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CARBON-CARBON COMPOSITES (CCC) - A HISTORICAL PERSPECTIVE

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Carbon-carbon composite (CCC) materials are typically composed of a fibrous carbon reinforcement, a carbonaceous or graphitic matrix, and sometimes other fillers or coatings to impart specialized properties. CCC materials have an outstanding balance of properties which have led to many important uses in the aerospace, defense, braking, industrial and other fields.

This report provides a historical perspective of CCC materials, including (a) the most important developmental events, (b) the present technology base, and (c) present and future uses.

The international materials community has assisted in compiling over 1400 historical events. Many of these events are listed in the report. Hopefully, they will assist in (a) recognizing major CCC events of the past, (b) stimulate new approaches and solutions for current problems and issues, and (c) provide a basis for forecasting future developments.

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FOREWORD

This report was prepared for the University of Dayton Research Institute under Air Force Contract F33615-95-D-5029, "Improved Technology for Advanced Composite Materials." The work was administered under the direction of the Nonmetallic Materials Division, Materials Directorate, Wright Laboratory, Air Force Materiel Command with Dr. James R. McCoy as the Project Engineer. This report was authored by a contractor of the U.S. Government. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes only. Every effort has been made by the author to insure that no inaccurate or misleading data, opinions, or statements appear in this technical report. The reader should understand that the author is reporting on an enormous amount of information which has been received from a variety of sources. Due to the voluminous quantity of information received, it was not possible to verify the accuracy of the data input. However, the reader is greatly encouraged to correspond with the author in a timely manner on (a) information believed to be inaccurate, (b) significant developments not reported herein, and (c) related matters. This information will be analyzed and used in future revisions of the technical report. All communications will remain on file at the Air Force Wright Laboratory/Materials Directorate, Wright-Patterson AFB OH 45433-7750, USA. Please address your correspondence to: Mr. Donald L. Schmidt, 1092 Lipton Lane, Beavercreek, OH 45430-1314.

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DEDICATION

This report is dedicated to the late Mr. Brennan A. Forcht. Mr. Forcht co-invented the family of carbon-carbon composites. He (a) personally conceived many new and novel forms of the material, (b) managed large materials and prototype developmental programs, (c) made many presentations, (d) published numerous articles, (e) strongly advocated new applications, and (f) tirelessly performed many other related technical and manufacturing tasks. No other individual has displayed greater initiative, leadership, and accomplishment in this field of advanced composite materials.

Mr. Brennan A. Forcht was born on January 21, 1922. He received a Bachelor of Chemical Engineering degree from the Polytechnic Institute of Brooklyn, N.Y., and a Master of Science degree in Chemical Engineering from the Rensselaer Polytechnic Institute, N. Y. Brennan joined Chance Vought in 1951 and later served as a Test Engineer, Lead Engineer, Engineering Specialist, and Program Manager. He also held a variety of other engineering and management positions in the field of structural materials. Mr. Forcht retired from the LTV Aerospace and Defense Company in August 1983 and then spent several years as a consultant. After a lengthy illness, he died on November 3, 1992 at the age of 70. His death was a great loss for the field of advanced composite materials in general and for carbon-carbon composite materials in particular.

Mr. Forcht is best known for his co-invention of the family of carbon-carbon composite (CCC) materials. Many of his other achievements are listed in this report under the organizational title of LTV Aerospace and Defense Company.

Brennan was a professional and personal friend of this author for over three decades. He was well known and liked by all of those in the carbon-carbon composites and related materials fields. He will continue to be missed by all of us.

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SECTION 1
INTRODUCTION

Advanced composites are "engineered materials," having high-performance properties and characteristics. Advanced composites are typically light in weight, strong, stiff, and thus suitable for structural applications. These properties are specifically sought in aerospace components where their high specific strengths and moduli (properties divided by density) can be advantageously used.

Composites are typically categorized according to their matrix material. Such categories include polymeric-matrix composites (PMCs), metal-matrix composites (MMCs), ceramic-matrix composites (CMCs), and carbon-carbon composites (CCCs). Each category of advanced composites has unique properties and application outlets. PMCs are the most mature of the advanced composites, and they are widely used in both defense and commercial applications. MMCs, CCCs, and CMCs are emerging technologies, and as such, their uses to date have been limited.

CCCs are a unique family of materials in that they combine the many desirable properties of fiber-reinforced composites (such as high specific strength, stiffness and toughness) with the refractory properties of carbon (namely, retention of strength and stiffness) at high temperatures in an inert atmosphere and resistance to thermal shock and creep. CCC materials are chemically composed of synthetic pure elemental carbon. Macro-properties can be varied greatly due to individual constituents, their microstructures, and the nature of the fiber-matrix interface.

A CCC material is composed of a discrete fibrous reinforcement, a carbonaceous matrix, and sometimes a specialty filler. Composite properties can be varied over great ranges by: (a) type, composition, percentage, and orientation of the constituents, and (b) processing effects. New and improved constituent materials are continually being developed, thus enabling the creation of new composite materials. Directional composite properties are influenced primarily by the fibrous reinforcement whose properties vary greatly in terms of density, strength, stiffness, thermal conductivity, and other properties. Simply stated, composites will generally outperform monolithic materials because of the intrinsic versatility of material design and the wide range of available constituent materials. A comparison of CCC materials and graphitic materials, both composed of an all-carbon composition, is a good example. CCC properties can equal or substantially exceed those of polycrystalline graphite except for bulk material costs. The rate of growth of monolithic materials is rather slow and predictable. By comparison, the growth rate for composite materials is high but rather unpredictable.

CCC materials are manufactured with various constituents and a variety of processes. The three major production schemes are illustrated in Figure 1.

CCC materials represent a "breakthrough" in modern materials technology in the sense that few individuals recognized their great applications potential. Polycrystalline and pyrolytic graphites were available to satisfy all of the "foreseeable" aerospace high-temperature requirements. Even after the early development of CCCs in the 1960s and 1970s, few program managers were interested in this new family of materials. They did not want to bear the risks associated with using a new material and its possible negative impact on systems or component performance, costs, and producibility. Fortunately, several United States (U.S.) individuals had the foresight, authority, commitment, and advocacy to insure the development of CCC materials and their transition from a "laboratory curiosity" to an "applications reality."

CCC materials are largely an American invention. The first decade of material development was primarily funded by the U.S. Department of Defense (DoD) organizations (mainly the Air Force Materials Laboratory). In the mid-1960s, the National Aeronautics and Space Administration (NASA) became interested in CCCs because they appeared to be the only suitable materials for the highest temperature components of the U.S. space shuttle orbiter. The U.S. DoD organizations focused on the development of uncoated CCCs for military applications like strategic reentry vehicles and rocket nozzles, whereas NASA pioneered the development of oxidation-protected carbon-carbon composites (OPCCC) materials for their hypersonic aerospace flight vehicle.

The U.S. development of CCCs during the first two decades was less than an orderly process. Some of the major reasons were:

(a) defense materials needs were ultracritical, complex, and poorly defined,

(b) applications development deadlines were shorter than typical materials developmental periods,

(c) the science base of CCC materials was virtually nonexistent,

(d) needed expertise was widely scattered throughout the U.S., and

(e) the materials development was "empirically" based.

In spite of these limitations, significant progress was made and various defense applications (nosetips and nozzles) moved closer to reality. Meanwhile, the aircraft braking systems

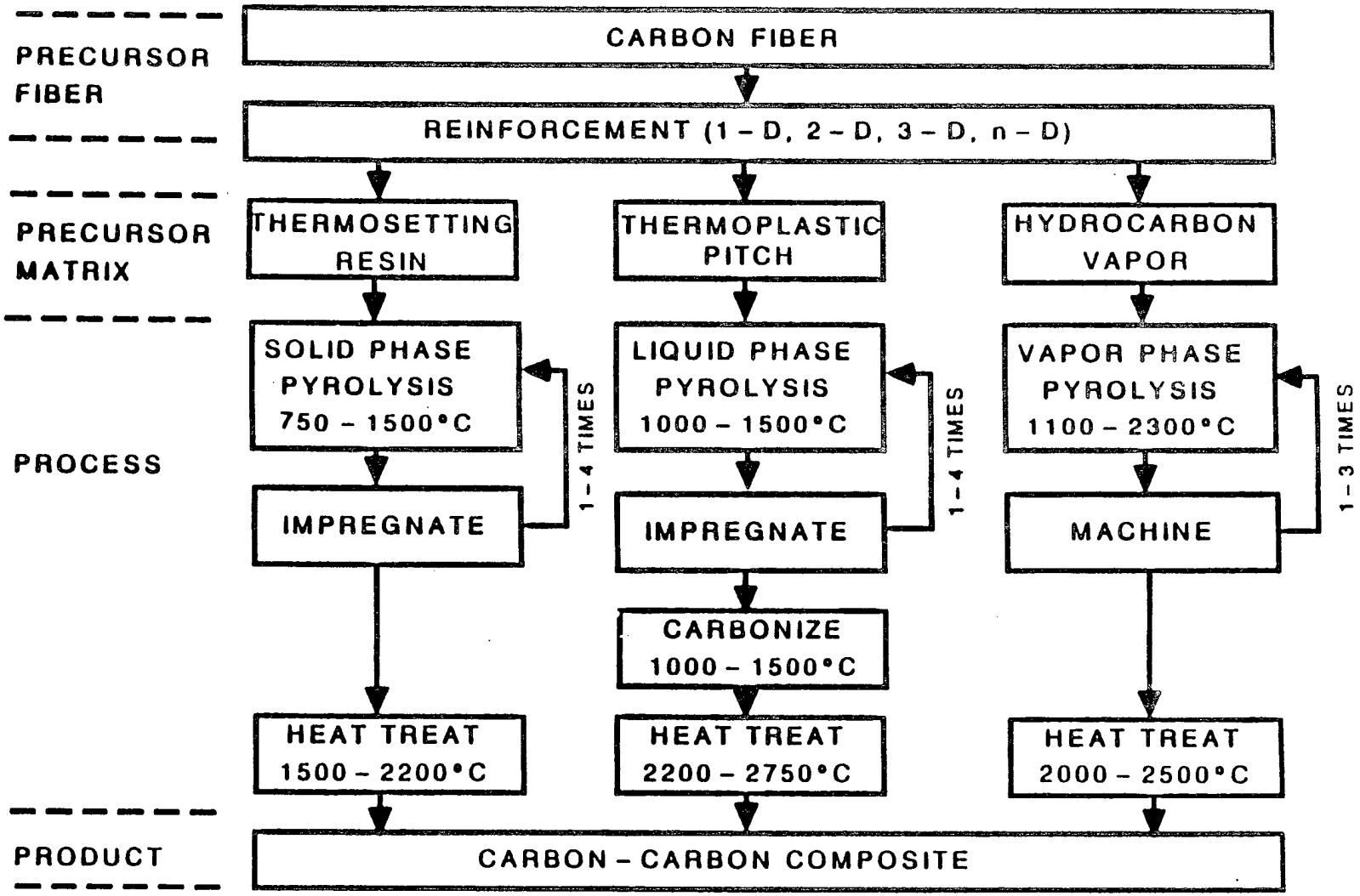


Figure 1. General Manufacturing Procedures for CCC Materials.

organizations were seeking a higher-performance and lighter weight frictional material. CCCs appeared to have many of the properties desired, and both materials upgrading and evaluation efforts were pursued. First-generation CCC braking materials were less than satisfactory due to their low density, variable frictional coefficient, influence of moisture on properties, and possibly other undesirable features. Technology created in defense programs was then transferred to the aircraft brake suppliers, and new cooperative agreements were initiated between the aircraft brake industry and domestic CCC developers. Within a few years CCC materials were tailored to the specific needs of aircraft brake systems and ultimately became the material of choice.

From 1960 until 1977, defense-funded and NASA-funded CCC technology achievements were published in "limited distribution" or "open literature" documents. A major fraction of the literature was published in releasable reports and technical journals. In 1977 the U.S. reaffirmed that the major applications for CCC materials were for critical defense components, and their future uses would provide enormous systems benefits. CCC materials technology, manufacturing and design data were therefore added to the International-in-Arms Regulations (ITAR) or Export Administration Regulations (EAR). Basic research results on CCCs continued to be published in the open literature, although there was very little of this work. U.S. corporations were funding CCC technology under their Independent Research and Development (IRAD) or Corporate Research and Development (CRAD) programs. Most corporations regarded this work as "proprietary" and thus little information found its way into the open literature. All of these situations impacted the flow of CCC technology from one source to another, and as a result, no single chronology of CCC technology was ever prepared. In 1990 the Air Force Wright Laboratory/ Materials Directorate requested the author to initiate this project.

Unified and comprehensive descriptions of CCC applications have not yet been published in the open literature. This report brings together, for the first time, essentially all of the conceptual and actual uses of CCC materials in modern day technology. It is anticipated that the reader will gain a greater understanding of CCC materials, their unique and varied properties, and how these properties and characteristics lend themselves to applied uses. Hopefully, these discussions will prompt ideas of new and expanded uses for CCC materials.

The CCC materials industry is entering an exciting and challenging time. The industry is focusing on diversification away from the traditional markets of defense and aerospace and moving into other specialized markets. North America is seeing record consumption levels and sales. Europe is also witnessing increased CCC production, mainly in the aircraft brake disc area. Intensive research and development is underway in the Far East, but commercialization efforts are

slowly evolving. With growth of the aircraft business in the Far East, CCC materials production will increase - especially in the aircraft brake sector.

This report should be useful to all individuals interested in CCC materials, especially management, engineering, and scientific personnel. The report can serve a number of purposes, including the:

(a) Identification of domestic and worldwide organizations that have contributed to the technology of CCC materials,

(b) Recognition of the most significant contributions of various organizations,

(c) Establishment of the general time frame for each of the significant events,

(d) Assessment of the relative level of domestic versus foreign contributions,

(e) Identification of major technological gaps,

(f) Existence of any previous work, and

(g) Establishment of organizations having common technology interests.

Technical terms, acronyms, abbreviations and symbols are defined in Appendices 1 through 4, respectively.

SECTION 2
MATERIAL ATTRIBUTES, LIMITATIONS, AND DEVELOPMENTAL NEEDS

CCC materials have essentially all of the desirable attributes of graphitic materials coupled with the inherent design versatility of composites. Table 1 presents the many attributes of current CCCs.

2.1 ATTRIBUTES

The major benefits of CCC materials are: (a) high thermal stability, (b) high strength, (c) high modulus (stiffness), (d) low density, (e) low coefficient of thermal expansion, and (f) self-lubricating.

2.1.1 Thermal Stability

CCC materials will slowly sublime or vaporize (nonmelting) in high-temperature inert atmospheres or in vacuums. They can be used at temperatures in excess of 3300°C (5972°F) in such environments. CCC materials can also survive long periods in 425°C (797°F) air, but the composite and its constituents will slowly oxidize and change dimensionally. Very high temperatures in oxidizing environments can be tolerated for only short periods. Any prolonged exposure to oxidizing environments will require oxidation protection.

CCC materials can withstand severe thermal gradients without catastrophic failure (fracture). CCCs can be thermally cycled from subzero temperatures to over 1900°C (3452°F) in seconds or suddenly exposed to 3300°C (5972°F) service temperatures without cracking or distorting. Intense transient heating associated with missile reentry heating, rocket nozzle firing, x-ray deposition and laser exposure produce high levels of thermally-induced stresses, but the composites have adequate strength to remain intact. There are no known cases of CCCs fracturing due to thermal shock or thermally-induced stresses.

2.1.2 Density

CCCs are very lightweight materials and, hence, they are very attractive for aerospace uses. The densities of CCCs range from about 1.55 g/cm^3 (0.056 lb/in^3) to 1.95 g/cm^3 (0.070 lb/in^3), although even lighter-weight materials have been manufactured for high-temperature insulation. Other high-temperature structural materials are considerably heavier, i.e., aluminum alloys (2.7 g/cm^3, 0.098 lb/in^3), titanium alloys (4.4 g/cm^3, 0.160 lb/in^3), nickel-based

TABLE 1
ATTRIBUTES OF CCC MATERIALS

PROPERTIES	*CHARACTERISTICS*
• High Strength and Modulus (Stiffness) at very High Temperatures (Vacuum & Inert Gaseous Environments)	• Near Constant Coefficient of Friction
• Low Density	• High Thermal Stability (Nonoxidizing Environments)
• High Specific Properties (Property Divided by Density)	• Nonmelting
• Fracture Toughness	• Thermal Shock Resistance
• High Thermal Conductivity	• Nonflammable
• Low Thermal Expansion Coefficient	• Nontoxic Fumes when Burned
• High Thermal Emissivity	• Radiation Resistance (X-rays, Gamma Rays, Neutrons, and Laser Energy)
• High Specific Heat	• Not Wet by Most Molten Metals
• Low Creep Rate	• Damage Tolerant
• Chemically Inert (except in Oxidizing Fluids)	• Low Wear Rate
• High Electrical Conductivity	• Biocompatible
• Nonmagnetic	• Low Vacuum Outgassing
	• Vibration Dampening
	• Machinable
	• Available in Many Different Shapes, Sizes, and Thicknesses
	• Numerous Worldwide Sources

superalloys (7.8 g/cm^3, 0.28 lb/in^3), graphite-aluminum MMC (2.50 g/cm^3, 0.090 lb/in^3), silicon carbide/glass CMC (2.70 g/cm^3, 0.098 lb/in^3), and silicon carbide/silicon carbide CMC (2.50 g/cm^3, 0.090 lb/in^3).

2.1.3 Mechanical Properties

CCC materials are very strong and stiff compared to polycrystalline graphites. See Table 2. Composite strength and stiffness is derived primarily from the fibrous reinforcement, and their values can be varied greatly depending upon the type, amount, and orientation of the fibers. The highest strength and stiffness values are exhibited parallel to the longitudinal axis of the fibers. As noted in Table 3, tensile strengths up to about 565 MPa (82 ksi) have been measured with unidirectionally-reinforced composites. Other reinforcing schemes result in lower in-plane strengths. For example, 2-D fabric-reinforced CCC materials exhibit tensile strengths about 330 to 400 MPa (48 to 58 ksi) when measured parallel to the fabric warp direction. CCCs are relatively high modulus (stiff) materials. The tensile modulus is maximum when measured parallel to the fiber axis. Unidirectionally-reinforced CCCs have exhibited moduli values in excess of 565 GPa (82 Msi), but 69 to 124 GPa (10 to 18 Msi) values are more representative of 2-D and 3-D composites. The mechanical behavior of CCCs at elevated temperatures is similar to that of polycrystalline graphites. The tensile strength increases with temperature up to about 1650°C (3002°F) and then decreases with further increases in temperature. At 1900°C (3500°F), 2-D CCC material is stronger and stiffer than aluminum at room temperature. The tensile moduli value remains essentially unchanged from room temperature to about 1650°C (3002°F), and thereafter decreases with temperature increases. Compressive and flexural properties also follow the same general trend.

As previously noted, very high mechanical properties are obtained parallel to the fiber axis in unidirectionally-reinforced CCC composites. Such composites, however, are seldom used due to their poor transverse and in-plane shear properties. Fabric-reinforced composites have a better balance of directional properties, and they are usually specified for structural applications. Tridirectionally-reinforced or 3-D CCC materials exhibit more isotropy. They are generally used when both thermal and mechanical performance are important. Four directionally-reinforced composites (4-D) have even greater isotropy of properties in all directions but are more difficult to fabricate. Up to 11-D reinforced CCC materials have been manufactured, but their higher complexity and costs have generally not warranted their use.

TABLE 2
TYPICAL PROPERTIES OF GRAPHITIC AND CCC MATERIALS

Properties	Test Direction	Polycrystalline Graphite (ATJ-S)	Pyrolytic Graphite	2-D CCC (T-300 HT 8HSW/ Phenolic Char)	3-D FWPF CCC (HM Yarn-Fabric/ Pitch Coke)
DENSITY, g/cm^3 (lb/in^3)		1.83 (0.066)	2.22 (0.080)	1.63 (0.059)	1.95 (0.070)
TENSILE STRENGTH,	X	37 (5.4)	124 (18)	330 (48)	228 (33)
MPa (ksi)	Z	30 (4.4)	6.9 (1.0)	4.5 (0.65)	172 (25)
TENSILE MODULUS,	X	12 (1.7)	29 (4.2)	117 (17)	83 (12)
GPa (Msi)	Z	7.6 (1.1)	10 (1.5)	3.1 (0.45)	69 (10)
TENSILE ULTIMATE	X	0.44	0.4	0.33	0.25
STRAIN, %	Z	0.54	-	-	0.19
COMPRESSIVE STRENGTH,	X	52 (7.5)	97 (14)	200 (29)	138 (20)
MPa (ksi)	Z	41 (6.0)	345 (50)	255 (37)	117 (17)
COMPRESSIVE MODULUS,	X	9.6 (1.4)	17 (2.5)	110 (16)	83 (12)
GPa (Msi)	Z	7.3 (1.1)	23 (3.3)	8.3 (1.2)	66 (9.5)
INPLANE SHEAR STRENGTH, MPa (ksi)	X	19 (2.8)	3.5 (0.5)	41 (6.0)	9.7 (1.4)
THERMAL CONDUCTIVITY,	X	161 (93)	415 (240)	45 (26)	159 (92)
W/m·K (Btu/ft·h·°F)	Z	121 (70)	23 (13)	4.7 (2.7)	130 (75)
THERMAL EXPANSION COEFFICIENT,					
RT to 1650°C (3002°F)	X	3.8 (2.1)	2.2 (1.2)	1.3 (0.73)	1.1 (0.63)
ppm/°C (ppm/°F)	Z	4.9 (2.7)	25 (14)	5.9 (3.3)	1.2 (0.65)

X - Parallel to with-grain in graphite or major fiber/fabric axes in composites.
Z - Parallel to across-grain in graphite or perpendicular (transverse) to major fiber/fabric axes.
Room temperature values; not for design purposes.

TABLE 3
TYPICAL PROPERTIES OF CCC MATERIALS

Properties	Test Direction	1-D CCC (P-100/Pitch Coke)	2-D CCC (T-300 HT 8HSW/ Phenolic Char)	3-D FWPF CCC (HM Yarn-Fabric/ Pitch Coke)	4-D ORTHOTROPIC CCC (HM Tow Rods/ Pitch Coke)
DENSITY, g/cm^3 (lb/in^3)		1.87 (0.068)	1.63 (0.059)	1.95 (0.070)	1.89 (0.068)
TENSILE STRENGTH, MPa (ksi)	X Z	565 (82) 14 (2.0)	330 (48) 4.5 (0.65)	228 (33) 172 (25)	303 (44) 103 (15)
TENSILE MODULUS, GPa (Msi)	X Z	303 (44) 10 (1.5)	117 (17) 3.1 (0.45)	83 (12) 69 (10)	37 (5.3) 97 (14)
TENSILE ULTIMATE STRAIN, %	X Z	0.23 0.21	0.33 -	0.25 0.19	0.31 0.42
COMPRESSIVE STRENGTH, MPa (ksi)	X Z	331 (48) 32 (4.6)	200 (29) 255 (37)	138 (20) 117 (17)	38 (5.5) 200 (29)
COMPRESSIVE MODULUS, GPa (Msi)	X Z	269 (39) 9 (1.3)	110 (16) 8.3 (1.2)	83 (12) 66 (9.5)	15 (2.1) 200 (29)
INPLANE SHEAR STRENGTH, MPa (ksi)	X	34 (4.9)	41 (6.0)	9.7 (1.4)	62 (9.0)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	X Z	204 (118) 17 (10)	45 (26) 4.7 (2.7)	159 (92) 130 (75)	100 (58) 195 (113)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	X Z	-1.8 (-1.0)	1.3 (0.73) 5.9 (3.3)	1.1 (0.63) 1.2 (0.65)	1.5 (0.85) 1.3 (0.73)

X - Parallel to with-grain in graphite or major fiber/fabric axes in composites.
Z - Parallel to across-grain in graphite or perpendicular (transverse) to major fiber/fabric axes.
Room temperature values; not for design purposes.

CCC materials are particularly attractive for aerospace uses because they have high specific structural characteristics (property divided by material density). Figure 2 illustrates the specific strength of 2-D and 3-D CCCs as a function of increasing temperature. Note that only CCC materials exhibit useful strengths above 1375°C (2507°F). Figure 3 presents the specific moduli of various aerospace materials and CCCs as a function of increasing temperature. Note that the modulus of CCC only decreases slightly with increasing temperature. Above about 1375°C (2507°F), only CCC materials offer a high degree of specific stiffness.

The fracture toughness of CCC materials is outstanding. Unlike polycrystalline graphite and other monolithic ceramics, CCCs do not exhibit catastrophic fracture and failure. Instead, they undergo progressive fracture of the matrix and reinforcement with increasing stress. Cracks are first initiated in the brittle-matrix material and then propagate toward the fibrous reinforcement. Fibers loosely bonded to the matrix deflect the cracks and impede their progress. Hence, composite failure is typically slow and sequential.

Other important structural attributes of CCC materials include: low creep rates, high fatigue resistance, vibration dampening, and damage tolerance. CCCs exhibit virtually no creep under loading and very long periods of time, and permanent strain resulting from long-term loading is virtually negligible. CCC materials also exhibit great resistance to fatigue loads. They can often be designed to have an unlimited service life. The stiffness of CCCs allows for greater vibration dampening than with metallic materials. This unique characteristic is exhibited over a wide spectrum of conditions. CCC materials also accommodate low-to-high strain rate loading. Because of the fiber toughening mechanism previously noted, CCCs have good impact strengths (low strain rate) provided the fibers are not well bonded to the matrix. Typical Izod impact test values are about 0.134 kJ/m (2.5 ft-lb/in) or higher. These impact values are almost 10 times those of nonreinforced carbons and graphites. At higher strain loading associated with supersonic and hypersonic particulate or planar impact, CCC materials also respond in a noncatastrophic manner. Damage is typically localized about the region of impact, and subsurface damage is usually minimal. Bullets fired through 3-D CCC plates resulted in holes the size of the projectiles and caused minimal damage to the adjacent material. This unique feature of CCCs has been successfully exploited in the development of hypervelocity impact-resistant flight vehicle surfaces.

2.1.4 Thermal Properties

CCC materials exhibit relatively high thermal conductivities like other carbonaceous materials. The conductivity values are highly directional depending upon the orientation of the fibers in the composite. Composite thermal conductivity values remain

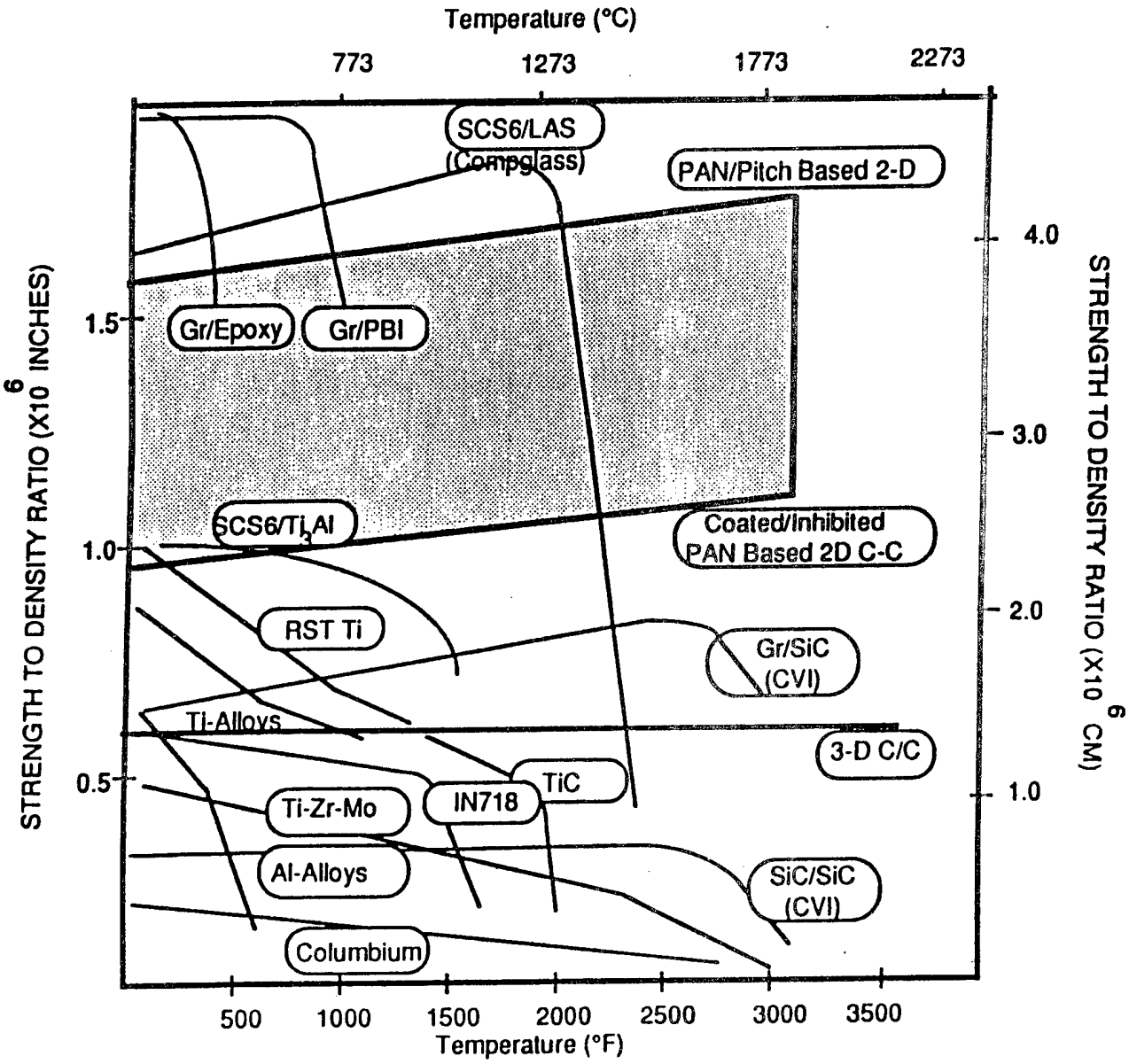


Figure 2. Specific Tensile Strengths of Aerospace Materials at Elevated Temperatures.

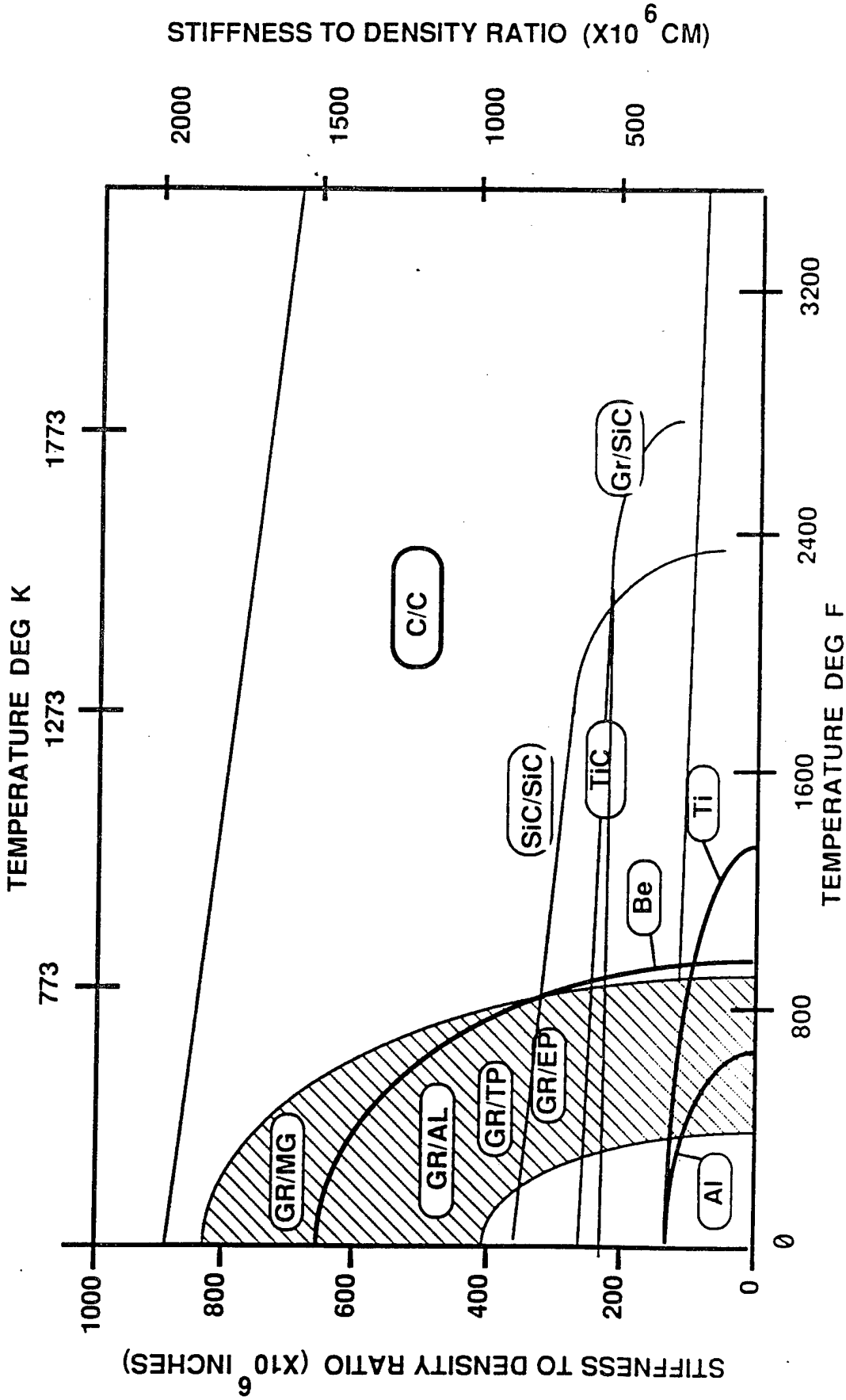


Figure 3. Specific Stiffnesses (Moduli) of Aerospace Materials at Elevated Temperatures.

essentially constant or increase slightly from room temperature to about 2204°C (4000°F), and thereafter they decrease with increasing temperature. For 2-D fabric-reinforced CCCs, the warp-fill direction room temperature thermal conductivities are about 43-46 W/m·K (25-27 Btu/ft·h·°F) and about the same values at 1649°C (3000°F). At higher temperatures, the thermal conductivity values tend to decrease slightly. In the X-ply or transverse direction, 2-D composite thermal conductivities are considerably less. At room temperature the through-the-thickness thermal conductivity of 2-D CCC materials is about 2.7 W/m·K (4.7 Btu/ft·h·°F). At 1649°C (3000°F) the thermal conductivity increases to 7.9 W/m·K (13.8 Btu/ft·h·°F) and reflects the values typical of porous carbonaceous materials.

CCC materials are dimensionally stable over a wide range of temperatures. Their coefficients of thermal expansion are very low, particularly when measured parallel to the fibers. Low thermal expansion coupled with high mechanical and high thermal properties produce a high resistance to thermal shock. Unlike monolithic ceramics and graphites, CCC materials can be heated red hot and plunged into a cold fluid without catastrophic fracture and failure. Conversely, CCC materials at room temperature can be suddenly exposed to extreme temperature conditions without macro-cracking. Matrix cracking takes place on the microscale, and crack propagation is interrupted at the matrix-fiber interface.

For 2-D fabric-reinforced CCCs, thermal expansion values are highly anisotropic. The warp and fill direction thermal expansion values are slightly negative from room temperature to about 650°C (1202°F). This unique property reflects the negative thermal expansion of carbonaceous fibers. With increasing temperature, the thermal expansion values turn positive and increase rapidly. From room temperature to 1649°C (3000°F), the thermal expansion coefficients for 2-D fabric-reinforced CCC materials are about 1.2-1.4 ppm/°C (0.67-0.76 ppm/°F) in the warp and fill directions. Since there are no fibers to restrain the composite in the X-ply or transverse direction, the thermal expansion is considerably higher. Typical values for the transverse direction of 2-D composites are about 5.9-6.3 ppm/°C (3.3-3.5 ppm/°F).

CCCs are composed entirely of carbonaceous constituents, and thus their specific heat or heat capacity is the same as traditional carbonaceous or graphitic materials. Near room temperature, the specific heat is about 0.18 cal/g·°C (0.18 Btu/lb·°F) and about 0.5 cal/g·°C (0.50 Btu/lb·°F) at 1650°C (3002°F).

2.1.5 Frictional Characteristics

CCC materials are self-lubricating like their carbonaceous homologues, and this property is exhibited over wide temperature ranges. Composite materials have been developed with near constant coefficient of friction values for a range of environmental conditions and temperatures. This property, coupled with low wear rate and high temperature performance, lends itself to aircraft brake discs. Today, frictional CCCs are the highest-volume CCC materials being manufactured.

2.1.6 Chemical and Corrosion Resistance

CCC materials, like other carbonaceous materials, are highly resistant to chemicals, except strongly oxidizing agents. They are not wet and do not react with a variety of molten materials including metals and ceramics. CCCs are compatible with body fluids. This property, coupled with tailorable strength and stiffness, has resulted in new applications involving bone replacements.

2.1.7 Other Properties and Characteristics

CCC materials also have other characteristics of interest. Most of their properties can be highly tailored in accordance with the needs of the specific application, thus imparting great design flexibility. The CCC materials can be fabricated into a variety of configurations, sizes, and thicknesses. They can be machined, drilled, sawed, and joined with existing methods. CCC materials are manufactured by most of the high-tech nations in the world, but the quality and quantity may differ greatly.

In space environments, CCCs exhibit good resistance to environmental effects. Vacuum outgassing is essentially nonexistent, but some material loss can be encountered in low earth orbits containing atomic oxygen (coating protection is required). CCC materials are also non-magnetic.

2.2 INTRINSIC LIMITATIONS

CCC materials have three basic property limitations, i.e.

(a) low resistance to oxidizing environments,
(b) low strain-to-failure, and
(c) low matrix-dominated mechanical properties.

2.2.1 Oxidation Resistance

CCC materials, like other carbonaceous and graphitic materials, are susceptible to oxidation, particularly at high temperatures or in strongly-oxidizing media. Nevertheless, they exhibit satisfactory performance if the exposure is short in duration (like a ballistic missile reentry vehicle nosetip). Longer exposure times and repeated exposures to oxidizing species generally result in excessive surface material loss and the need for oxidation protection. Oxidation-resistant coatings and oxidation-inhibited substrates have been developed to extend the life of CCC materials in oxidizing environments, but more advanced protective approaches are required to minimize this service limitation.

2.2.2 Elongation-at-Fracture

CCC materials, like other ceramic-based materials, have relatively low strain-to-failure (elongation-at-fracture) values. Typical values are about 0.3 to 1.1 percent. Both constituent materials have low elongation-at-fracture values. Minimum values are typically measured parallel to the fibers, but some relief can be effected by altering the fiber-to-matrix bond. CCC materials containing strongly bonded fibers-to-matrix tend to be "brittle" or low in elongation-at-fracture. Weaker fiber-matrix bonding generally permits some slippage of the fibers during stressing and maximum utilization of the fiber strength. This phenomenon was first discovered in CCCs, and after many years was extended to other ceramic- matrix composite materials.

2.2.3 Matrix-Dominated Mechanical Properties

CCC materials exhibit low matrix-dominated mechanical properties. In the transverse (cross-ply) direction of 2-D materials, the tensile strength values are only about 4.5 MPa (0.65 ksi) to 14 MPa (2.0 ksi) or the intrinsic tensile strength of the carbon matrix itself. The interlaminar shear strength is about 9.0 to 21 MPa (1.3 to 3.0 ksi). These properties are essentially those of the matrix itself, because there are no reinforcing fibers in the direction of stress to help carry the load. Novel design procedures can sometimes minimize or circumvent these composite limitations, but for the most part these low value properties remain "troublesome" for the designer. The advent of three directionally-reinforced composites largely eliminated the "matrix-dominated" composite problem and provided reasonably high mechanical properties along the principal orthogonal axes. A greater number of fiber orientations are also possible, ranging from four-directional (4-D) to 11-directional (11-D). These types of composites provided closer-to-isotropic properties, but at the expense of increased manufacturing costs and

lower composite fiber volumes. Four directional-reinforced composites are the most widely used of the n-D composites.

2.3 TECHNOLOGICAL NEEDS

The development and application of CCC materials during the past three decades has uncovered a number of technological problems, many of which have only been partially solved. Table 4 is a list of the general, manufacturing, data generation, and oxidation-resistant composite needs. While significant progress is required in all of the areas cited, the most critical needs appear to be those given in Table 5. Major advances in these particular needs would greatly accelerate a designer's confidence in existing materials and provide new composites for expanded applications.

TABLE 4

TECHNOLOGICAL NEEDS OF CCC MATERIALS

- *GENERAL*
  - HIGHER TRANSVERSE MECHANICAL PROPERTIES
  - IMPROVED OXIDATION RESISTANCE
  - LOWER COST MATERIALS
  - SHORTER FABRICATION AND PROCESSING TIMES
  - MATERIALS/FABRICATION/PROCESSING/PROPERTY RELATIONSHIPS
  - UPGRADED DESIGN METHODOLOGY ACCOMMODATING ANISOTROPIC PROPERTIES AND OTHER UNIQUE MATERIAL FEATURES
  - IMPROVED NONDESTRUCTIVE EVALUATION AND INSPECTION METHODS
  - IMPROVED FRACTURE/FAILURE PREDICTION MODELS
  - IMPROVED ATTACHMENT AND JOINING TECHNIQUES
  - ON-SITE REPAIR PROCEDURES
  - IMPROVED TECHNOLOGY AND INFORMATION TRANSFER PROCEDURES
- *MANUFACTURING*
  - LOWER COST FABRICATION AND PROCESSING
  - REPRODUCIBLE MANUFACTURING PROCESSES
  - NET SHAPE FABRICATION AND PROCESSING
  - AUTOMATED IN-PROCESS MANUFACTURING CONTROLS
  - INTRINSICALLY SCALABLE PROCESSES
  - NONPROPRIETARY MATERIALS AND PROCESS SPECIFICATIONS

TABLE 4 (Concluded)

TECHNOLOGICAL NEEDS OF CCC MATERIALS

- *DATA GENERATION*
    - CONSTITUENT AND COMPOSITE PROPERTIES AT HIGHER TEMPERATURES AND SPECIALIZED ENVIRONMENTAL CONDITIONS
    - STATISTICAL DESIGN DATA
    - TEST METHODS STANDARDIZATION
    - COMPUTERIZED DATA BANK

- *OXIDATION-INHIBITED COMPOSITES*
    - PROTECTIVE COATINGS WITH A WIDER TEMPERATURE RANGE CAPABILITY, HIGHER SERVICE TEMPERATURE, AND MULTIFUNCTIONAL IN PERFORMANCE
    - CRACK SEALING, NONHYDROSCOPIC SEALANTS FOR CARBONACEOUS SUBSTRATES
    - MORE ADHERENT COATINGS
    - REPRODUCIBLE COATING COMPOSITIONS AND THICKNESSES

TABLE 5

FUTURE NEEDS OF CCC MATERIALS

- ***MATERIALS***
  - LOWER-COST COMPOSITES
  - WIDER TEMPERATURE RANGE, LONG-LIFE OXIDATION-PROTECTED MATERIALS
- ***TECHNOLOGY***
  - UNDERSTAND MATERIALS:PROPERTIES:PERFORMANCE RELATIONSHIPS
  - RELIABLE LIFE PREDICTION MODELS
- ***APPLICATIONS***
  - STATISTICAL DESIGN DATA
  - PROTOTYPE EVALUATIONS

SECTION 3
SOURCES OF INFORMATION

3.1 APPROACH

The chronology of CCC materials was assembled from an analysis of:

(a) published articles, presentations, and company brochures,

(b) national and international abstracting documents,

(c) private communications with leading national and international CCC authorities, and

(d) personal knowledge of virtually every significant CCC event for over three decades.

An exhaustive search of various library records was conducted, and many hundreds of references to CCC technology were identified. Each significant item was documented in terms of:

(a) the year(s) of achievement,

(b) a short description of the event,

(c) the significance of the accomplishment, and

(d) organization responsible for the achievement.

Each of the events was categorized as either:

(a) basic and fundamental research efforts,

(b) new materials constituents, constructions, and concepts,

(c) nondestructive inspection methods for assuring quality control and the measurement of composite properties,

(d) analytical techniques and modeling for predicting composite properties and performance, and for guiding materials developmental efforts,

(e) new fabrication and processing methods,

(f) laboratory testing and evaluations,

(g) fabrication of subscale or full-scale components for verification of fabrication feasibility, property generation, or performance features, or

(h) manufacturing and marketing.

After assembling the CCC chronology, it was apparent that a complete chronology was beyond the knowledge and skills of a single individual. In order to obtain as complete a coverage as possible, a formal letter request was sent to several hundred organizations for additional input. The author's listing of organization's accomplishments were also forwarded for possible additions, amendments, and changes. Follow-up letters were also sent to non-responding organizations.

A limited number of entries were received from individuals throughout the world. In order to improve readability, some of the entries were slightly changed. No attempt was made to verify the accuracy and completeness of the entries received because of time constraints and difficulties involved. Although the intent of this document was to report only the most significant events, several organizations apparently listed all of their achievements. Rather than pass judgment on the importance of the information received, it was decided to publish all of the data.

Most of the organization's contributions are listed by a single year for achievement. It should be recognized that many events took place over a number of years, and that the year listed is likely the most significant date for the accomplishment. Large materials programs generally involved several different participating organizations. When possible, the individual contributions were cited. No attempt was made to delete duplicate entries received from different organizations.

Over 1400 entries have been received to date or formulated by the author. All entries received from participating organizations will be listed in this document. Most of the author's entries were also included in this report.

3.2 CONTRIBUTING ORGANIZATIONS

Appendix 5 contains a listing of worldwide organizations that have or are conducting CCC materials research, development, manufacturing, test, evaluation or utilizing these composites in various applications. Each organization is listed with its current address and their major (not all) areas of contribution.

Each organization has been listed in one of five categories to facilitate ease of using the appendix. They are:

(a) Section A. U.S. Academic Organizations,

(b) Section B. U.S. Research Institutes & Federal Contract Research Centers,

(c) Section C. U.S. Industrial Organizations,

(d) Section D. U.S. Government Organizations, and

(e) Section E. Overseas Organizations.

SECTION 4
HISTORICAL OVERVIEW

4.1 DISCOVERY

Carbon-carbon composite (CCC) materials originated in the United States. Precursory composites were first made in 1958 by the pyrolysis of oxide fiber-reinforced resinous composites. With the advent of commercially-available rayon-based graphitic fabrics one-to-two years later, an all-carbon composite became a reality.

Four separate aerospace, industrial, and government organizations played a key role in creating a new form of advanced composites: namely, CCC materials. Each of these organizations pursued a different route in co-inventing CCC materials.

In 1958, a laboratory technician at Chance Vought Aircraft, Inc., Astronautics Division attempted to measure the resin content of an oxide fiber-reinforced phenolic composite by the "resin burnout technique." He inadvertently covered the heated crucible containing the plastic specimen, and in the process, the pyrolyzing material was surrounded by hydrocarbon (nonoxidizing) gases. Instead of air oxidizing the resin char, a porous composite was formed (1-4). See Section 8. Mr. Brennan Forcht, the technician's supervisor, called the material "burnt toast" or "reduced resin laminate." He decided to keep the specimen and showed it to the author a short time later. I can recall our excitement in demonstrating the high impact resistance and high strength of the material through crude tests like dropping and pounding on it. Both of us recognized that the temperature limitation of the composite was the oxide fiber, and a carbonaceous fiber would be needed to survive much higher temperatures. This requirement turned out to be rather easy. Mr. Rex Farmer and the author (of the Air Force Materials Laboratory) were creating a wide variety of fibrous carbons during an evening-hour, government-funded laboratory research project. Different organic fibers were successfully pyrolyzed into low-strength and low-modulus carbon fibers. Similar experiments were also being carried out by the tobacco industry to develop an improved carbon filter for cigarettes. 0ther investigators were also active in this field, and they submitted a number of patent applications. In the same time period, the Union Carbide Corporation was developing a cellulosic (viscous rayon-based) "graphite" fabric. Their flexible fibrous material was later commercialized as "WCA" fabric. Their process for graphitizing woven and nonwoven cellulosic fibers was later described in U.S. Patent 3,107,152, which was filed on September 12, 1960 (5). The graphitized fabrics contained fibers with a tensile strength of about 0.745 to 0.897 GPa (108 to 130 ksi) and a Young's modulus from about 414 to 690 GPa (6 to 10 Msi). At this point in time, it was apparent that all

of the necessary carbonaceous constituents would soon be available, and a government-funded developmental program would be desirable to explore various composite types, processing methods, and materials properties. Chance Vought Corporation/Vought Astronautics Division took the initiative and submitted an unsolicited proposal to the U.S. Air Force Materials Laboratory. This proposal was technically acceptable, but it was not funded because of insufficient funds (middle of the fiscal year procurement cycle). The proposal was later upgraded and resubmitted. The author in behalf of the Air Force Materials Laboratory funded the materials development program. First effort (began 1 March 1961) involved various fibrous oxide reinforcements, but with the availability of UCC "WCA" graphite fabric, all succeeding efforts were centered on totally carbonaceous (CCC) materials. Hence, this effort was likely the first "dedicated" CCC material developmental program.

Meanwhile at the Air Force Materials Laboratory, the author and his co-workers were measuring the properties of surface chars excised from ablated plastic composites (6). The virgin phenolic-graphite fabric composites were in the form of reentry missile nosetip shapes, and after exposure to ground-based reentry heating conditions in a water-stabilized electric arc, charred material remained on the surface of the specimens. Properties of the surface chars were needed to improve their ablation and erosion resistance, thermal conductivity, and other properties. It was noted by the author that these surface chars had a balance of properties not found in any other class of materials. But of greater importance, it was documented that "charred" plastic composites or "pyrolyzed plastics" could be created in the laboratory under more controlled thermal and environmental conditions, and the resultant properties would be more predictable and desirable. It was now apparent to the author that the technologies of the graphite industry and the new organic matrix composite industry could be married to form all sorts of new CCC materials. The intrinsic brittleness (and other limitations) of monolithic graphitic materials could (at last) be overcome via fibrous reinforcement, and the design flexibility of "composites" could enable a balance of properties not previously found in typical engineering materials.

In the same (possibly sooner) general time period, the Union Carbide Corporation/ National Carbon Company was developing their first commercial CCC materials (7-12). Composite development was proceeding slowly, but with the initiation of the U.S. Air Force "Advanced Development Program On Graphites," the "fiber-reinforced graphite" development was greatly accelerated. A new family of "PT"-TM grade materials were developed, characterized and commercialized. According to U.S. Patent 3,174,895 filed on September 7, 1960, laminates of graphitized cellulosic sheets were produced with a carbonized or graphitized binder. Precursor carbonaceous matrices mentioned included (a) furfuraldehyde-furfural alcohol,

and (b) furfuraldehyde-ketone condensation products and furane-phenolic resins. The CCCs were prepared from laminated material cured under pressure at about 165°C (329°F), carbonized in a nonoxidizing atmosphere at 800-900°C (1472-1652°F) and further heat treated at 2800-2900°C (5072-5252°F) in an inert atmosphere. These baseline CCC production materials were also further densified with a furane resin, cured, carbonized, and graphitized.

Other CCC materials were later manufactured based on (a) higher char-yielding resins like phenolics, and (b) plain (square) woven graphite cloth in continuous form, diced, or macerated. The developmental composites were sold as cured, pyrolyzed, or graphitized materials. Most of the commercial products were in the form of solid blocks which had to be machined to the desired shape. Some materials were fabricated to shape. These "PT" CCC products attracted few customers because (a) CCC properties generally have to be tailored to meet the requirements of specific applications, (b) high costs, and (c) designers of high-temperature components were focusing their attention on polycrystalline graphites and not CCC materials.

About the same time, the United Kingdom Atomic Energy Authority was seeking a method of forming massive fibrous carbon products for encapsulation of uranium and other nuclear materials. One of the first successful CCC methods involved the pyrolization of cotton wool to form the fibrous carbon and then densifying it with either pyrolytic carbon or a carbonizable (furfural alcohol, phenolic, etc.) thermosetting resin. Low-strength and low-modulus CCC materials were fabricated with a maximum density of 1.66 g/cm^3 (13). Although this pioneering research was cited later in other CCC patents, its significance remained rather obscure and under appreciated for several decades.

It is interesting to note that the discovery and initial development of CCC materials took place in different locations and by various groups with dissimilar objectives. There was little (if any) interaction between the various research groups, and it took quite a few years for the technical community to fully appreciate these pathfinding developments. Each of the materials development groups had a different name for their carbonaceous composites, but over the years the designation "carbon-carbon composites" became a standard in the industry.

It has been widely reported that CCC materials were discovered in 1958. The concept of "pyrolyzed plastic composites" was discovered in 1958, not CCC materials. Carbonaceous reinforcements did not become commercially available until about 1959, thus enabling the development of the first "all-carbon" CCC material.

In the following years, it should be noted that the advocacy and development of CCCs was mainly due to the aerospace and plastic composites companies. CCCs were viewed as a specialty product by the domestic graphite industries, and thus represented only limited opportunities for profit. As a consequence, the domestic CCC industry grew mainly outside of the graphite industry, and the needed graphite technology had to be learned by the plastic composite companies. This situation is unlike that of foreign countries in which CCC developments have been centered within their carbon and graphite companies.

4.2 COMPOSITE CONSTITUENTS AND CONCEPTS

The development of various constituent materials and their successful incorporation into composites played a vital role in providing many new and unique CCC materials. The following sections are devoted to the background role and first reported development and chronology of development for (a) fibrous carbons and graphites, (b) fibrous textile preforms, and (c) carbon and graphite matrices. These constituents were incorporated into unique composites through the use of existing or new fabrication and processing technologies. These developmental activities have also been reported. Oxidation-protected CCC materials are discussed in a separate section because their constituents start to include materials other than carbon. Finally, hybrid composites containing major fractions of noncarbon ceramic constituents will be discussed.

4.2.1 Fibrous Carbon and Graphite

Carbon fibers are filaments consisting of nongraphitic carbon obtained by carbonization either of synthetic or natural fibers, or of fibers drawn from organic precursors such as resins or graphitic carbons. The fibers are typically 92 percent or higher in carbon content and from about 5-15 microns (0.20 to 0.59 mils) in diameter. They are also characterized by flexibility, low density, high thermal stability, chemical inertness except to oxidation, corrosion resistance, low thermal expansion, low-to-very-high thermal conductivity, very low thermal expansion, and a broad range of tensile strengths, moduli, and elongation values. See Figure 4. These properties are highly anisotropic with respect to the fiber axis. Properties of major interest are those in the longitudinal direction, and distinctly different properties are exhibited in the transverse fiber direction. Many properties are related to the degree of microstructural orientation along the fiber axis. With increasing orientation of the graphitic crystallites, the following properties also increase in value: (a) tensile modulus, density, thermal conductivity, and electrical conductivity, and (b) tensile strength and elongation properties decrease in value.

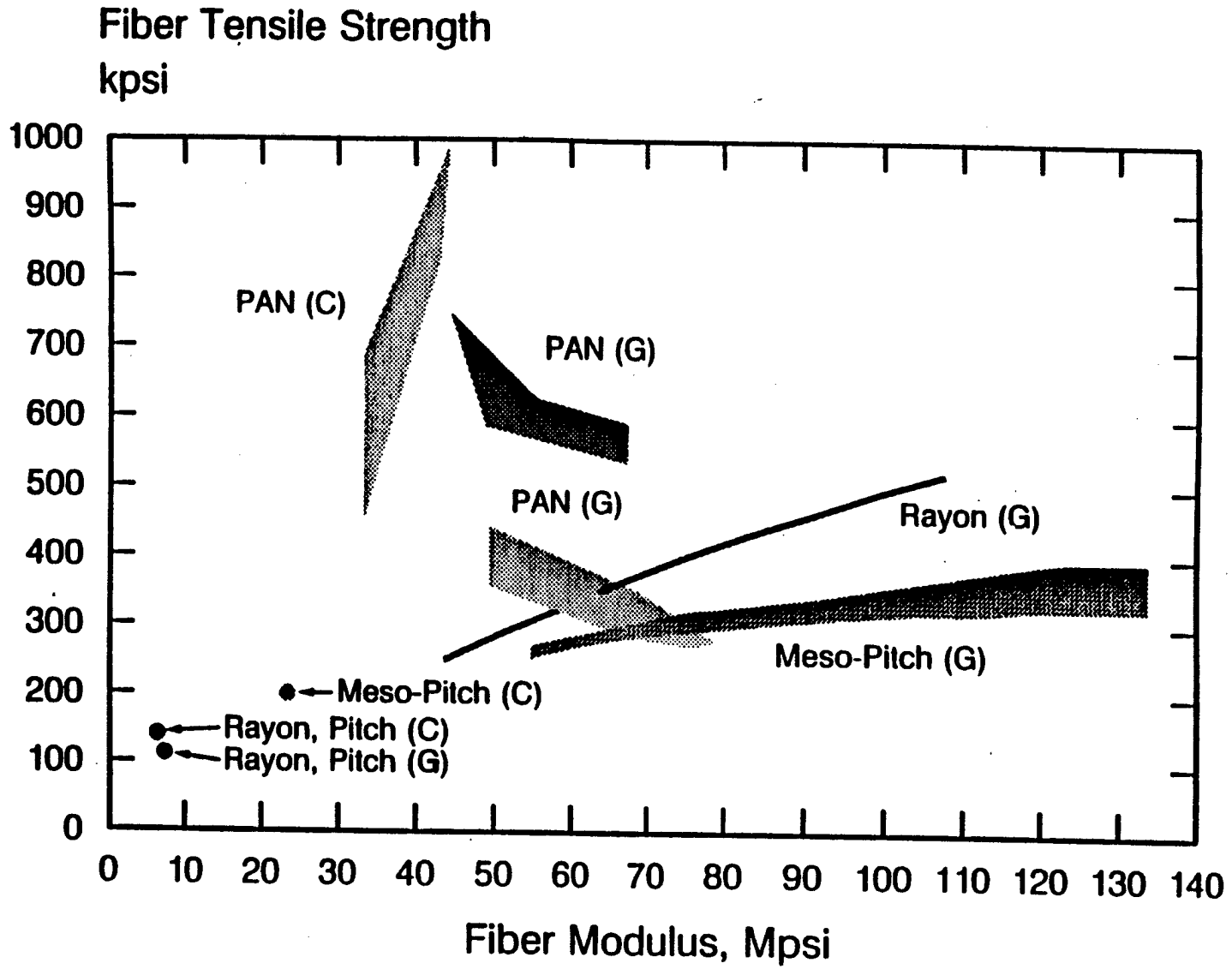


Figure 4. Tensile Strengths and Moduli Values of Available Carbon (C) and Graphite (G) Fibers.

Virtually all carbon fibers are formed by a "solid-phase" pyrolysis process, and thus they should be called "carbon" fibers. Unfortunately, the terms "carbon fiber" and "graphite fiber" were used since the advent of this class of fibers. This terminology has been retained in this report since it is more meaningful to worldwide readers.

Carbon fibers are manufactured by the constructive pyrolysis of precursor oxidized organic fibers. See Figure 5. Polyacrylonitrile (PAN) is the dominant precursory material, and it is widely used to manufacture high-strength and intermediate-modulus products. Mesophase pitch (petroleum, coal tar, or synthetic) is the dominant precursor for high-modulus carbon fibers, and isotropic pitch is used for low-strength, low-modulus carbon fibers. Viscose rayon also serves as a precursor for low-strength, low-modulus carbon fibers, although hot stress-graphitization processing will yield intermediate-strength, high-modulus carbon fibers. Production processes are proprietary, but many details have been disclosed in hundreds of published patents. In all cases the precursor organic fiber is first oxidized to a crosslinked thermosetting state to prevent melting or slumping during the subsequent carbonization cycle. The fibers may be further heat treated to a "graphite fiber" stage. The pyrolyzed fiber may then be surface treated with an oxidative process to enhance composite fiber-to-matrix bond or left in the non-surface-treated condition. The next process step is to apply a surface size (finish) to the fibers to preserve the surface treatment and enhance handleability of the fibrous products. The strands are then wound on spools, environmentally protected with a plastic film, and stored in boxes.

Carbon fibers are loosely classified according to their (a) maximum heat treatment temperature, (b) carbon content, (c) strength, (d) modulus, or (e) precursor fiber from which they were produced. Carbon fibers are generally manufactured at less than 1400°C (2552°F), and their carbon contents are about 92 to 96 percent. Graphite fibers are routinely manufactured at much higher temperatures. Strength and modulus designations, however, are the most commonly used. High tensile strength fibers are classified HT (tensile strengths above 3.0 GPa, 435 ksi). Intermediate modulus (IM) fibers have a tensile modulus from about 228 to 303 GPa (33 to 44 Msi). High- modulus (HM) fibers have stiffness values from about 350 to 524 GPa (50 to 76 Msi). UHM stands for ultrahigh modulus, and these fibers have moduli values of 689 GPa (100 Msi) or higher. High-modulus carbon fibers are sometimes called "Type I," and high-strength carbon fibers are designated "Type II." The latter fiber designations are now only infrequently used.

Carbon and graphite filaments are available in tow, yarn, plied yarn, staple yarn, cordage, fiber felts, tapes, nonwoven and woven fabrics, and other fibrous forms. The filament

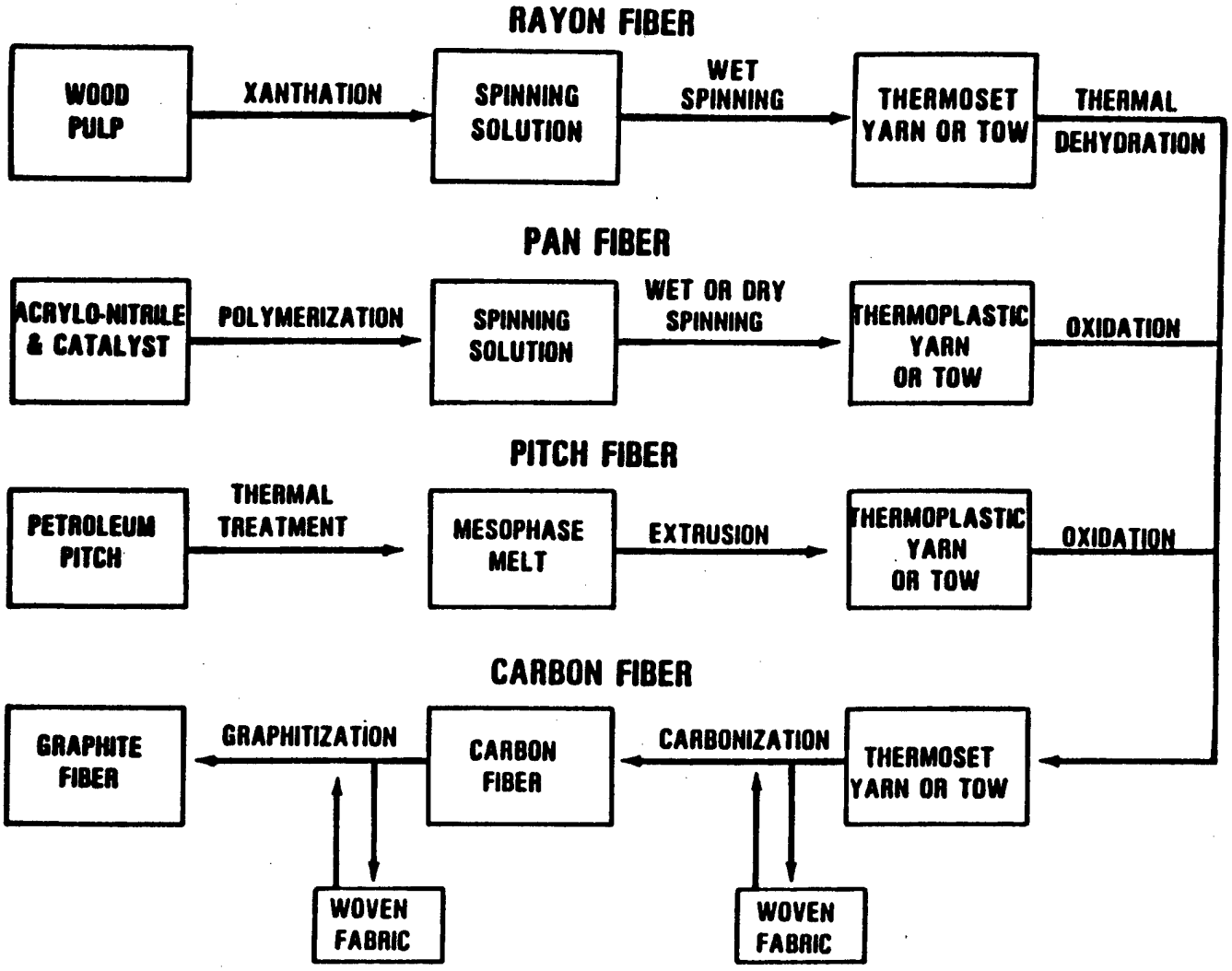


Figure 5. Schematic of Carbon Fiber Manufacturing Processes.

lengths range from continuous to any other shorter length. The number of filaments per strand generally ranges from about 500 to about 160,000, but 2,000 to 12,000 filament strands are most commonly used.

The price of carbon fibers depends upon many factors, including the precursor material, number of filaments per strand, number and type of process steps involved, physical form of the product, market volume, and other parameters. In general, low-modulus carbon fibers cost about $5.50/kg to $45/kg ($12/lb to $99/lb); intermediate- to high-modulus carbon fibers are about $18/kg to $475/kg ($40/lb to $1045/lb); and ultrahigh-modulus carbon fibers cost about $430/kg to $1000/kg ($946/lb to $2200/lb). Strands containing less than 3,000 filaments are quite expensive, and, of course, woven fabrics and preforms are more expensive because of the added labor involved in preparing the fibrous materials.

Table 6 lists the room temperature properties of carbon and graphite fibers which have been used in the manufacture of U.S. CCC materials. The first commercially-available carbon fibers were based on viscose rayon. Their low strength and low moduli values limited their use to ablative types of components (low stress or nonstructural). Typical applications included the nosecap and leading edges of the U.S. space shuttle, rocket nozzle throats and exit cones, and others. With the advent of high-strength, high-modulus stretch-graphitized yarns, the applications for rayon-based carbon fiber increased greatly. Their use in CCC components was short-lived, however, because of the introduction of high-modulus PAN-based graphite fibers. PAN-based carbon fibers are the most widely used. They offer high strength with intermediate-to-high modulus properties, relatively low price, availability in many strand sizes, and produced by many commercial sources throughout the world. PAN-based carbon fibers are presently marketed with room temperature tensile strengths of up to 6.85 GPa (1000 ksi). The fiber moduli values generally range from about 2.3 to 5.5 GPa (33 to 80 Msi). Intermediate- modulus PAN-based carbon fiber can be further heat treated to significantly higher moduli values while preserving most of the intrinsic tensile strength of the fiber. PAN-based carbon fibers are well known for their use in aircraft structures and golf shafts, but they have also been employed in various CCCs like missile nosetips, rocket nozzle throats, aircraft brake discs and others.

Pitch-based carbon fibers range from general purpose, low-cost materials to high-performance, high-cost materials. The properties and characteristics of this class of carbon fibers are the direct result of the precursors and processes employed to produce them. General purpose fibers are manufactured from a purified isotropic pitch. The resultant carbon fibers are typically low in strength and modulus, but relatively inexpensive. These characteristics lend themselves to

TABLE 6
PROPERTIES OF CARBON FIBERS USED IN CCC MATERIALS

	Rayon-Based			PAN-Based			Pitch-Based		
Fiber Properties*	*VYB*	*WYB*	*T-50*	*T-300*	*T-300HT***	*HMU*	*P-25*	*P-100*	*P-120*
CARBON CONTENT, %	90	99	99+	92	99	99+	97+	99+	99+
DENSITY, g/cm^3 (lb/in^3)	1.53 (0.055)	1.32 (0.048)	1.67 (0.060)	1.76 (0.064)	1.86 (0.067)	1.84 (0.067)	2.00 (0.072)	2.15 (0.078)	2.18 (0.079)
FIBER DIAMETER, micron (mils)	9.5 (0.37)	8.9 (0.35)	6.6 (0.26)	6.9 (0.27)	5.9 (0.23)	8.0 (0.31)	9.0 (0.35)	10.0 (0.39)	10.0 (0.39)
TENSILE STRENGTH, GPa (ksi)	0.836 (120)	0.621 (90)	2.21 (320)	3.65 (530)	2.41 (350)	2.76 (400)	1.38 (200)	2.24 (325)	2.24 (325)
TENSILE MODULUS, GPa (Msi)	41.4 (6.0)	41.4 (6.0)	393 (57)	234 (34)	317 (46)	379 (55)	159 (23)	724 (105)	827 (120)
TENSILE ULTIMATE STRAIN, %	2.00	1.57	0.56	1.58	0.76	0.73	0.87	0.31	0.27
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	- -	- -	- -	8.5 (5.0)	70 (40.5)	- -	- -	520 (300)	640 (370)
THERMAL EXPANSION, ppm/°C (ppm/°F)	- -	- -	- -	-0.06 (-0.33)	-0.11 (-0.61)	- -	- -	-1.45 (-0.80)	-1.45 (-0.80)

*Room Temperature values.
**HT - Heat treated above the usual processing temperature.

various uses in aircraft CCC brake discs, thermal insulation, static dissipation and other commercial applications. Future uses will likely involve the reinforcement of concrete products, filtration and purification of fluids, static dissipation, and many others. High-performance, pitch-based carbon fibers are formed from a liquid-crystalline (mesophase) pitch precursor or a blend or mesophase and isotropic pitches. In either case the fibers are melt spun, stabilized by oxidation, carbonized and finally graphitized. Fibers based on high mesophase content precursory pitches typically have very high axial tensile moduli and thermal conductivity values. These fiber attributes lend themselves to various structural and thermal management applications. High stiffness composites are especially important in spacecraft structures where weight is a great premium. The highly-ordered, pitch-based carbon fibers also offer unique heat transfer capabilities in various thermal management applications. Prototype spacecraft radiators have been fabricated and are being evaluated.

Table 7 presents an abbreviated chronology of carbonaceous and graphite fibers in terms of their first recorded development, year of achievement, and responsible organization for these types of constituent materials.

4.2.1.1 The 1950s

Pioneering research was conducted on carbon fibers during the 1950s. Hundreds of different organic fibers were pyrolyzed in an inert atmosphere to form carbon fibers typically having low density, low tensile strength, and low tensile modulus. Certain viscose rayon fibers were found to be ideal precursors because of their very low costs, moderate carbon yields, and availability from several sources.

In the late 1950s to early 1960s, the Union Carbide Corporation (UCC)/National Carbon Company commercialized their pyrolyzed viscose rayon fabrics. The very high temperature processed rayon fabrics, i.e., graphite fabrics, were first available in a plain woven cloth. The all-carbon fabric was initially used as a reinforcement for ablative plastic composites and for first generation CCCs.

4.2.1.2 The 1960s

Other forms of rayon-based carbon reinforcements became available in the 1960s. Five-harness and eight-harness fabrics were added to the list of available reinforcements. Carbon fabrics with a lower thermal conductivity were developed for the ablative thermal protection industry, while the more thermally stable "graphite" fabrics remained the choice for rocket nozzle throats and CCC materials. Rayon-based graphite felts, battings, yarns,

TABLE 7
CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC FIBERS

YEAR	FIBER EVENTS	IMPORTANCE	ORGANIZATION
1959	Rayon-based graphite fabric became commercially available	Reinforcement for the first all-carbon composite (CCC)	Union Carbide Corporation/Carbon Products Division/USA
1959	PAN-based carbon tows produced in a laboratory	First intermediate-modulus, low-strength carbon tows for composites	Government Industrial Research Institute/ JAPAN
1961	Rayon-based carbon/graphite yarns became commercially available	Continuous carbon fibers for production of 1-D and 2-D composites	Union Carbide Corporation/Carbon Products Division/USA
1962	PAN-based carbon tows became commercially available	First world production of PAN-based carbon tows	Nippon Carbon/JAPAN
1965	Low-strength, low-modulus pitch-based (polyvinylchloride) isotropic carbon fibers produced in the laboratory	First low-cost, pitch-based carbon fibers for reinforcement of advanced composites	Gumma University/JAPAN
1965	Hot-stretched, rayon-based graphite yarn became commercially available	First high-modulus, high-strength carbon yarn for structural CCCs	Union Carbide Corporation/Carbon Products Division/USA
1968/69	Hot stretching of PAN-based carbon fibers was demonstrated in a laboratory	Low modulus carbon fibers were transformed to high-modulus graphite fibers	Royal Aircraft Establishment/ENGLAND
1969/70	PAN-based carbon tows (meter lengths) with intermediate modulus and intermediate strength properties became commercially available	Higher-quality and lower-cost carbon tows	Courtaulds, Ltd./ENGLAND Morgan Crucible/ENGLAND Royal Aircraft Establishment/ENGLAND
1970/73	Pyrolytic graphite and metal carbide coated (rayon-based) graphite yarns were produced in a laboratory	Coating produced increased fiber strength, modulus, and oxidation resistance	Oak Ridge National Laboratory/USA
1974	Continuous filament graphite yarns from mesophase pitch were produced in a laboratory	High-density, high-modulus and low-strength graphite yarns	Union Carbide Corporation/Carbon Products Division/USA
1982	Mesophase pitch-based graphite fiber plant reached a production capacity of 0.023 Mkg (0.50 Mlb)	Graphite fibrous products with the highest available density, Young's modulus and axial thermal conductivity	Union Carbide Corporation/Carbon Products Division/USA

TABLE 7 (Concluded)
CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC FIBERS

YEAR	FIBER EVENTS	IMPORTANCE	ORGANIZATION
1983	Noncircular, mesophase pitch-based graphite fibers were developed in a laboratory	Unique, very high axial thermal conductivity fibers for thermal management CCC materials	Clemson University/USA
1985/87	Heat treatment of PAN-based carbon tows above their normal manufacturing temperature altered various fiber properties	High temperature processing of CCC materials reduced the fiber tensile strength and increased the fiber modulus	Acurex Corporation/Aerotherm Division/ USA
1987	Mesophase coal tar pitch-based graphite fibers were produced in a laboratory	First pitch-based carbon tows with both high strength and high modulus	Mitsubishi Kasei Corporation/JAPAN
1989	PAN fibers containing metal-boron compounds were produced in a laboratory and pyrolyzed into hybrid carbon fibers	Oxidation resistance of PAN-based carbon fibers was increased with boron additions	Hoechst Celanese Corporation/USA

and tows were also manufactured. Of particular importance, however, was the development of a hot-stretched rayon-based graphite yarn having high strength and intermediate modulus. This yarn was the first "true" structural carbon reinforcement. It had sufficient strength and abrasion resistance for weaving into various fabric geometries, but its high costs limited the material to only the most demanding aerospace products.

In the mid-1960s, graphite yarns, tows, and fabrics were coated with a fraction of one micron thickness of various refractory carbides, borides, and nitrides in an effort to improve their tensile strength and bonding to various matrices. These specialty fibers were never used in large quantities, although they later found applications in the nuclear and metal matrix composite industries. Other unique hybrid carbon fibers that were produced for the first time included whisker-containing graphite fibers and silica-coated carbon fibers. The latter fibers were probably the first oxidation-resistant carbon reinforcements produced in the laboratory, but they were never commercialized.

Research on PAN-based carbon fibers was initiated in 1961 at the Osaka Government Industrial Research Institute in Japan. Intermediate-strength and low-modulus carbon tows and yarns were produced. In the mid-1960s, research underway at the Royal Aircraft Establishment in England produced higher modulus fibrous products by restraining the PAN fiber during the oxidation (stabilization) process. These technologies were further developed, and commercial products were made available in the early 1970s.

Research on pitch-based carbon fibers was initiated in the early 1960s. The Union Carbide-Corporation/National Carbon Company successfully produced isotropic/mesophase pitch-based carbon fibers in the laboratory, and isotropic pitch-based carbon fibers were synthesized by researchers at the Gumma University in Japan.

4.2.1.3 The 1970s

The 1970s were very exciting years for the fibrous carbon and graphite industries. A wide range of fibrous products based on viscose rayon were commercially available from several domestic commercial sources. Manufacturing facilities for PAN-based fibrous carbons were built in Japan and England. Very high strength, intermediate-modulus, and low-cost carbon tows, yarns, and fabrics became available. Plans for licensing the manufacturing technology to domestic sources were also underway. Higher-modulus versions of the PAN-based fibrous carbon products were produced by raising the pyrolysis temperature, thus yielding a more dimensionally stable, lower outgassing, and higher thermally-conductive material. The technology

for creating PAN-based fibrous carbons with a very wide range of thermal conductivities was demonstrated, but the more thermally unstable, low thermal conductivity fibrous products were not commercialized nor used in CCC materials. Significant improvements were made in raising the modulus of petroleum pitch-based graphite fibers, but their high costs limited their use to ultrahigh performance CCCs like missile reentry nosetips.

4.2.1.4 The 1980s

Fibrous carbon developments during the 1980s were centered primarily on PAN-based materials. Production volumes were greatly expanded with attendant decreases in fiber costs. Tensile strengths were dramatically increased to about 6.9 GPa (1.0 Msi), tow sizes became available with a very wide range of filaments per strand, and many other desirable improvements were made. Newly-dedicated PAN fiber plants were built in the U.S. in order to have a total domestic capability for fibrous PAN-based carbons. All of these developments were aimed at satisfying the ever-growing aerospace organic matrix composite markets, but nevertheless, the same products proved to be very useful in CCCs for both military and civilian applications.

Mesophase pitch-based fibrous carbons continued to be improved with respect to tensile strength, strain-to-fracture (elongation), modulus, axial thermal conductivity and other features. DuPont Corporation introduced commercial tows having very high strength and strain-to-failure, but due to the very small market for this type of high-performance fiber, they discontinued manufacturing in the early 1990s. Meanwhile in Japan five different organizations were producing petroleum and coal-tar based pitch fibers for the marketplace. All of these products were high strength, low-to-very high modulus, high elongation, and competitively priced. At least one of these producers has temporarily suspended operations due to lack of world demand; others will likely do the same.

The need for an oxidation-resistant carbon fiber became apparent during the 1980s as ORCCC materials were being developed for high-temperature air and exhaust environments. External protective coatings (metallic carbides or boron compounds) and internal submicron particulate oxygen scavengers were investigated in an effort to improve the long time, high-temperature survivability of carbonaceous fibers in CCCs.

4.2.1.5 The 1990s

Fibrous carbons represented a rather mature technology at this point in time because of the extensive worldwide developments over the past two decades. This is not to

say that further improvements are not required. Quite to the contrary, there exist many specialized technical needs, and continued research (but at a lower rate) is anticipated.

The enormous worldwide production capacity greatly exceeded demand during the early 1990s because of a downturn in defense business. Some fiber producers have discontinued their total product lines, and significant retrenching of the industry may continue for some time. Some low-volume specialty products will likely disappear from the marketplace. Hopefully, existing commercial fibrous carbons can be substituted without incurring large component requalification costs. It is anticipated that funds available for the development of new and improved fibers will also diminish both in the government and the industry. More emphasis will be placed on using commercially-available materials (at some reduction in composite performance) rather than the continued development of new specialized (low volume) fibrous carbons.

On a more positive note, the costs of fibrous carbons for CCC materials will likely decline in the near future. Ongoing research will provide a better understanding of the materials:process:property relationships needed to produce high-quality fibers with predetermined properties. Hybrid and other specialty fibers containing ceramic and carbon phases will continue to be developed, thus enabling a long functional life in oxidizing service environments.

4.2.2 Fibrous Textile Preforms

Textile preforming is the method of placing reinforcing fibers in a predetermined arrangement prior to the formation of a composite structure. The products of this process are known as fibrous preforms. They exhibit a broad spectrum of pore geometries, pore distributions, fiber orientations, and densities.

Fibrous textile preforms for CCC materials exist in many different forms including:

(a) unidirectional (1-D) tow or yarn,

(b) bidirectional (2-D) woven fabrics, chopped fabrics and fibers, angled tape wrapped or angled filament wound,

(c) three-directional (3-D) in-plane fabric, braided fabrics, or orthogonal constructions, and

(d) n-directional (n-D) constructions ranging from 4-D to 11-D.

Textile preforms based on short fibers are used in a variety of CCC materials. Typical examples of short fiber preforms are: (a) mats, (b) felts, (c) needled felts, (d) nonwoven fabrics, (e) tapes, and (f) woven fabrics. These fibrous constructions generally have a very high pore volume and a large fiber surface area, both of which are important for CVI densified composites.

Needled felt preforms were developed in the mid-1960s. They were manufactured by assembling layers of short rayon fiber felt and then needle punching in the through-the-thickness direction. Some of the in-plane felt fibers were thus reoriented in the third direction, thereby raising the interlaminar properties of the composite. The needled felt preforms were first fabricated in flat, cylindrical, frusta and other configurations, and then pyrolyzed into the corresponding carbonaceous textile preform. The resultant preform served as the reinforcement for CVI pyrocarbon deposits. Full-scale CCC missile heatshields were manufactured using this process.

The needled felt assembly process was upgraded in the early 1980s by automation and the use of PAN-based fibers. A short-fiber fabric was first prepared with oxidized PAN fibers and then layered into the desired configuration. The textile preform was then needled through successive layers of fabric/tape to provide third direction reinforcement. For circular or frusta configurations, the special textile was tape-wrapped onto a mandrel and needled during the tape-wrapping process to produce a pseudo 3-D preform. The textile preform was then heat treated to successively higher temperatures to convert the oxidized PAN to carbon. Maximum temperatures used were on the order of 1600°C (2912°F). The carbonaceous preform was then densified with CVI pyrocarbon. Multiple densification cycles were typically used to obtain the desired composite density. The CVI composite was then heat treated up to about 2500°C (4532°F), or the heat treatment cycle was accomplished prior to the last CVI process cycle. Textile preforms manufactured in this manner are widely used for CCC brake discs, nozzle exit cones, and other applications.

Discontinuous fibers are also used as the reinforcement in low-density carbonaceous insulation materials. The insulation is composed of randomly-oriented, rayon-based carbon fibers in the X-Y direction which have been lightly bonded together with a carbonizable organic material. The short fibers impart low thermal conductivity, thermal stability, dimensional stability, and sufficient rigidity for shape retention and machining.

The major advantages of short fiber preforms are their ease of manufacture, low costs, conformance to various end-item shapes, and numerous fibrous sites for deposition of

matrix material. The chief limitations are low strength properties of the short fibers and density gradients in the composites.

Woven fabrics based on staple (short) fibers are also a textile preform of interest. Compared to fabric-reinforced composites, they are typically lower in costs, bulkier, and provide lower mechanical properties. CCC materials have been produced with these reinforcements, but they have shown promise only in CCC nozzle parts.

Where the ultimate in performance or weight reduction is required, continuous fibers are the reinforcement of choice. They are typically used in tapes and woven fabrics, which are available in hundreds of styles. Fabric styles vary according to the basic weave pattern, the type of yarn, yarn spacing, yarn packing efficiency, and the volume percent of yarn or tow in each direction. Uniaxial tapes typically have the majority of fibers oriented in a single direction and with a few percent of fibers interwoven crosswise to provide handling characteristics. The uniaxial (1-D) tapes provide the most highly directional properties, especially parallel to the axis of the fibers. Naturally, their transverse mechanical properties are low. Uniaxial tapes are used primarily in spacecraft structures where the fiber modulus can be advantageously employed. The two weave patterns most widely used in CCC materials are plain weave and satin weave. Figure 6 illustrates the construction of plain, 5-harness, and 8-harness satin woven fabrics. In plain weaves, warp ends are alternately woven over one fill yarn and under the next. Plain weaves provide the firmest, most stable construction, and provide porosity and minimum slippage with uniform strength in both directions. Rayon-based plain woven carbon fabrics have been used in 2-D involute and tape-wrapped CCC parts. Eight-harness satin woven fabrics are commonly employed in 2-D structural and 3-D pierced fabric-reinforced CCC parts. In satin weaves, warp ends are woven over several successive fill yarns and then under one fill yarn. In an 8-harness satin weave, for example, warp ends pass over seven fill yarns and under one. Satin weaves are more pliable than the plain weave, and they conform readily to complex shapes. They can be woven to high densities and are less open than other weaves. Strength is high in both the warp and fill directions. Although woven fabrics are more expensive than short fiber constructions or unidirectional tapes, significant cost savings are often realized in composite fabrication because labor requirements are reduced. Easier-to-handle woven fabrics are frequently used for complex shapes and in processes requiring careful positioning of the fibrous reinforcement.

High-modulus carbon fibers with low tensile strength have been woven into conventional fabric constructions but with great difficulty. In the early 1990s, however, the tensile strength and elongation-at-break properties of high-modulus carbon fibers were significantly increased. Such fibers in yarn and tow forms were much easier to weave with

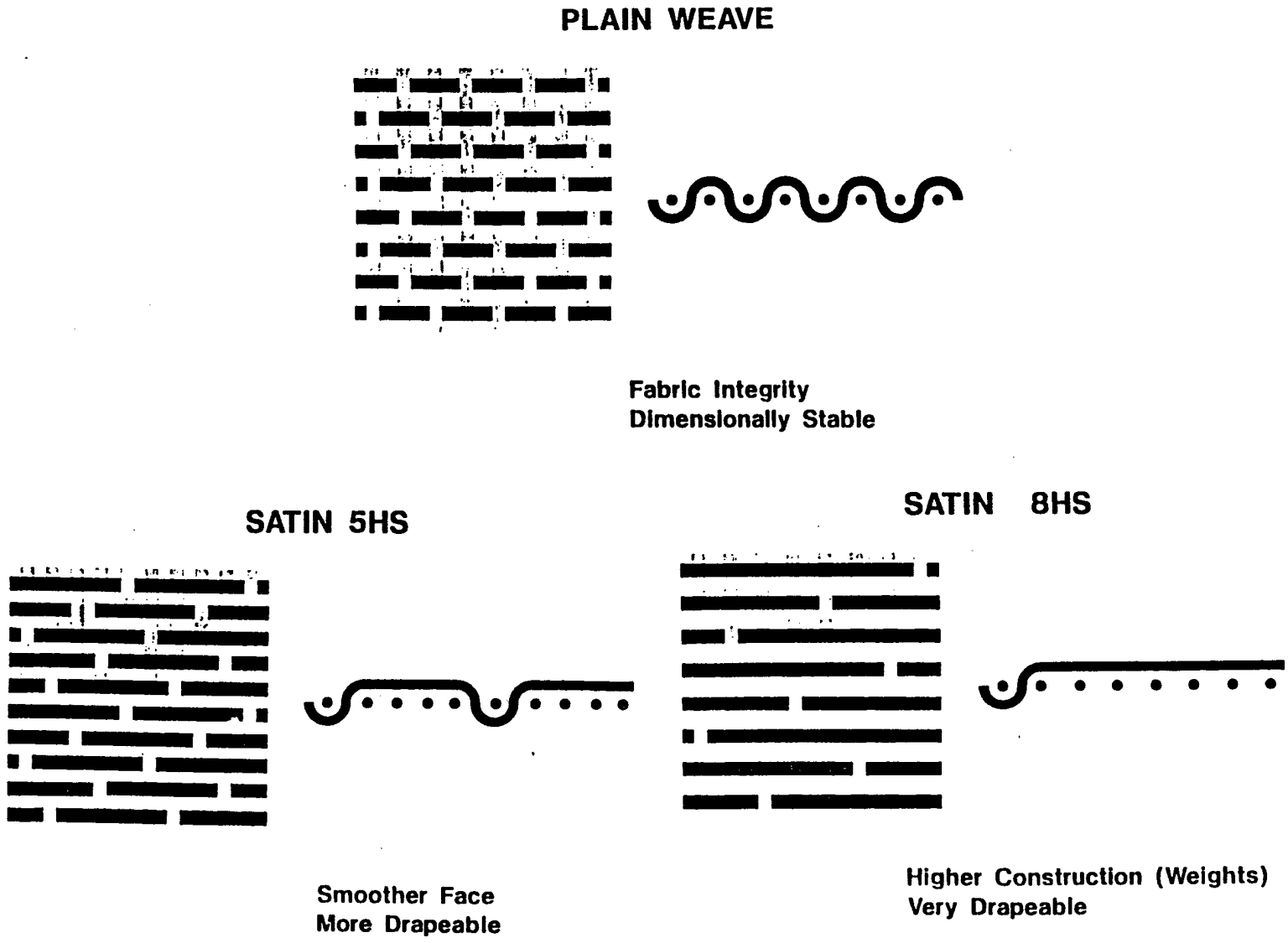


Figure 6. Illustrations of Woven Fabric Constructions.

conventional machinery. An alternate approach for obtaining high-modulus fibers in fabric forms was based on weaving low-modulus fibers and then heat treating the fabric construction to a relatively high temperature and in the presence of an inert gas. The advantage of the weave and heat treat approach was a product of moderate cost. Naturally, the crimp in the woven fabric was permanently set by the elevated temperature process.

Tows and yarns are also used to a limited extent in the production of CCC materials. First-generation rayon-based carbon and graphite yarns were low in strength and low in modulus, and hence they had limited use in fibrous textile preforms. Second-generation, stretch-graphitized, rayon-based graphite yarns were significantly higher in tensile strength, tensile modulus, and resistance to abrasion. They found uses in woven fabrics, unidirectional reinforcing rods in 3-D constructions, and filament-wound composites. As the first true structural graphite fibrous reinforcement, their performance was more than adequate for CCC materials. However, they were later and gradually replaced with PAN-based high-modulus carbon tows having lower costs, wider range of tow diameters (number of filaments), and multiple sources.

2-D CCC materials have been manufactured in a variety of constructions, including: parallel fabric laminates, chopped or mascerated fabrics, tapewrapped, spiral wrapped and filament wound. First-generation 2-D CCC materials were produced with woven or mascerated graphite fabrics. Plain woven fabrics were first used because of their availability, but later eight-harness and five-harness satin woven fabrics became commercially available and were utilized as the reinforcement. The advantages of woven fabric constructions are their high in-plane mechanical properties, conformance to simple shapes, and availability in a wide variety of woven constructions and thicknesses. The major composite limitations are typically associated with poor transverse properties. Mascerated fabrics are relatively inexpensive (scrap is sometimes used) and can be formed into just about any configuration. Principal limitations are low mechanical properties and a restriction to relatively thick parts.

Tapewrapped 2-D CCC materials were originally manufactured by pyrolysis of precursor 2-D plastic composites. This type of composite has not gained any popularity because of low interlaminar shear and low transverse strength properties.

The spiral involute is one of the most widely used 2-D CCC constructions. In the manufacturing process, prepreg carbon fabric gore patterns are cut and laid up on or in a mandrel. The fabric plies assume a spiral placement in which each ply goes from the inside to the outside in a spiral path (involute). The pattern shape is tailored to changes in the part contour and thickness. Both male and female tooling may be used. The major advantages of the involute construction

are: its higher interlaminar shear strength compared to conventional laminates, low through-the-thickness thermal conductivity, adaptability for contour changes and local hard points, and numerous manufacturing sources. The principal limitations are: sensitivity to fabrication errors like fabric wrinkles, low reinforcement tailorability, and complex analysis and testing. Most CCC exit cones are still manufactured with this type of construction.

2-D filament-wound preforms have also been used to manufacture CCC hollow cylinders and frusta (heatshield) configurations. Wet (liquid resin) or dry (prepreg) was wound onto a removable mandrel, the part cured, pyrolyzed and densified. The advantages of this type of construction are: automated and rapid placement of fiber, ability to vary lay-up angles over a wide range, minimum wall thicknesses, and availability of manufacturing equipment. The major disadvantages include: difficulty in maintaining the yarn or tow in their position during winding and processing, difficult to debulk without wrinkles, and others. Nevertheless, the filament winding process has been successfully used for the fabrication of missile heatshields and heat exchanger tubes.

Three-directional textile preforms exist in the form of through-the-thickness woven fabrics (like angle interlock), braided preforms, nonwoven orthogonal, and woven orthogonal constructions. Through-the-thickness woven fabrics have exhibited only limited property advantages (transverse tensile strength), and consequently they are not presently used. Braided textile preforms offer more promise. Triaxially-braided preforms consist of laying down plies with fixed axial reinforcements and quasi-hoop reinforcements in two helical directions. Layer thickness is built up by braiding multiple layers. The discrete layers of this braided preform rely solely on the strength of the matrix and the resin-fiber interface to transfer interlaminar stresses. Through-the-thickness braiding also uses fixed axial reinforcement, but the other fibers traverse in both the circumferential and radial directions. The through-the-thickness braided composite provides high through-the-thickness strength, but at the expense of lower hoop properties. The adjacent-layer interlock braiding is yet another process for manufacturing fibrous carbon textile preforms. In the process, yarns transverse only from one braid to an adjacent layer, and then back to the original layer, minimizing the out-of-plane angle of interlaminar connections. Regardless of the braiding process, the various textile preforms can be rapidly woven to net part shapes and subsequently densified by existing techniques. Braided CCC parts have been fabricated for rocket ramjet combustor chambers and solid propellant rocket nozzle exist cones. None of these applications have yet progressed to operational use. On the other hand, the nonwoven orthogonal constructions have been widely used in missile nosetip and nozzle applications. Nonwoven 3-D orthogonal preforms are produced with either dry yarns, prepreg tape, unidirectional composites,

woven fabrics, and various combinations thereof. Rectangular billet (block) preforms are prepared by interlacing dry yarns in the X, Y and Z direction; interlacing X and Y dry yarns around Z-oriented precured rods; or using woven fabric for the X-Y reinforcement and dry yarns or precured rods in the Z-direction. See Figure 7. 3-D preforms were also developed with cylindrical or polar coordinates. The manufacturing procedures are somewhat similar. The axial fibers provide the necessary tensile and compressive properties; the circumferential or hoop fibers provide strength in that direction; and the radial (through-the-thickness) fibers impart compressive strength, torsional shear strength, and low thermal conductivity. 3-D rectangular CCC billets have been the source of missile nosetips; thick-walled 3-D cylindrical CCC billets have provided nozzle throats and ITEs; and thin-walled 3-D frusta CCC configurations have been used for nozzle exit cones. First-generation 3-D CCC materials used stretch-graphitized rayon-based graphite yarns as reinforcements, but later composites were based on intermediate- or high-modulus PAN-based carbon fibers. Many improvements in 3-D orthogonal textile preforms were made in succeeding years including:

(a) utilization of newly-available PAN-based and pitch-based carbon yarns and tows,
(b) ability to weave smaller-diameter yarns and tows,
(c) ability to weave preforms with closer yarn/tow spacing,
(d) new configurations like hollow cylinders, frusta, contoured parts, etc., and
(e) semiautomated preform manufacturing.

The development of 3-D fibrous textile preforms probably did more to advance the use of CCC materials in defense applications than any other single development.

4-D to 11-D fibrous textile preforms enable a CCC composite to have greater isotropic properties, higher off-axis properties, and higher in-plane X-Y shear moduli compared to 3-D orthogonal fibrous constructions. The n-D preforms are assembled from precured unidirectionally-reinforced rods, and then the composite is densified by one of the standard matrix impregnation processes. The overall fiber volume of the preform is less than that of orthogonal constructions because of the numerous crossover points of the straight rods. Hence, the mechanical properties in each in-plane direction are less than those in 3-D CCCs. Extensive testing of n-D composites has shown that 4-D CCC composites are generally optimum on the basis of assembly complexity, manufacturing costs, and properties. Table 8 lists a condensed chronology of fibrous textile preforms.

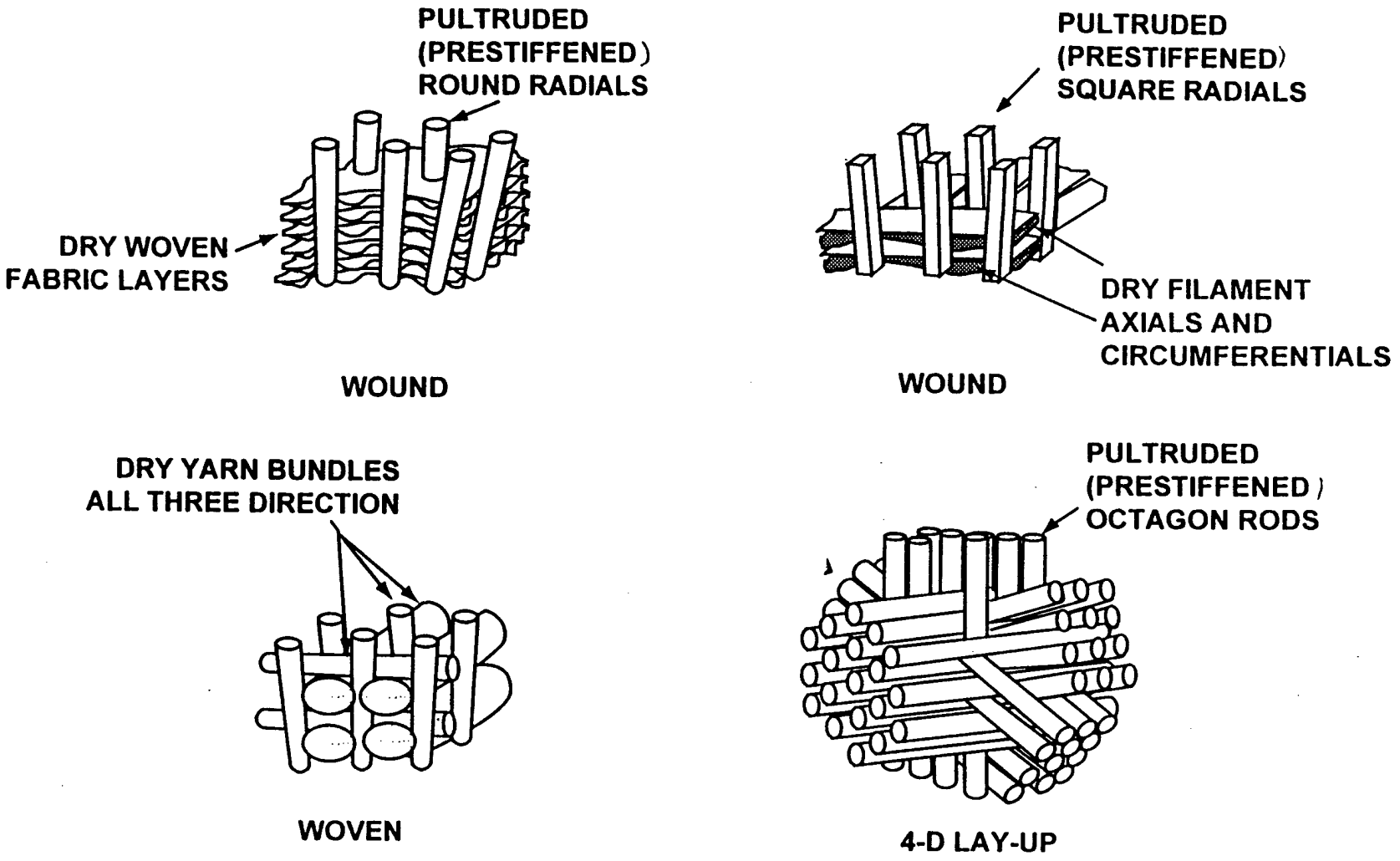


Figure 7. Illustrations of 3-D and 4-D Fibrous Textile Preforms.

TABLE 8
CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC FIBROUS PREFORMS

YEAR	PREFORM EVENTS	IMPORTANCE	ORGANIZATION
1964	Hand-operated loom was developed for weaving 3-D orthogonal fibrous yarn preforms	First thick-walled 3-D orthogonal fibrous (quartz) reinforcement for potential composite uses	Avco Corporation/Research and Advanced Development Division/USA
1965	3-D orthogonal graphite (rayon-based) needled felt block, cylinder and frusta were prepared in a laboratory	First short-fiber 3-D orthogonal fibrous graphite reinforcement for CCC materials	Sandia National Laboratories/USA
1966	3-D orthogonal and pierced fabric graphite (rayon-based) yarn preforms woven in a laboratory	First continuous graphite filament 3-D preform reinforcement for CCC materials	Avco Corporation/Space Systems Division/ USA
1968	3-D orthogonal fibrous graphite preforms were rigidized with CVD pyrolytic graphite matrix	Prevented yarn bundle movement during high pressure matrix infiltration	General Electric Company/Re-Entry Systems/USA
1969	3-D fine-woven, pierced fabric graphite (rayon-based) yarn preforms were prepared in the laboratory	Fibrous graphite preform suitable for a shape stable CCC nosetip of a missile reentry system	Avco Corporation/Space Systems Division/USA
1969	Precured graphite fiber/resin rods were used to assemble 4-D and 7-D preforms in a laboratory	Composite directional properties expanded beyond three principal (3-D) axes	Fiber Materials, Inc./USA
1969	4-D and 7-D graphite (rayon-based) yarn preforms prepared in the laboratory	Reinforcement provided less directional properties than 3-D orthogonal constructions	Societe Europeenne de Propulsion/ FRANCE
1971	3-D orthogonal graphite (PAN-based) needled felt preforms were fabricated in rectangular shapes	High strength and higher modulus fibrous graphite preform for CCC materials	Super-Temp Corporation/USA
1972	Automated machinery was developed for weaving 3-D orthogonal fibrous graphite block and cylindrical preforms	Faster and lower-cost approach for fabricating high-quality 3-D fibrous reinforcement	Brochier/FRANCE Aerospatiale/FRANCE

TABLE 8 (Concluded)
CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC FIBROUS PREFORMS

YEAR	PREFORM EVENTS	IMPORTANCE	ORGANIZATION
1974	3-D ultrafine-weave orthogonal graphite (PAN-based) tow preforms were assembled in block configurations	Smaller-diameter, closely-spaced yarns or tows used in fibrous carbon and graphite reinforcements for higher-performance CCC materials	Avco Corporation/Systems Division/USA Fiber Materials, Inc./USA
1976	3-D fine-woven orthogonal (pitch-based) graphite yarn preforms were woven in the laboratory	Higher-density, higher-modulus 3-D reinforcement for CCC materials	Fiber Materials, Inc./USA
1977	Automated woven 3-D cylindrical fibrous graphite tow preforms were manufactured	Faster woven and lower-cost fibrous graphite preforms for high-performance CCC materials	Aerospatiale/FRANCE Brochier/FRANCE
1980	Automated woven, contoured 3-D fibrous graphite preforms were woven in cylindrical shapes	Manufacture-to-shape fibrous graphite preform for reduced machining of CCC materials	Fiber Materials, Inc./USA
1981	Exact involute, fabric ply patterns were developed for 2-D CCC exit cones	Minimized fabric wrinkles and ply pattern distortions during exit cone fabrication	AF Wright Aeronautical Laboratories/ Materials Directorate/USA
1982	Automated 3-D needled fibrous graphite tape preform assembled	Fast carbon and graphite fiber preform assembly method for low-cost CCC materials	Societe Europeenne de Propulsion/ FRANCE
1983	3-D pierced fabric, fibrous (PAN-based) graphite reinforcements were fabricated in frusta configurations	Very large 3-D fibrous graphite reinforcement configurations for missile reentry CCC heatshields	Textron Specialty Materials/USA
1989	Largest (218 cm, 86 in. O.D.) 3-D thick-walled fibrous carbon (PAN-based) preform was woven with automated machinery	Polar woven fibrous carbon preform for a nozzle CCC ITE of a large solid propellant motor	Fiber Materials, Inc./USA

4.2.2.1 The 1960s

During the mid-1960s, the concept of 3-D fibrous graphite preforms became a reality in the forms of rectangular, circular, and frusta configurations. 3-D needled felt, 3-D orthogonal continuous filament, and 3-D woven fabric (continuous yarns in the through-the-thickness) preforms were first developed in the U.S. All of these developments utilized rayon-based graphite fibers/yarns/tows. In the late 1960s, wool-based carbon fibers were investigated, but their properties were not superior to the previously-developed rayon-based carbon fibrous preforms. Of greater importance were the developments of 3-D pierced fabric and two sources for 3-D orthogonal fibrous graphite preforms. Rectangular preform billets having 10.2x10.2 cm (4x4 in.) dimensions were woven, rigidized by CVD or pitch/resin impregnation techniques, and then densified. Four- and seven-directionally reinforced CCC billets were also manufactured and evaluated for composite properties. Another major materials development involved the concept of "fine woven" preforms. Small diameter yarns/tows and close yarn/tow spacing were required to insure original part-shape stability and delay the smooth-to-rough boundary layer transition (BLT) flow and heating. Interest in obtaining a more isotropic balance of CCC properties heightened in the late 1960s. A U.S. company manufactured 4-D fibrous graphite braided preforms and attendant CCC materials were produced. These particular preforms were low cost and could be quickly woven, but the attendant CCC materials apparently did not offer any significant property advantages.

4.2.2.2 The 1970s

The development of 3-D and n-D fibrous graphite preforms reached their peak in the early 1970s. 3-D orthogonal, 3-D pierced fabric, 4-D, 7-D, and 11-D fibrous preforms were produced in a variety of sizes and shapes. Automation of the 3-D dry yarn and pierced fabric preform assemblies was achieved. The use of precured rods in the manufacture of n-D fibrous graphite preforms also became highly developed.

During the late 1970s, one exceptionally skilled, foreign company (Brochier) developed an automated process for weaving 3-D fibrous graphite preforms in a variety of configurations. Several previous attempts by U.S. industries were not successful. U.S. 3-D fibrous preforms could be manufactured in high quality, but at slow speeds, and high costs. Any attempt to speed up the weaving process resulted in a reduction of preform quality. The foreign source weaving technology has since been used in a number of important U.S. aerospace CCC components.

4.2.2.3 The 1980s

The 1980s were devoted to the acquisition of an automatic fibrous graphite preform manufacturing capability in the U.S. based in part on overseas technology. Fibrous graphite preforms in many different configurations were demonstrated and successfully utilized in U.S. aerospace CCCs. Large 3-D rectangular fibrous graphite billets were manufactured, densified, and then sectioned into appropriate sizes with significant cost savings for ultimate use in missile reentry nosetips. Metal (metal carbide) fiber-reinforced CCC materials were developed with superior particulate erosion resistance and made available for an all-weather missile nosetips. 3-D CCC for solid rocket motors was optimized by contour weaving of the preforms, thus reducing the absolute surface ablation rate.

More refined developmental efforts began to be devoted to 5-D, 6-D and 8-D fibrous preforms. The 5-D fibrous construction was evaluated for CCC laser mirror substrates, but the effort was later abandoned.

To summarize, 2-D, 3-D, and 4-D preform constructions appear to have the greatest utility for both current and future CCC materials. The textile weaving technology and manufacturing of fibrous graphite preforms are now highly developed in the U.S. and France and, to a lesser extent, Russia, Korea, and the People's Republic of China (PRC).

4.2.3 Carbonaceous and Graphitic Matrices

Carbonaceous matrices are one of the important constituents in a CCC material. They are typically low in strength, contain voids and cracks, and may differ greatly with respect to microstructure and other properties.

The main function of a matrix is to transfer mechanical loads to the stronger fibrous reinforcement, but they also have other functions. They preserve the original placement of the reinforcement in the composite, and they provide environmental protection for the fibers. They may also have specialized purposes like enhancing the frictional characteristics in CCC brake discs.

CCC materials contain different amounts of matrix depending upon the final composite properties desired. Structural CCC materials are typically composed of one-third matrix which provides a maximum amount of fibers for high mechanical properties. On the other hand, CVI pyrocarbon may constitute up to four-fifths of the composite to optimize wear and heat dissipation.

Matrix requirements vary but, in general, they should:

(a) yield a high carbon content upon pyrolysis,
(b) undergo pyrolysis in an orderly manner,
(c) exhibit minimal shrinkage during pyrolysis,
(d) be readily processible and reproducible,
(e) be relatively low in cost,
(f) be available from multiple sources, and
(g) possibly other characteristics including graphitizability.

Carbonaceous and graphitic matrices are typically derived from three types of precursors. The first type is based on thermosetting resins. The liquid impregnating resin is cured and then undergoes solid phase pyrolysis to form a char of moderate porosity and relatively low density. Phenolic and epoxy resins are two types of commonly-used thermosetting resins. The second type of matrix precursor is based on pitch materials. Pitch materials are solid at room temperature and are heated to a molten state in order to have a viscosity suitable for impregnation. Pitches undergo a liquid phase pyrolysis to form a coke of moderate density. Coal tar and petroleum pitches are two types of commonly-used infiltrants. The third type of carbon matrix is derived by the chemical vapor deposition/infiltration process. Hydrocarbon gases are the source of the deposited carbon. The deposits are typically high in density and may range from isotropic to highly anisotropic in properties. Heat treatment of the CVD/CVI deposit at temperatures above the process temperature may alter their properties.

Solid-state pyrolysis of synthetic or natural thermosetting polymers allows the retention of the morphology of the precursor material. Carbonaceous char products produced in this manner are isotropic in properties, due to the random orientation of the small and grossly-defective lamellar domains. At processing temperatures above 1000°C (1832°F) and high pressures, the highly crosslinked resinous material forms an impermeable glassy form of carbon.

Resins and resinous blends are the precursory material for many carbonaceous matrices. Phenolics, epoxy novolacs, furfural alcohol, and blends thereof have been used since the advent of CCC materials. Phenolic resins are the most widely used, particularly for prepreg employed in manufacturing 2-D fabric-reinforced structural CCC materials. Phenolic resins are chemically pure, readily available from numerous sources, and relatively inexpensive. Phenolic resins undergo high shrinkage during pyrolysis, and they have only a moderate carbon yield (50 percent). The char formed is typically glassy (brittle), amorphous, contains numerous microcracks and pores, and it is nongraphitizable. Char yields have been improved by increasing

the aromatic content of the resins. Such products are used commercially in the manufacture of 2-D fabric-reinforced CCC materials.

Higher carbon-yielding matrices have also been derived by blending thermosetting resins with higher aromatic content pitch materials. A low viscosity resin is typically used to reduce the viscosity and turn solid pitches into liquid impregnating fluids. The carbon yields of these blended matrices are higher than those of phenolics, i.e., about 70 percent vs. 50 percent.

Thermoplastic aromatic materials are also used as matrix precursors. The matrices are polynuclear aromatic hydrocarbons in the form of coal tar or petroleum pitches. The outstanding advantage of these matrices is their high coke (carbon) contents, i.e. about 85 percent. However, the molten matrix must be retained in the preform during carbonization to realize the high density coke structure. Pitches are very low-cost materials, available from numerous sources, pass through a liquid state during pyrolysis, exhibit minimal shrinkage and gas evolution during carbonization, and form a graphitizable matrix. The matrix generally is higher in density and contains less porosity than chars formed from thermosetting resinous materials. In addition the pitch-based coke matrix can be altered significantly by further heat treatment. Since the precursor pitch is chemically impure, some contaminants may be retained in the coke depending upon the final heat treatment temperature. Three approaches have been developed to upgrade the features of pitches. In the first approach, the pitch material was heat treated to reduce the low-temperature volatiles and increase the mesophase content. These specialty pitches exhibited a reduced exotherm during high-pressure carbonization, decreased outgassing, and the coke residue was more uniform and contained smaller pores. The second approach was based on the synthesis of synthetic pitch structures. Chemically pure pitch precursors were synthesized in the form of cinnamylidene indene, isotruxene, and acenaphthylene. These synthetic pitches processed much like regular pitches, but they were more expensive. In addition they did not exhibit any outstanding properties. The materials were therefore not commercialized. CCC materials developers were quick to realize that blends of resinous and pitch materials may yield useful products. The materials were chemically compatible due to their similar aromatic chemistries. Infiltrant viscosity could be varied greatly depending upon the amount of lower-viscosity resin used. In all cases, however, the carbon yield of resinous materials was increased by the addition of pitch material. Some of these blended precursory carbon-matrix materials are still used in CCC manufacturing. The third development involving thermoplastic pitches has been its use as a prepreg matrix followed by oxidative crosslinking to a thermoset. The process is similar to the oxidative stabilization of pitch fibers prior to the first pyrolysis step. Table 9 lists a condensed chronology of carbonaceous and graphitic matrices.

TABLE 9
CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC MATRICES

YEAR	MATRIX EVENTS	IMPORTANCE	ORGANIZATION
1960	Phenolic and phenolic-furfuryl alcohol resins were used to produce resin chars	Commercially-available resins produced adequate char matrices for first-generation 2-D CCC materials	LTV Aerospace and Defense Company/ USA
1962	Petroleum pitch-furfuryl resin blends provided the proper impregnant viscosity and a higher char yield	Fewer matrix impregnation-carbonization cycles needed to reach fully dense graphite composites	Union Carbide Corporation/Carbon Products Division/USA
1965	CVD/CVI pyrolytic carbon and graphite matrices infiltrated into fibrous graphite preforms	High-density matrices produced with existing processing equipment	AEC/Sandia Laboratories/USA
1965	Mesophase pitch formation mechanism demonstrated in a laboratory	High-density, graphitizable coke matrix for CCC materials	CSIRO/Division of Coal Research/ AUSTRALIA
1965	Highly aromatic phenolic resin impregnants were synthesized in a laboratory	Higher char-yielding matrices compared to commercially-available phenolic resins	Hughes Aircraft Company/USA
1966	Intractable high-carbon polyphenylene resin powders were dissolved in phenolic resins	Greatly increased the char yield of phenolic impregnating matrices	Air Force Materials Laboratory/USA
1967	Pitch matrices were combined with commercial epoxy or phenolic resins to yield new fibrous preform infiltrants	Higher carbon yields coupled with suitable infiltrant properties were demonstrated	AEC/Sandia National Laboratories/USA
1969	Synthetic pitch matrices were prepared in a laboratory	High-purity, high coke-yielding matrix impregnant for CCC materials	Union Carbide Corporation/Nuclear Division/Y-12 Plant/USA
1972	High-pressure infiltration-carbonization process (HIPIC) using coal tar pitch for densification of porous graphites was adapted for use with fibrous graphite preforms	HIPIC process enabled the production of high-density CCCs with fewer densification process cycles	Union Carbide Corporation/Oak Ridge Y-12 Plant/USA Fiber Materials, Inc./USA Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1980	Solvent-extracted petroleum pitches were developed for densification of fibrous carbon preforms	High coke-yielding matrix for low-pressure infiltration of porous fibrous preforms	Acurex Corporation/Aerotherm Division/ USA

TABLE 9 (Concluded)

CHRONOLOGY OF CARBONACEOUS AND GRAPHITIC MATRICES

YEAR	MATRIX EVENTS	IMPORTANCE	ORGANIZATION
1984	Improved petroleum pitch infiltrant became commercially available for CCC materials	High coke yielding matrix with superior processing properties	Ashland Petroleum Company/USA
1987/90	Highly-aromatic, polyarylacetylene resins were used for densifying CCC materials	Processible, low-shrinkage char-forming matrix for CCC materials	The Aerospace Corporation/Materials Sciences Laboratory/USA Gencorp/Aerojet Propulsion Division/USA
1988/89	Molecularly-dispersed inhibitors or oxygen scavengers were incorporated into resinous char-forming matrices	Oxidation inhibition was provided at the molecular level	Aerojet Solid Propulsion Company/USA
1989	Oxidative stabilization process was originated for thermosetting molten pitch in 3-D fibrous pitch	Molten pitch expulsion at low ambient pressures was prevented	University of California/Department of Mechanics and Engineering Sciences/USA
1991	Very high char-yielding (71%) phenolic resin impregnant was synthesized in a laboratory	Fewer densification process cycles were needed to produce full-density CCC materials	Chung-San Institute of Science and Technology (CSIST)/TAIWAN
1991	Predetermined molecular weight fractions of pitch matrices were obtained by using a supercritical fluid extraction process	Enabled the identification of desirable pitch fractions for carbon fiber and matrix research	Clemson University/USA
1991	Naphthalene-based mesophase pitches were developed for preform densification	New and processible coke-forming matrix for 2-D and 3-D CCCs	Kyushu University/USA

4.2.3.1 The 1960s

Phenolic and phenolic-based resins served as the first carbon-matrix precursory materials. The phenolic resin was typically used in the form of a prepreg, cured, and then pyrolyzed. Subsequent resin impregnations were needed to densify the CCC and to reduce the porosity as low as possible. Furfural alcohol was used to reduce the viscosity of the impregnating solution. In the mid-1960s developmental efforts were expended to increase the char (carbon) yield of the resinous impregnants. Phenolic resins, which were originally developed for ablative plastic composites, were blended with higher carbon-containing materials like epoxy novolac resins or pitches. Higher aromatic content phenolic resins were also synthesized, some of which were commercialized by the resin industry.

Graphitizable, high-density matrices were also available via CVD and CVI processes. These processes were developed prior to the 1960s by the graphite industry. Carbon-matrix yielding processes, however, were significantly improved during the 1960s in support of aircraft CCC brake discs and missile reentry CCC heatshield programs.

4.2.3.2 The 1970s

The development of higher carbon-containing matrices reached its peak during the 1970s. Highly-aromatic polyphenylene resins were synthesized, but their lack of processibility kept them in the "research curiosity and test tube" phase. The author found an early use for polyphenylene resin by adding the powdered resin to liquid phenolic resin, thereby increasing the total carbon content of the blended resinous mixture. This concept was subsequently used by other researchers in their efforts to develop improved CCC matrices. Another unique approach for high-coking matrices was developed by the AEC Oak Ridge National Laboratory. Their personnel reasoned that the purity level and processibility of coal tar and petroleum pitches could be greatly improved by chemical synthesis of synthetic pitches. Acenaphthylene, cinnamylidene, isotruxene, and similar aromatic compounds were prepared and evaluated. The attributes of the new synthetic pitches (compared to natural pitches) unfortunately were insufficient to warrant further development.

Chemical synthesis efforts on processible, high-aromatic polymers was also accomplished in the late 1970s. Ethynylated aromatic resins were prepared and evaluated. They offered many processing advantages and char-forming characteristics, but their higher costs (compared to phenolics) and lack of commercial sources has precluded their use in CCC production.

4.2.3.3 The 1980s

The 1980s involved only limited improvements in the properties and processibility of resinous and pitch infiltrant materials. Petroleum pitches were solvent extracted or mechanically filtered to improve their purity and carbon microstructural features. A new petroleum pitch product having improved coking characteristics also became commercially available. Techniques were developed for oxidative stabilization of pitch matrices in fibrous preforms. This approach was akin to similar processes used to stabilize pitch fibers. Perhaps the most exciting new process involved a very fast densification process based on the pyrolysis of hydrocarbon fluids. Preform densification was reduced from many cycles and many hours to only several hours and possibly two cycles. This process was acquired by the U.S. from French developers, but as yet it has not been used in a production mode.

4.2.3.4 The 1990s

Research on high char-forming, processible polyarylacetylene resins continued into the early 1990s. Most matrix efforts, however, were centered on improving the oxidation resistance of carbonaceous matrices. Ceramic forming precursory materials and submicron particulate containing matrices were developed and evaluated.

4.2.4 Composite Fabrication and Processing

The fabrication and processing of CCC materials are complex, labor intensive, lengthy, and expensive. More than 100 materials and process variables must be defined and controlled in order to produce a product having the desired properties .

CCC materials are fabricated and processed by a series of steps which involve (a) selection or preparation of the fibrous reinforcement, (b) selection and use of a carbon-forming organic compound, (c) manufacture of the matrix-impregnated fabric or infiltrated fibrous preform reinforcement, (d) pyrolysis of the composite in the absence of oxidizing species, (e) redensification with a carbon-forming matrix at low-to-high pressures, (f) repeated impregnation and pyrolysis until the desired density is reached, and (g) an optional ceramic coating and infiltrant if the article is to be used in a hot oxidizing atmosphere.

CCC materials are densified by either (a) chemical vapor infiltration (CVI) processes, (b) liquid matrix infiltration (LIP) techniques, or (c) combinations thereof. The specific process selected depends upon the (a) part thickness, (b) part size, (c) composite properties desired, (d) economic factors, (e) available equipment, and (f) time considerations.

4.2.4.1 The CVI Process

In the CVI process a reactive gaseous mixture is introduced into a chamber so that it surrounds the components to be coated or infiltrated. Precursory carbonaceous gases are either (a) city gas, (b) methane, (c) propane, (d) propylene, (e) benzene, or (f) others. The components and the chamber are usually heated in order to initiate the necessary thermochemical reactions. As the gas contacts the hot preform surfaces, pyrolytic carbon is deposited onto the hot surface and the volatile by-products (mainly hydrogen) are swept away. The type or pyrocarbon formed as well as the deposition rate depends upon many parameters, including (a) temperature, geometry and thickness of the substrate, (b) reactant and carrier gas composition and temperature, (c) processing pressure, and (d) possibly other factors. A fibrous preform is rigidized prior to a CVI/CVD process, or it is supported on a tool (usually graphite) to prevent deformation during heat treating operations. A typical CVD densification process is carried out at 1100°C (2012°F) and with pressures ranging from 500 to 3000 Pa (0.07 to 0.43 psi). The total deposition time is about 650 hours to reach a density of 1.6 g/cm^3 (0.058 lb/in^3) for a 1.0 cm (0.4 in) part. Parts up to 1300 mm (51 in) diameter and 1500 mm (59 in) length have been infiltrated and coated.

There are four basic CVI processes and combinations thereof. They include (a) isothermal, (b) thermal gradient, (c) pressure gradient, (d) rapid densification, and (e) various modifications and combinations of the techniques.

4.2.4.1.1 *Isothermal Process*

The isothermal CVD/CVI process is illustrated in Figure 8. In the process a fibrous preform or porous substrate is placed within a furnace susceptor. The preform is then radiantly and uniformly heated to about 990-1150°C (1814 -3708°F). The furnace temperature and pressure (typically 6 kPa, 50 torr) are kept constant throughout the deposition process. Pyrocarbon is deposited from the gaseous phase, and the carbonaceous deposit is preferentially contained on and near the surface region of the heated part. Surface bottleneck pores are gradually closed off as the process continues. Consequently, the material open porosity decreases with deposition time. All of the open pores and cracks are eventually closed, and a surface crust builds up. The part must then be cooled, removed from the furnace, and the surface machined to open up porosity under the surface crust. The partially densified part is then placed in the furnace again, reheated, and the deposition process continued. Substrates with thicknesses over 2.54 cm (1.0 in) may require surface machining up to three times before a

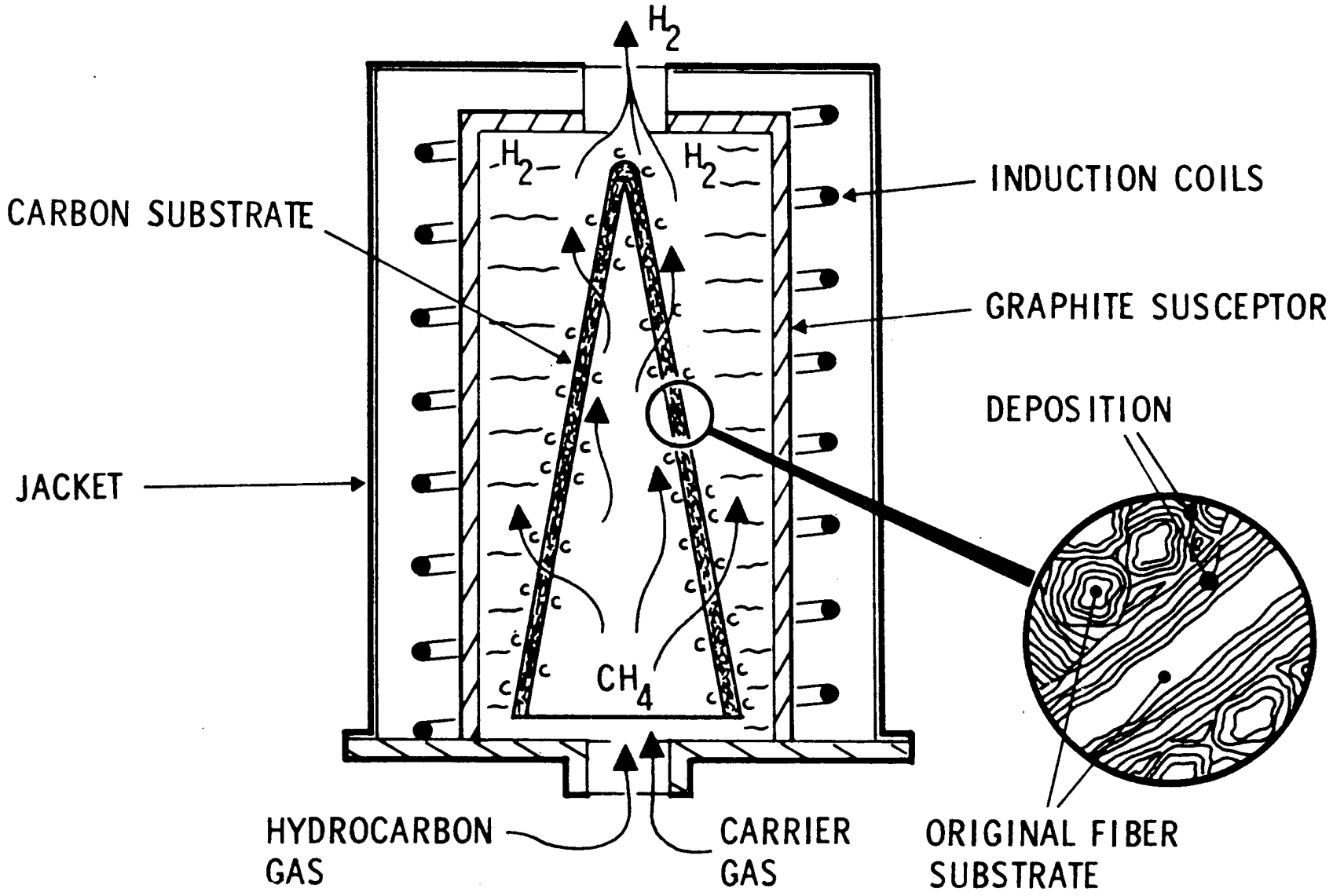


Figure 8. Schematic of the Isothermal Chemical Vapor Infiltration (CVI) Process.

sufficient amount of matrix is deposited into the substrate material. Pyrocarbon deposits obtained by the isothermal method are typically of high density and modulus, reproducible, and graphitizable. Similar and dissimilar parts can be simultaneously processed. The major limitations of the isothermal CVI method are: (a) long infiltration times (50 to 120 hr/cycle), and (b) preferential filling of pores near the substrate surface.

4.2.4.1.2 *Thermal Gradient Process*

In the thermal gradient process, a porous textile carbon preform is placed on a graphite mandrel. The purpose of the mandrel is to insure the required shape of the final part and to prevent deformation and movement of the part during processing. Inductive coils heat the mandrel surface, with the hottest portion of the preform in contact with the mandrel. Hydrocarbon gas is passed through the heated preform, and deposition occurs mainly on the hottest region near the mandrel. As pyrocarbon builds up on the inner surfaces, the highest temperature region moves toward the outside of the preform and the deposition follows this thermal front. A more uniform through-the-thickness deposit is obtained in this manner.

The thermal gradient process (a) is suitable only for large individual parts, (b) is relatively low in reproducibility, (c) requires a separate coil for each part, and (d) has an inability to process dissimilar or multiple parts at one time.

One variant of the thermal gradient process involves added forced flow. In the forced flow-thermal gradient system, carbon-containing vapor is passed through a fibrous preform. The porous preform is heated to a temperature of about 1200°C (2192°F) in an electric furnace. The flow provides faster infiltration and finishes a 1-cm (0.39-in) thick section in as little as eight hours. The temperature gradient insures vapor flow and uniform formation of carbon matrix throughout the part. This modified process reportedly allows more specific control over materials characteristics, and produces parts thicker than those being made with conventional processes.

4.2.4.1.3 *Pressure Gradient Process*

The third major CVI deposition method involves differential pressures or a vapor pressure gradient within the substrate. In this variant of the isothermal process, the inner portion of the preform is sealed off from the furnace at the base. Hydrocarbon or other precursory gases at a positive pressure (compared to the furnace pressure) flow through the porous preform and react with the heated substrate. The carbon or ceramic matrix is thus deposited in a uniform manner. As in the thermal gradient process, an outer pyrocarbon crust

does not build up on the reactive surfaces. The attributes of the pressure gradient process are: (a) infiltration times are short, (b) carbon deposits are uniform, and (c) the product has the same shape and size as the preform and thus expensive machining to final shape can be minimized.

4.2.4.1.4 *Rapid Matrix Densification Process*

Carbon-matrix densification processes that are fast and economical have been sought for many years. In recent years a French originated process has been demonstrated to greatly shorten the carbon-matrix deposition time. In the process a porous preform (typically a 2-D or 3-D fibrous carbon substrate) is placed in a reactor. The porous preform, which acts as the carbon susceptor, is immersed in a liquid hydrocarbon or molten precursor. The preform is inductively heated to a high temperature by means of a coiled tube outside the reactor. During heating, the carbon precursor boils and the vapor is forced into the porous substrate. Thermal decomposition of the hydrocarbon gases results in a carbon deposit on the highest temperature surfaces. The noncracked vapors are condensed within a cooling system located above the reactor. High carbon densification rates are due to: (a) high process pressures compared to other CVI methods, (b) strong convection due to the thermal gradient, and (c) densification from the internal to the external part of the preform (avoids plugging and reduced densification in the external pores). A densification of rate of about 1-10 mm/hr (0.0039-0.039 in/hr) has been achieved which is many times faster than conventional CVI processes.

4 2.4.2 The Liquid Infiltration Process

A liquid infiltration process (LIP) is used to coat or impregnate fibrous carbon reinforcements with a precursory carbon-forming matrix. As the process name infers, a liquid carbon-containing matrix like a thermosetting resin or a thermoplastic pitch is used to coat or infiltrate a fibrous structure. The matrix impregnation process is carried out at atmospheric-to-low pressures, or very high gas pressures.

4.2.4.2.1 *Low Pressure Infiltration (LPI)*

The fabrication of a 2-D fabric-reinforced CCC composite by atmospheric pressure resin infiltration and carbonization is illustrated in Figure 9. Resin-impregnated carbon cloth is laid up to form a 2-D laminate. The solid part is usually cured in an autoclave and then removed. After cure, the laminate is postcured to remove any remaining resinous volatiles. The part is then placed in an inert (nonoxidizing) atmosphere furnace and slowly carbonized. For dimensionally-critical CCC parts, the cured plastic part is left on a

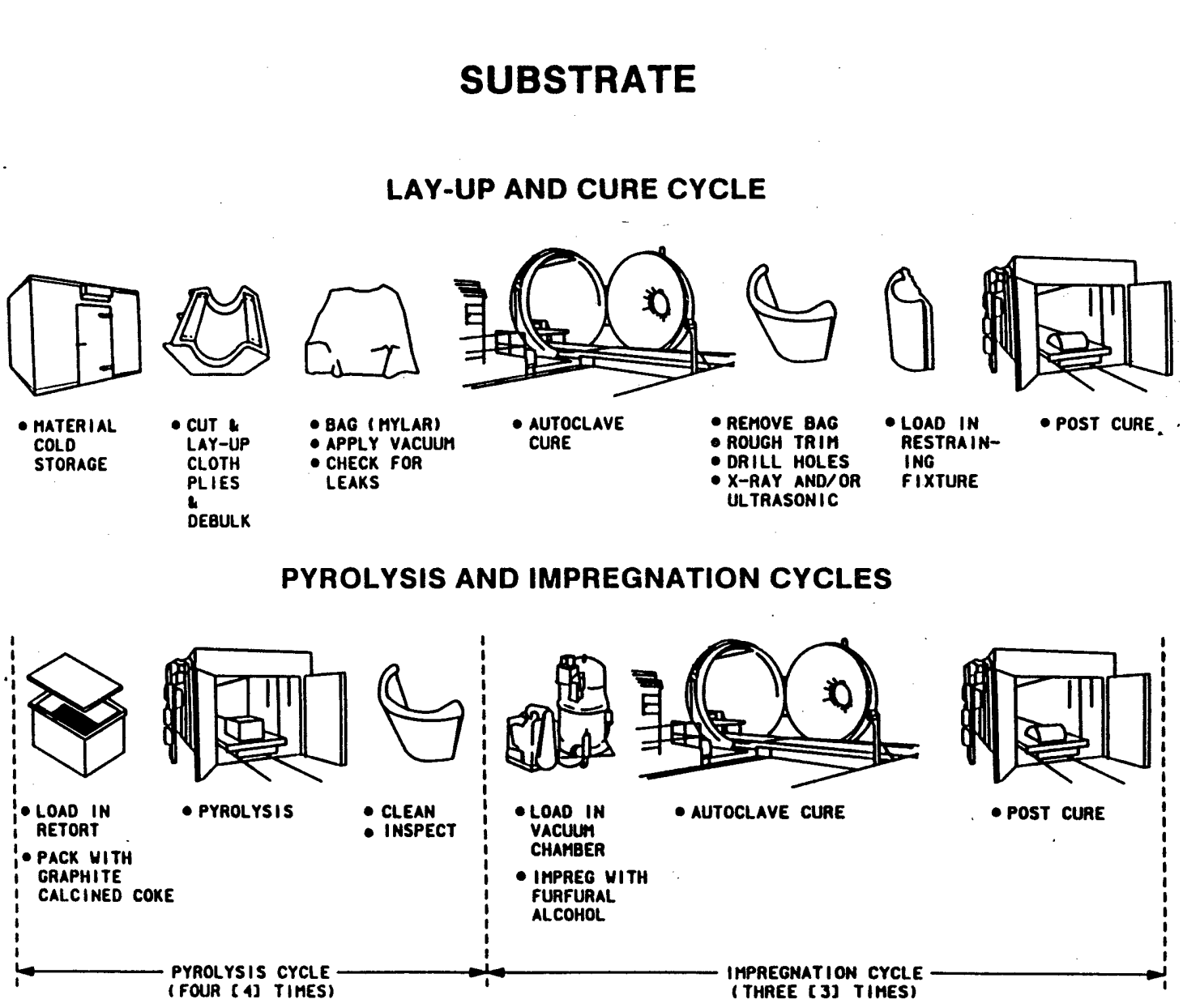


Figure 9. Schematic of a 2-D Fabric-Reinforced CCC Manufacturing Method.

high-temperature tool to restrain expansion and contraction during the carbonization process. In either case the carbon-matrix-forming process is the most critical step in the manufacture of any CCC material (particularly thick-walled articles). During the first carbonization cycle, the highest percentage conversion of organic matrix-to-carbon generally takes place. If the first carbonization process step is not conducted properly, the voluminous pyrolysis gases evolving from decomposing organic matrix may induce composite delamination and yarn misalignment. Extensive matrix cracking and fiber-matrix debonding may also be encountered. Carbonization is generally performed in either ambient or positive pressure conditions. The carbonization process is spread over a long period of time and discontinued at maximum temperatures of about 1200°C (2192°F). The material may be further heat treated to increase its dimensional and thermal stabilities. Typical graphitization temperatures are between 1650°C (3002°F) and 2760°C (5000°F). At this point one densification cycle is complete. The CCC material is usually not useful at this stage because of its high porosity and poor mechanical properties. Additional cycles of resin or pitch infiltration and pyrolysis cycles are thus necessary to obtain the desired composite density. Three or four additional impregnation and pyrolysis cycles are typically adequate to obtain a structurally sound and acceptable density CCC material.

2-D CCC articles prepared by the previously-described low pressure infiltration process are shown in Figure 10. Many CCC sizes and configurations were fabricated using predominantly thermosetting resins as the precursory char material.

LIP processes have also been developed for densification of 3-D and n-D fibrous preforms. First-generation 3-D CCC materials utilized only moderate pressures to infiltrate the porous preform with a thermosetting resin (typically phenolic or phenolic-furfural alcohol blend). The resin was then cured, postcured, and carbonized to a char. Figure 11 is a schematic of a 3-D pierced fabric rectangular preform densification process which utilized phenolic resin impregnation. Figure 12 depicts the assembly of a cylindrical 3-D pierced fabric preform and subsequent densification with a thermosetting polymeric matrix.

4.2.4.2.2 *High-Pressure Impregnation*

Pressure impregnation carbonization (PIC) and high pressure impregnation carbonization (HIPIC) processes have been developed to obtain very high density CCC materials. These processes are based on liquid matrix impregnation of porous carbonaceous bodies or fibrous carbon preforms, usually employing thermoplastic pitch as the precursory carbon matrix. External pressures may range from about 6.9 MPa (1 ksi) to about 103 MPa (15 ksi). The major advantages of these densification processes are: (a) the matrix



Figure 10. Configurations of First-Generation CCC Materials.

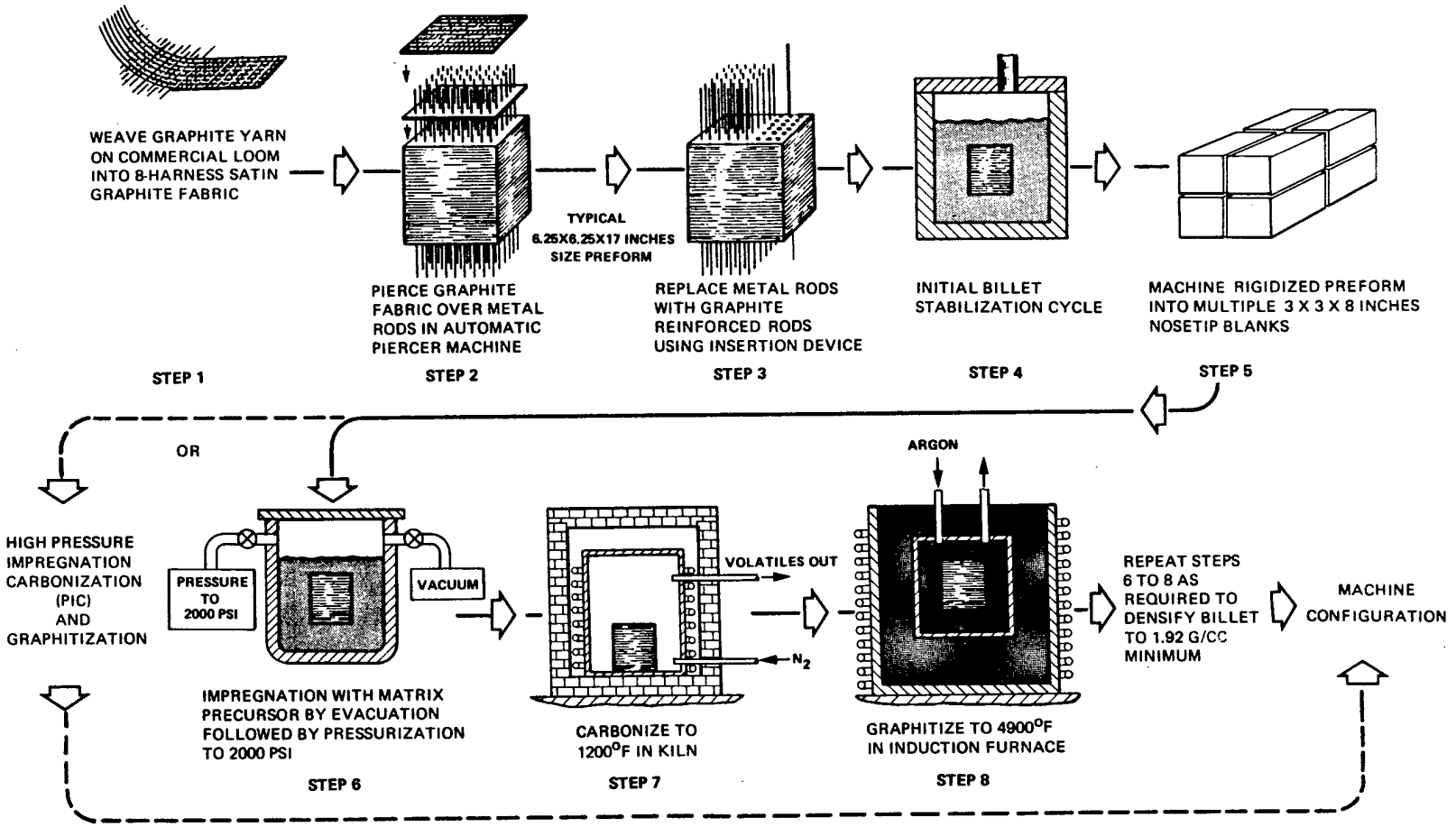


Figure 11. Schematic of a 3-D Rectangular CCC Billet Production Process.

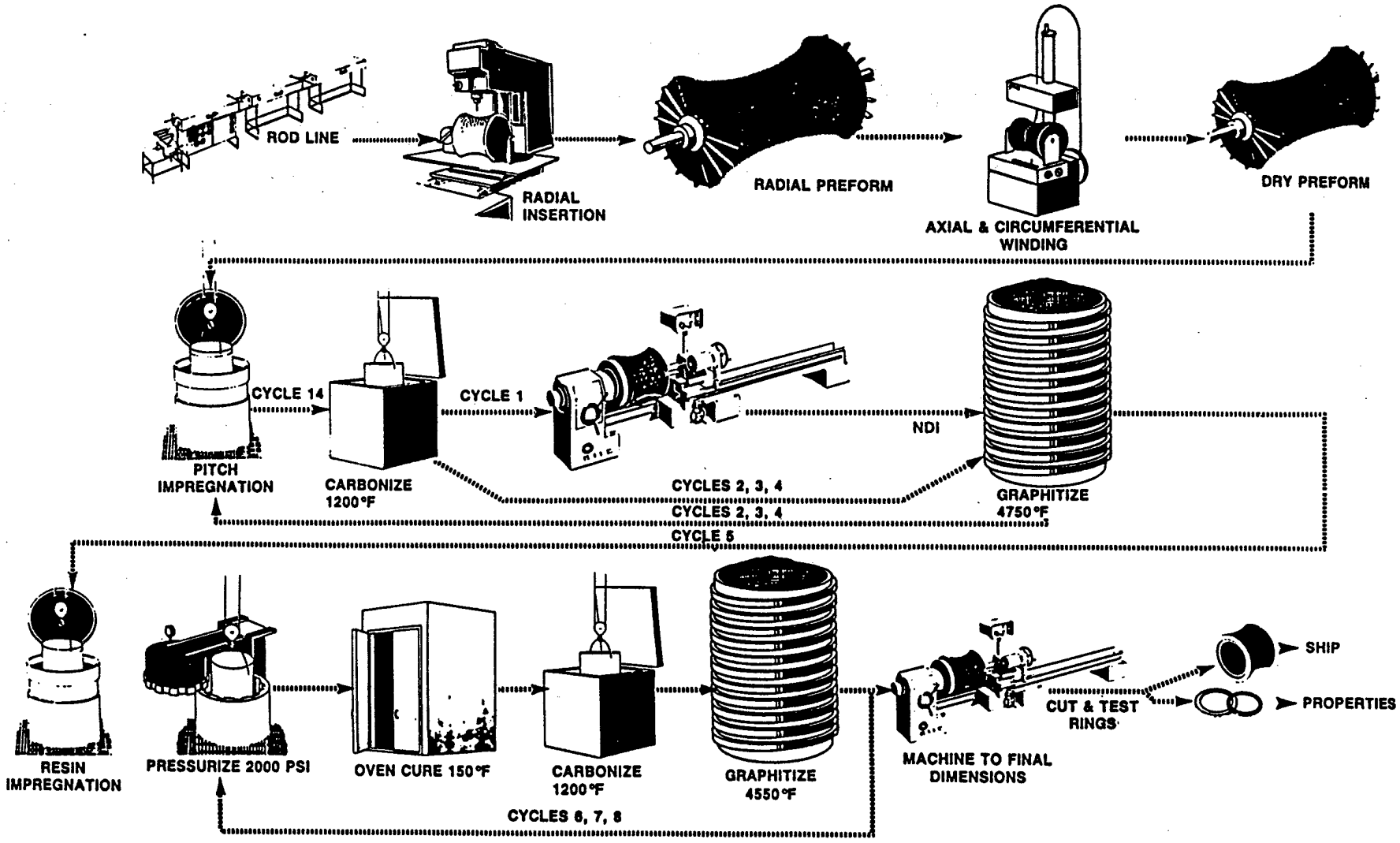


Figure 12. Schematic of a 3-D Cylindrical CCC Manufacturing Method.

thoroughly penetrates thick preforms and small interconnected pores, (b) more of the volatile pitch constituents are kept in the condensed stage with no or little bloating, and (c) retention of the molten pitch in the porous preform results in a higher carbon-matrix yield. The coke yield of coal tar pitch, for example, is increased from about 52 percent at atmospheric pressure pyrolysis (0.15 MPa, 15 psi) to approximately 82 percent with 69.0 MPa (10 ksi) pyrolysis pressure. Consequently, only four or five HIPIC cycles are needed to reach maximum composite density. It is common practice to use a final resin impregnation and carbonization to seal off any remaining part porosity. The process pressure level selected depends greatly upon the (a) size of the part, (b) available equipment, and (c) CCC density and properties desired. Small parts like nosetips and nozzle throats have been typically processed at 35 MPa (5 ksi) to 103 MPa (15 ksi). The larger the part, the lower the pressure employed and the greater the number of process cycles. The graphitization temperature used is generally above the maximum use temperature to minimize further property changes during material exposure. The last or second last graphitization cycle is like a structural proof test in that the most severe fiber strain states during the entire processing cycle are generated. The highest risk of billet cracking thus occurs during the final several graphitization cycles.

PIC or HIPIC processing is typically used to densify 3-D and n-D preforms. The PIC procedure is carried out in a specially-designed high pressure impregnation (HIP) unit. A dry fibrous preform or porous CCC material is first vacuum-impregnated with molten coal tar or petroleum pitch. It is then placed inside a metal (stainless steel) can (container) and surrounded with an excess of granular pitch particles. The metal can is then evacuated and sealed with an electron beam weld. After placing the can within the work zone of the HIP unit, the temperature is raised at a programmed rate above the melting point of the pitch. The temperature and isostatic pressure are then increased to force the molten pitch into the preform, hold it there, and eventually induce carbonization of the matrix. The sealed metal container deforms under pressure and forces the molten pitch into the preform. Hydrogen gas arising from the decomposing pitch penetrates the hot stainless-steel can and is released from the furnace unit. Once the PIC cycle is complete, the can is removed from the furnace and the densified preform taken from the container. Excess carbonized matrix is machined away from the preform surface, and in the process additional pores are exposed for subsequent impregnation. The densified preform is usually heat treated to high graphitization temperatures after the first PIC cycle to stabilize the preform and open up additional pores. The final processing step is usually a heat treatment, but at slightly lower graphitization temperatures, to maximize composite properties and minimize surface porosity.

PIC processing has also recently been performed without the need for a container. Net-shaped CCC components were prepared at pressures of around 200 MPa (29 ksi).

4.2.4.3 Chronology

Many types of CCC materials have been created and their varied compositions are reported in Table 10. Also given is the first year the material became available, its importance, and the organization responsible for the material creation.

Many fabrication processes were also developed to produce unique forms of CCC materials. Table 11 is a condensed chronology of CCC material processing.

First-generation CCC materials were based on phenolic and furfural char matrices as previously noted. Many densification and carbonization cycles were required to reach intermediate composite densities of 1.63 g/cm^3 (0.059 lb/in^3). Higher carbon yielding precursory materials and processes were needed to significantly upgrade composite properties. This search for new materials and processing was essentially completed when the author visited the U.S. Atomic Energy Commission Oak Ridge National Laboratory. A unique process for densifying graphitic porous substrates was observed. In the process molten pitch infiltrant was forced under very high pressure into the pores of the graphite substrate. Pressures up to 207 MPa (30 ksi) were possible, but 35 MPa (5 ksi) to 69 MPa (10 ksi) were more economical and produced acceptable part densities. Upon learning of this specialized technology, the author initiated a U.S. Air Force project to have the A.E.C. Oak Ridge National Laboratory densify various 3-D fibrous preforms. Just prior to the first HIPIC runs, the U.S. Navy expressed an interest in densifying their first-generation 3-D orthogonal fibrous graphite performs. The Air Force-funded effort was therefore delayed, and both the Air Force and the Navy billets were processed simultaneously. For the first time, high-performance 3-D CCC materials became available with densities up to about 1.88 g/cm^3 (0.068 lb/in^3). This breakthrough meant that high-density 3-D CCC materials could now compete with polycrystalline graphites in terms of low ablation rate and high shape stability. The CCC materials possessed other attributes like high in-plane strengths and moduli values, low thermal expansion, and high resistance to nuclear weapons effects. There was some concern within the aerospace industry that the new high-density 3-D CCCs might exhibit brittleness and thermal stress fracture similar to polycrystalline graphites. Extensive ground-based testing revealed that the composite failed in a noncatastrophic manner. No facilities were capable of thermostructurally failing the material. This phenomenon was due mainly to the poor bonding

TABLE 10
CHRONOLOGY OF CCC MATERIALS DEVELOPMENT

YEAR	MATERIAL	IMPORTANCE	ORGANIZATION
1960/61	2-D graphite (rayon-based) fabric/phenyl silane resin char CCC	First CCC produced in a government laboratory	AF Wright Laboratory/Materials Directorate USA
1960/61	2-D carbon (cotton wool-based) fiber/CVI PG or resin char CCC	Potential impermeable container material for storage of radioactive materials	Atomic Energy Authority/GREAT BRITAIN
1960/61	2-D involute construction, graphite (rayon-based) fabric/resin char CCC	First CCC exit cone configuration fabricated	Hitco/USA
1960/61	2-D graphite (rayon-based) fabric/phenolic resin char CCC	First-generation, porous and low-strength CCC	LTV Aerospace and Defense Company/ USA
1960/61	2-D graphite (rayon-based) fabric/phenolic-furfuryl alcohol resin char CCC	First commercially-available 2-D CCC materials	Union Carbide Corporation/National Carbon Company/USA
1962	3-D multilayered graphite (rayon-based) preform/resin char CCC	CCC material with higher interlaminar shear strength	LTV Aerospace and Defense Company/ USA
1962	CCC honeycomb construction prepared by pyrolyzing a precursory phenolic-graphite fabric honeycomb	Unique CCC material for possible structural applications	LTV Aerospace and Defense Company/ USA
1963	2-D mascerated graphite (rayon-based) fabric/phenolic-furfuryl alcohol resin char CCC surface coated with CVD pyrolytic graphite	First graphite-coated CCC material with enhanced ablation and erosion resistances	Union Carbide Corporation/National Carbon Company/USA
1965	Isotropic, castable graphite (rayon-based) fiber/resin char CCC	Low-cost, insulation CCC material for potential nozzle applications	Atlantic Research Corporation/USA
1965	3-D needled fibrous graphite (rayon-based) felt/CVI PG matrix CCC	First-generation 3-D CCC amenable to production sizes and volumes	Atomic Energy Commission/Sandia National Laboratories/USA
1966	2-D filament-wound graphite (rayon-based) yarn/CVI PG matrix CCC	First-generation, structural 2-D CCC amenable to production sizes and quantities	Atomic Energy Commission/Sandia National Laboratories/USA Union Carbide Corporation/Oak Ridge Y-12 Plant/USA

TABLE 10 (Continued)
CHRONOLOGY OF CCC MATERIALS DEVELOPMENT

YEAR	MATERIAL	IMPORTANCE	ORGANIZATION
1966	3-D orthogonal graphite (rayon-based) yarn/resin char CCC	First-generation 3-D CCC material with attractive ablation and mechanical properties	Avco Corporation/Space Systems Division/ USA
1966	2-D graphite (rayon-based) fabric/phenolic char matrix CCC reimpregnated with phenolic resin	Combined insulative-structural material for transient high-temperature environments	San Rafael Plastics Company/USA
1967	3-D orthogonal graphite (rayon-based) yarn/coal tar pitch coke CCC	Higher-density matrix and CCC composite	Avco Corporation/Space Systems Division/ USA
1968	2-D filament-wound graphite (rayon-based) yarn/CVI PG matrix CCC	Commercial source for first-generation structural CCC materials	Atlantic Research Corporation/USA Atomic Energy Commission/Sandia National Laboratories/USA
1968	2-D graphite (rayon-based) short-fiber construction bonded together with a resin char	Very low density CCC material provided excellent thermal insulation and was later commercialized	Union Carbide Corporation/Oak Ridge Y-12 Plant/USA
1969	4-D and 7-D graphite (rayon-based) yarn/ resin char matrix CCC	First-generation CCC materials with 4- or 7-D properties and providing potential for use on advanced missile nosetips and nozzle throats	Fiber Materials, Inc./USA Societe Europeenne de Propulsion/ FRANCE
1970	2-D moldable, staple graphite (rayon-based) fiber/carbon powder/furfuryl ester resin char CCC	An approach for lowering the cost of CCC materials	Illinois Institute of Technology Research Institute/USA
1970	2-D carbon (PAN-based) tow/phenolic-epoxy novolac char matrix CCC	First CCC material utilizing newly-available, higher-strength and intermediate modulus carbon tows	Atomic Weapons Research Establishment/ ENGLAND
1971	3-D needled fibrous carbon (PAN-based) felt/CVI PG matrix CCC	Upgraded CCC construction based on higher-performance fibers	Atomic Energy Commission/Sandia Laboratories/USA
1971	CCC woven truss core construction prepared by pyrolyzing a precursory graphite fabric-yarn/resin char material	Unique CCC material for possible high-temperature structural applications	General Dynamics/Convair Aerospace/ USA

TABLE 10 (Continued)
CHRONOLOGY OF CCC MATERIALS DEVELOPMENT

YEAR	MATERIAL	IMPORTANCE	ORGANIZATION
1971	All-carbon foam-containing carbon hollow microspheres and a resin char matrix	Lightweight, high-temperature insulation material	Union Carbide Corporation/Oak Ridge Y-12 Plant/USA
1971/72	3-D pierced fabric and orthogonal graphite (PAN-based) carbon tow/HIPIC-processed coal tar pitch coke matrix CCC	High-density, high-strength, and high-modulus CCC for missile nosetips	Union Carbide Corporation/Oak Ridge Y-12 Plant (Densification)/USA Avco Corporation (Preform)/USA
1972	7-D fine-textured graphite tow (PAN-based)/HIPIC coal tar pitch coke CCC	Upgraded 7-D CCC construction with higher-strength fibers and higher-density matrix	Fiber Materials, Inc./USA
1973	11-D graphite (rayon-based) yarn/resin char matrix CCC	Demonstrated an approach for more isotropic composite properties	Fiber Materials, Inc./USA
1974	Random dispersed graphite (rayon-based) fiber/resin char matrix CCC	Promising low-cost frictional material for future braking systems	Bendix Corporation/Energy Controls Division/USA
1976	3-D fine-woven graphite (pitch-based) yarn/coal tar pitch coke matrix CCC	Very high stiffness and high-density composite for various military uses	Fiber Materials, Inc./USA
1976/78	4-D graphite (rayon-based) yarn/graphite powder/pitch coke matrix CCC	Inexpensive graphite powder replaced some graphite yarn for a lower-cost, faster processed material	Science Application International/Materials Sciences Operation/USA
1977	3-D coarse woven carbon (rayon-based or PAN-based) fiber tapered pin-helix wound/ resin-pitch coke matrix CCC	Multidirectional reinforced CCC for cylindrical or frusta shapes	Avco Corporation/Systems Division/USA
1978	5-D, 6-D, 7-D, and 8-D rigid-rods/carbon matrix CCCs	Additional n-D reinforced materials for uses requiring more isotropic properties	Societe Europeenne de Propulsion/ FRANCE
1981	2-D graphite (rayon-based) fabric/phenolic char CCC surface coated with CVD silicon-carbide and containing a sealant	Second-generation, oxidation-resistant 2-D CCC materials for high-temperature oxidizing and mechanically-stressed uses	Vought Corporation/USA
1984	2-D carbon (PAN-based) fabric/phenolic char CCC surface coated with CVD silicon nitride	Alternate ceramic coating for CCCs having more compatible thermophysical properties with the structural substrate	United Technologies Research Center (Coating)/USA Hitco (Substrate)/USA

TABLE 10 (Concluded)
CHRONOLOGY OF CCC MATERIALS DEVELOPMENT

YEAR	MATERIAL	IMPORTANCE	ORGANIZATION
1985	5-D pierced/carbon (PAN-based) fabric/pitch coke CCCs	Candidate material with low ablation and high bend stiffness for maneuvering reentry vehicle nosetips	Textron Specialty Materials/USA
1987	2-D carbon (PAN-based) staple fiber knit/graphite matrix CCC	Low-cost, formable and high thermal conductivity CCC for potential uses in plasma facing components	BFGoodrich Aerospace/Super-Temp/USA
1990	3-D staple fiber (PAN-based) fabric/resin char or CVI PG matrix CCCs	High through-the-thickness thermal conductivity material for plasma facing components	Societe Europeenne de Propulsion/ FRANCE
1990/92	3-D orthogonal carbon (PAN-based) tow and graphite (pitch-based) yarn/pitch coke matrix CCCs	Very high directional (in-plane) thermal conductivity for plasma facing components of fusion reactors	Fiber Materials, Inc./USA

TABLE 11
CHRONOLOGY OF CCC MATERIALS PROCESSING

YEAR	PROCESSING EVENTS	IMPORTANCE	ORGANIZATION
1960/61	Constructive pyrolysis of 2-D graphite fabric/phenolic resin composites in the absence of oxygen produced a CCC material	First process used to produce a 2-D CCC material	Chance Vought Corporation/USA
1962	CVI pyrolytic graphite process was demonstrated for densifying 2-D resin char/graphite fabric CCC materials in a laboratory	Process was later modified for the production of 2-D involute CCC exit cones	AF Aeronautical Systems Division/ Directorate of Materials and Processes/ USA
1966	Hot-pressed, 3-D needled fibrous graphite (rayon-based) felt/CVI PG matrix CCC produced in a laboratory	Process approach for reducing composite porosity and increasing density while improving mechanical properties	Sandia National Laboratories/USA
1969	Co-pyrolyzed, matched shrinkage constituents process was developed	Faster and less-expensive process for fabricating CCC materials	LTV Aerospace Corporation/USA
1970/71	High-pressure infiltration-carbonization (HIPIC) process was used to densify fibrous graphite 3-D preforms	CCC materials with high density, low ablation and high mechanical properties	Philco-Ford Corporation/Aeronutronic Division/USA UCC Oak Ridge Y-12 Plant/USA
1977	Billet overwrapping technique was developed for processing 3-D cylindrical CCC materials	Billet cracking during heat treatment was avoided by lowering process stress levels	Material Sciences Corporation/USA
1981	Film boiling process was developed for densification of fibrous carbon preforms	Very fast and economical densification process for CCC materials	Commissariat a l'Energie Atomique/ FRANCE
1982	CVI carbon welding process was developed for joining two worn (machined surfaces) CCC brake discs	Greatly extended brake disc life and lowered the cost per aircraft landing	Dunlop Limited/Aviation Division/ ENGLAND
1983	Direct current plasma enhanced CVI carbon process was developed for densifying carbon (PAN-based) fabric preforms	Novel CVI process with less severe processing conditions	Domaine Universitaire/FRANCE

TABLE 11 (Concluded)
CHRONOLOGY OF CCC MATERIALS PROCESSING

YEAR	PROCESSING EVENTS	IMPORTANCE	ORGANIZATION
1983	A CCC process was developed based on finely pulverized coke mixed into a binder pitch, fiber added, and the composite hot pressed and heat treated	A simple and low-cost process for producing high toughness CCC materials	University of Tokyo/Institute of Industrial Sciences/JAPAN
1988	Single densification process was developed in a laboratory	Fast, low-cost process for obtaining inexpensive CCC materials	Acurex Corporation/Aerotherm Division/ USA
1989	An oxidative stabilization process was developed for mesophase pitch matrices used in CCC materials	Converting the thermoplastic pitch to a thermoset prevented its expulsion during 3-D preform densification	University of California/Department of Mechanics and Engineering Sciences/USA The Aerospace Corporation/Materials Sciences Laboratory/USA
1990	Artificial intelligence controllers and *in situ* sensors were used for real-time control of CCC processing	CCC processing times were reduced and part reproducibility was improved	Science Applications International Corporation/Materials Sciences Operation/ USA
1991	Hot press molding process was developed for obtaining very low-cost CCC materials	CCC materials reportedly had lower cost (one-third to one-fifth) and higher mechanical properties compared to conventional CCC materials	Osaka Gas Company, Ltd./JAPAN

of fiber and matrix, low expansion coefficients of the constituent materials, and the high strengths imparted by the reinforcement. These outstanding attributes ultimately led to the use of 3-D CCCs in missile reentry nosetips. Later, the 3-D orthogonal fibrous preform processes were modified to obtain polar 3-D fibrous constructions. These preforms were densified by methods previously described, and the resultant 3-D CCCs were applied extensively to rocket motor throats and integral-throat-entrance (ITE) sections.

4.2.4.3.1 *The 1960s*

First-generation CCC materials were prepared in the early 1960s as previously noted. The CCC materials were based on pyrolyzed plastic laminates and molded composites which were subsequently densified with organic matrices and re-carbonized. A wide variety of CCC materials were prepared in the laboratory, including honeycomb sandwich constructions and a multilayered fabric-reinforced CCC.

By the mid-1960s, CCC research and development had spread to a number of domestic organizations and at least one overseas company. Carbon matrices derived from resinous materials continued to be emphasized, but pyrolytic carbons and graphites obtained by chemical vapor infiltration processes were used for the first time to obtain high-density composites. The usual forms of rayon-based carbon reinforcements continued to be used which included woven fabrics, chopped yarns, and felts. A limited effort was also devoted to filament-wound composites, but for the most part this particular reinforcement scheme proved to be less than promising.

The most exciting CCC developments during the mid-1960s concerned the invention of a usable 3-D fibrous-reinforced composite. Previously fabricated 2-D CCCs were found to have acceptable mechanical properties in the plane of reinforcement, but their interlaminar shear strengths were very low, and this was a major limiting design parameter. A third directional fibrous-reinforcing scheme was needed to upgrade the interlaminar shear strength, transverse tensile properties, and through-the-thickness thermal conductivity. In 1965, the A.E.C. Sandia National Laboratories perfected a 3-D needled fibrous graphite felt and successfully infiltrated the preform with CVI pyrolytic graphite. The reinforcement content of the CCC was quite low, especially in the third direction. Nevertheless, the properties of the CCC were quite respectable because of the high-density CVI matrix. This type of composite was later scaled up to missile reentry vehicle heatshield sizes and then successfully flown. A second type of 3-D CCC was created in 1966 by U.S. Textron Specialty Materials, Inc. A hand loom originally developed to weave 3-D quartz yarn preforms was adapted to the weaving of 3-D orthogonal

fibrous graphite preforms. The preforms were then densified with resin char to form a composite having a density of about 1.5 g/cm^3 (0.054 lb/in^3). Several years later, Textron Specialty Materials created a 3-D pierced fabric preform in which the X and Y yarns of the orthogonal construction were replaced with woven fabric. Semiautomated weaving processes were also developed, and preform sizes were increased to satisfy the needs of the aerospace industry. Densification with pitch matrices became a routine operation, and with the introduction of HIPIC processing in the early 1970s, very uniform, high-density (1.9 g/cm^3, 0.069 lb/in^3) CCCs were produced and successfully used for missile reentry vehicle nosetips.

A number of interesting CCC materials were also fabricated in the late 1960s. The first silicon carbide-coated CCC was prepared, and with later NASA-funded developmental efforts, this basic type of composite was scaled-up and used on the space shuttle orbiter. First attempts to improve the oxidation resistance of carbonaceous matrices were also initiated. Using a metallic-containing resinous approach, chars containing molecularly-dispersed silicon carbide or zirconium carbide particles were prepared and evaluated. Another very significant development was the invention of a low-density carbon insulation having a low thermal conductivity. The material was composed of short pyrolyzed rayon fibers lightly bonded together with a small amount of pyrolyzed organic matrix.

Although 3-D CCC materials proved to have very high in-plane mechanical and thermal properties, certain future applications required higher off-axis properties. To meet this need, 4-D and 7-D fibrous graphite constructions were developed by the French Societe Europeenne de Propulsion (SEP) and domestically by U.S. Fiber Materials, Inc. and the U.S. General Electric Company. Four-directional interlocked braided constructions were woven into rectangular and hollow cylindrical preform shapes and then densified with a high coke-yielding matrix. Of all the n-D (4-D to 11-D) fibrous preforms developed, the original 4-D constructions proved to be the most advantageous from both a composite property and process economic standpoint. Increased CCC isotropy with 5-D or higher directional reinforcements were associated with (a) increased preform assembly complexity, (b) higher preform costs, (c) lower in-plane properties, and (d) more complex data generation needs.

4.2.4.3.2 *The 1970s*

Most of the basic CCC concepts were originated during the 1960s, and therefore the 1970s were devoted to (a) modifying these concepts in accordance with systems needs, (b) improving the preform and matrix densification processes, (c) developing other composite configurations, (d) scaling up CCC sizes for prototype evaluations, (e) generating

property data for preliminary design of systems components, and (f) demonstrating the utility of CCCs in various ground-based and actual service environments.

Developmental activities in the early 1970s were indeed intensive as the U.S. Air Force sought a lasting solution to the strategic missile reentry nosetip problem. These technical problems involved high ablation rates, poor nosetip shape stability during reentry, and unpredictable performance. 3-D CCC materials were upgraded with respect to their texture. Smaller diameter yarns and tows were used, and the yarn-to-yarn spacing was reduced. These advanced fibrous carbon preforms along with the newly-available HIPIC pitch processing method resulted in very high density CCCs. In subsequent times, rayon-based carbon fibers were replaced with PAN-based carbon fibers. The PAN-based tows were treated at high process temperatures to induce thermal and expansion stabilities. They were also of higher quality and higher modulus. Three-directional cylindrical and frusta shapes were demonstrated with continuous carbon and graphite tows. Thus, a second and more promising type of 3-D CCC construction (continuous fibers versus short fibers) became available in useful configurations. The prospects for CCC missile heatshields and rocket propulsion nozzle throats began to take on new meaning. Interest in n-D preforms and composites continued, and during this period an 11-D preform with precured rods was manufactured. It should be noted that the U.S. defense materials philosophy at that time was to create a wide variety of new and possibly useful materials, measure their properties, identify unique features, and then begin to tailor the composites to the specific needs of the application. This approach was most successful in that (a) creativity was at its zenith, (b) a wide variety of potential concepts were always available for potential development, (c) the most cost-effective activities were accomplished, (d) backup CCC materials were available as systems options, and (e) developmental risks and resources were much easier to forecast. As a result many composite materials were created before a recognizable need existed for them.

During the mid-1970s, the Air Force continued to focus on the development of shape stable CCC missile nosetips. A second domestic source for 3-D fibrous preforms became available, thus intensifying the competition for future business. Three-directional CCC missile heatshield developments were also continued at the Sandia National Laboratories under Atomic Energy Commission (now DOE) sponsorship. The Air Force/Defense Nuclear Agency sponsored work on 3-D orthogonal frusta configurations culminated in full-scale, nuclear-hardened missile reentry heatshields. The development of alternate fibrous-reinforcing schemes and matrix densification processes in support of CCC brake discs continued to proliferate. Overseas, the French SEP organization was perfecting its high-density 4-D CCC and originating new fabrication methods for n-D CCC materials.

During the late 1970s, the major attributes of 2-D, 3-D, and 4-D CCC were known, and there was little U.S. incentive to create additional new concepts. Instead, developments focused on refining CCC concepts. Alternate forms of 3-D cylindrical woven CCCs were fabricated, and a lower-cost (carbon powder-filled) 4-D CCC was developed for potential solid rocket motor uses.

A major new DOD thrust on an all-weather missile reentry nosetip material was established in the late 1970s. The best candidate material appeared to be a form of CCC which had been modified to accommodate hypervelocity particle (rain, snow and ice) impacts without significant shape change. Developmental efforts were initiated on new 3-D CCCs containing metallic-, metallic-carbide-, and refractory compounds.

Meanwhile, the potential use of CCC for biomedical applications was gaining substantial interest in both France and Germany. It was known that pyrolytic graphite was an excellent biocompatible material. CCC materials potentially offered a better balance of properties because their features could be tailored to the specific structural needs of bone replacements. The bio-CCC materials were fabricated overseas, initial tests conducted with animals, and the results shown to be most promising. Similar research was not conducted within the U.S.

During the late 1970s, it became apparent that high-performance CCC materials were a key ingredient to the successful development of strategic and tactical missile systems. Some industrialized nations, recognizing the U.S. leadership in this materials field, began to acquire manufacturing technology and equipment from domestic sources. In an effort to remain cognizant of the nature and extent of these commercial agreements, the U.S. placed CCC technology and certain manufacturing equipment on the International Traffic in Arms Regulations (ITAR) list. Except for basic research, most of the other CCC technologies were subject to the Department of State regulations. As a result of this action, there was a dramatic decrease in the number of open literature CCC publications and a general slowing down of the technology-transfers from the U.S. to foreign-owned organizations. Technical documents with limited distribution restrictions became the order of the day, and more orderly and visible technology transfer arrangement procedures were perfected for the benefit of both government and industry.

4.2.4.3.3 *The 1980s*

There were few CCC material concepts developed in the United States during the 1980s because of (a) a fundamental change in the U.S. defense materials developmental approach, and (b) minimal research activities both within and external to the CCC companies. A more systems applications orientation became dominant during the 1980s. Materials concepts expecting government support would now have to describe (a) the basic materials composite, (b) anticipated composite properties, (c) unique composite features, (d) anticipated systems benefits, and (e) total developmental time and costs. A multiyear CCC developmental roadmap was needed, and planning was the key to obtaining defense fiscal support. This "roadmap" concept had many desirable features, but it was limited by the visionary capabilities of the originator. Needless to say, few new composite concepts could be programmatically described in such great detail, and thus "concept refinement" rather than "new concepts" became commonplace.

In the 1980s, about the only new and useful CCC concept was the development of a 5-D pierced fabric material. This composite was based on 3-D pierced fabric with additional reinforcing planes to improve the bend stiffness. Such a material was expected to have better structural properties for maneuvering flight vehicle nosetips.

In the early 1980s, a French organization made a major breakthrough in the densification of fibrous carbon textiles. A rapid densification process was conceived and reduced to practice. During the rapid densification process, a carbon fiber preform was immersed in a liquid hydrocarbon. The liquid was then heated to the boiling point, and the preform enveloped in a vapor film. The hydrocarbon vapor infiltrated the porous preform, and when in contact with the hot preform, pyrolytic carbon was rapidly deposited from the inside out. Unlike chemical vapor deposition, the vaporization of the liquid hydrocarbon acted to cool the preform surface while the preform core remained hot. This condition allowed carbon deposition to initiate within the specimen and proceed towards the surface. The surface pores were not sealed off which resulted in a uniform density composite. This process technology was later licensed to a U.S. defense firm, and with the aid of a large government contract, a manufacturing process is being developed for commercialization of rapidly processed CCC materials.

4.2.4.3.4 *The 1990s*

Prospects for using CCC materials in space applications became more likely during the early 1990s. Specialized composite constructions were needed for

such applications as intrinsically hardened (survivable) spacecraft structures, high efficiency radiators, and other uses.

Candidate spacecraft structures were developed in the early 1990s. Very thin 2-D CCC materials were fabricated with high specific modulus and strength, low thermal expansion, low vacuum outgassing, and capable of service over a very wide temperature range and thermal gradient conditions. The lightweight CCC structural materials were also successfully coated for protection against atomic oxygen (low earth orbits).

Spacecraft CCC radiators were also developed in the early 1990s. Pitch-based graphite tows having outstanding axial thermal conduction were used to rapidly transport waste heat (from spacecraft electronic components) and then radiate it to the surrounding space environment. Two-directional fibrous constructions with significant third direction (through-the-thickness) fibers were created by novel methods and successfully processed into thermal management composites. Improved third direction heat transfer schemes are presently being sought.

4.2.5 Oxidation Protected Materials

CCC materials altered to impart oxidation resistance are known as oxidation protected materials. Oxidation protected CCC materials are the only class of high-temperature composites that exhibit considerable mechanical properties when exposed to cyclical air temperatures over 985°C (1805°F) for hundreds of hours, and for over 10 hours at 1850°C (3300°F). Material performance depends greatly on the specific environmental parameters and service conditions. At present, it appears that adequate structural properties can be retained for about 80-100 h (maximum two percent weight loss) at sustained air temperatures of 1370°C (2498°F). Separation of the external coating from the underlying CCC substrate was the identified major problem, but failures were not precipitous. They tended to occur over a period exceeding five hours. This type of behavior can be attributed to the positive action of surface sealants and matrix inhibitors that collectively formed protective borate glasses upon oxidation. The key to effective and acceptable oxidation protection appears to be a reliable, self-sealing external coating system.

4.2.5.1 Mechanisms of Oxidation

Carbonaceous materials vaporize when exposed to oxidizing species, particularly at high temperatures. Hence, their utilization in high-temperature air applications may require some form of environmental protection.

Carbonaceous materials including CCCs will react at high temperatures with oxygen, oxidizing species, water vapor, various oxides, metals, hydrogen, and other compounds. Unprotected CCCs start to vaporize in high-temperature air as low as 400°C (752°F). The rate of carbon vaporization is primarily kinetically controlled up to about 1375°C (2507°F), and at higher temperatures, it is diffusion controlled (rate of oxidizing species diffusion to the reactive surface). In addition, the rate of CCC oxidation is influenced by impurities, active sites, available surface area, microstructure, and other parameters.

High-temperature air enters a coated CCC through the surface crack grid. See Figure 13. Air penetration into the substrate is primarily by passage through subsurface fiber-bundle cracks and porous fiber bundles. Oxidation takes place at all exposed surfaces, but in general the carbonaceous matrix is more susceptible than the fiber. Weakly-bonded (often separated) fiber-matrix interfaces are particularly susceptible to oxidation. Material loss is generally not visible at low magnifications (up to 100 X). Nevertheless, the composite matrix-dominated properties may be significantly affected.

4.2.5.2 Oxidation Protection Approaches

Three key approaches have been developed to prevent or delay the carbon-oxygen reactions. These approaches include (a) a thin outer layer of ceramic coating, (b) inhibitors within the carbonaceous matrix or the fibrous reinforcement, and (c) a sealant layer on exposed carbonaceous surfaces to block ingress of the oxidizing species.

The general fabrication and processing approach for an oxidation-protected CCC material is as follows. The surface of the substrate is first prepared by thermal etching, chemical etching, or mechanical abrading. The purpose of the surface treatment is to increase coating adherence via a modified surface layer. An optional layer is then deposited on the substrate surface. It is generally composed of a thin carbon film or a silicon carbide conversion material. Various sealants or interlayers are next (optionally) deposited. The coating is then deposited onto the substrate. It is generally composed of silicon carbide or silicon nitride.

The protective surface layer is generally composed of different layered materials. This type of layered structure is required because of microcracking in the outer ceramic coating. See Figure 14. Silicon-based coatings are deposited in and onto the highly anisotropic CCC material at relatively high temperatures (about 1100°C, 1832°F). During cool-down, the

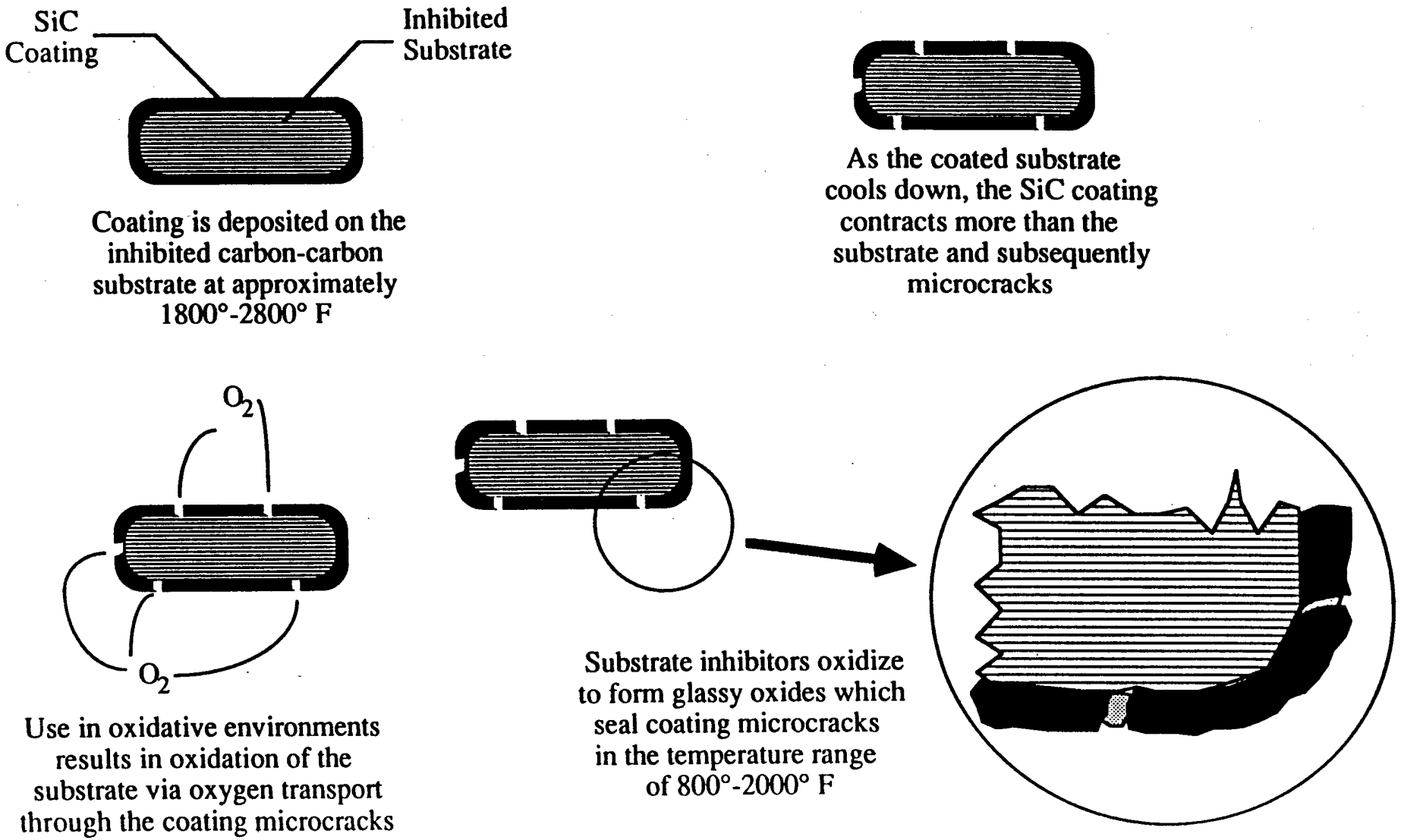


Figure 13. Oxidation Mechanisms of a Coated 2-D CCC Material.

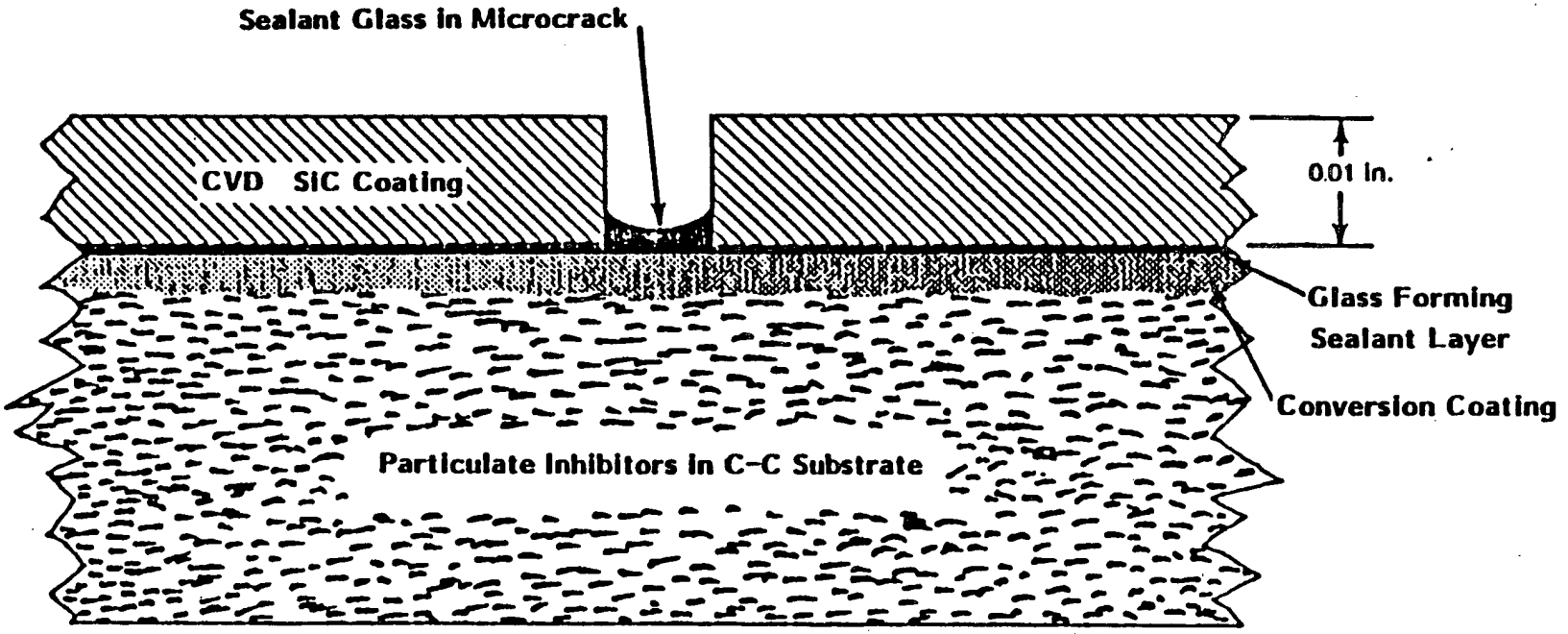


Figure 14. Schematic of an Oxidation-Inhibited CCC Material Cross Section.

brittle coating usually cracks. These microcracks relieve the induced stresses which are caused by a large difference in the coefficients of thermal expansion of the coating and the substrate. Various sealants have been developed to fill crack openings and substrate pores but, as expected, their efficiencies are reduced with exposure time and thermal cycling. Particulates capable of being converted to a glass and forming an added barrier have also been incorporated into the carbon matrix. Likewise, their efficiencies are time dependent as the material is consumed.

4.2.5.3 Coatings

The primary oxidation barrier of a protected CCC material is the coating. Its function is to completely encapsulate the part and prevent any portion of it from coming into direct contact with an oxidizing atmosphere. Four categories of coatings have been developed for CCC materials, namely: pack diffusion, liquid infiltration, chemical vapor deposition/infiltration, and slurry coating processes. The pack diffusion coating processes are advantageous because of the diffuse interface between the coating and the substrate and the improved matching of thermal expansion coefficients of the respective layers. Some line-of-sight coating processes have also been developed, but they are limited to simple shapes and small sizes.

The selection of a coating for a particular application involves many factors such as:

(a) adherence of the protective coating to the substrate,
(b) minimal thermal expansion mismatch between the coating and the substrate,
(c) minimal chemical reaction between the coating and the environmental gases,
(d) toughness of the coating interface to resist thermal shock,
(e) low gas permeation through the coating,
(f) resistance to particle erosion,
(g) low vapor pressure of coating and newly-formed products,
(h) chemical and strain compatibility with the fibers and substrate, and
(i) maximum use temperature.

The most widely used coating process is based on chemical vapor deposition (CVD). Major advantages of this process are: (a) controlled crystallinity and morphology, (b) good adherence to underlying substrate material, (c) high purity of the deposited material, (d) high density of the deposit, (e) good control of the deposit composition, (f) adequate

deposition rates, (g) good deposit uniformity over odd-shaped parts, and (h) mobility of gaseous reactants.

In the CVD silicon-carbide coating process, a silane-based gas is decomposed on the hot carbonaceous substrate to form the desired ceramic coating. Typical processing temperatures are about 1050-1875°C (1922-3407°F), but deposition temperatures are normally closer to the lower processing temperature. Up to 10 CVD deposition cycles may be needed to obtain coatings having a thickness of about 0.26-0.36 mm (0.010-0.014 in). Total coating times are on the order of 100 hours. Multilayered silicon-carbide coatings generally contain an inner silicon-rich layer having an appropriate thickness of 0.03 mm (0.001 in), an intermediate boron-rich layer having a thickness of about 0.080 mm (0.003 in) and final outer CVD silicon carbide layer of about 0.250 mm (0.010 in). After coating deposition, it is common practice to heat treat the material at a typical temperature of 1400°C (2552°F) and in an inert gas.

Diffusion coating (also known as pack or conversion) processes were developed during the 1960s to provide an oxidation-resistant silicon-carbide coating for 2-D CCC materials. In the process the porous CCC part is placed in a high-temperature graphite retort and surrounded with reactive dry-pack materials. A typical mixture contains approximately 30 percent silicon powder, 60 percent silicon carbide, and 10 percent alumina. The retort is placed in a furnace and heated with a stepped time-temperature cycle up to about 1650-1760°C (3002-3200°F). An argon atmosphere is used in the retort to keep oxidizing species away from the CCC material. At high temperatures, alumina vapors etch the CCC surface, and silicon vapors are deposited onto the available surface areas. Reaction between the deposited silicon and the carbonaceous material causes the outer layers of the CCC to convert to silicon carbide (whitish-gray color) with essentially no thickness increase of the uncoated part.

CVD and reaction bonded (conversion) processes have also been used to deposit very high-temperature ceramic coatings on various CCC substrates. Hafnium carbide, tantalum carbide, and their alloys were successfully applied (deposition or infiltration) to 2-D and other CCC materials.

Paint-on coatings are applied in liquid form to a carbon substrate and then converted to a ceramic coating by curing and subsequent pyrolysis. The liquid coating is typically a preceramic polymer or an oxide-based sol-gel. The major use for paint-on coatings to date has been on selected areas of CCC brake discs.

Two problems that significantly affect the performance of a coated CCC material are: (a) spallation and (b) weak adherence to the underlying substrate. In general coating spallation is most pronounced when (a) the coating is thick, (b) the expansion coefficients of the coating and substrate are very different, (c) parts are curved or complex, and (d) deposition rates are high. Coating spallation from 3-D composites is usually much more pronounced than with 2-D materials. Weak coating adherence, of course, contributes to spallation. Very little is known about the physical and chemical rules for coating adherence, and much additional research is required to minimize this problem.

4.2.5.4 Sealants

Sealants are needed to fill the many cracks in a coated CCC material. Cracks occur in the ceramic coating because of the high deposition temperatures followed by cool-down to room temperature. The CCC substrate has a lower coefficient of thermal expansion than the coating, thus giving rise to coating cracks. During subsequent heating of the coated part, the cracks remain open up to the original temperature of crack formation [typically 1000°C (1800°F)]. At higher temperatures the cracks close, and the coating becomes a very effective protective layer.

Sealants are categorized as glasses or glass precursors. Perhaps the first CCC sealant was tetraethylorthosilicate (TEOS) which was used on the U.S. Shuttle nosecap and wing leading-edge parts. The liquid TEOS material was forced under pressure into the porous CCC part and thermally cured. A silicon-dioxide residue was thus left throughout the coating and substrate to further reduce the exposed area of carbon.

Sealant glasses are typically based on various oxides which have been modified with other constituents for viscosity control and to promote wetting of the CCC substrate. Glassy sealants are generally used to fill the pores and cracks of porous conversion coatings. The sealant also serves as a reservoir of protective glass. During high-temperature exposure, the glassy sealant softens and flows into the coating cracks, thereby sealing the substrate from the external atmosphere. Boria and borosilicate glasses are frequently used to perform this function. Unfortunately, these sealants contain substantial amounts of boron which absorb moisture in humid environments. If rapidly heated, high pressures in the substrate can result, and the steam may cause coating spallation. Moisture absorption can also lead to swelling and crumbling. When hydrated, boria is converted to boric acid. At elevated temperatures the boric acid and water form gases which rapidly expand and may delaminate the composite. The glassy sealants also have rather low softening temperatures, and they may not provide adequate

sealing up to the crack closure temperature. Lastly, the glass sealants are limited to temperatures below the carbon-silica reaction temperature. Silica reacts with carbon at about 1575°C (2867°F) to form silicon carbide and gaseous carbon monoxide. In recent times, however, the moisture resistance of boria has been greatly improved with alkali additions like lithia and silica.

Glass precursors represent the second type of sealants. When oxidized, they perform a similar oxygen-blocking function as the glassy sealants. A typical sealant precursor is boron carbide. It is applied via the CVD process and thinly coats the CCC substrate. The primary coating is then applied. The purpose of the boron carbide is to react with oxygen that penetrates the primary coating and form a boria glass. The sealant then wets the carbon and inhibits further oxidation.

Sealants are applied either before or after the application of a coating. When the sealant is placed on the outside of the coating (overcoat glaze), the glass only contacts carbon at the base of cracking it penetrates in the coating. Oxidation-protected CCC materials with an exterior sealant are capable of surviving a few hours up to about 1700°C (3092°F), but their performance is greatly diminished at higher temperatures or multiple thermal cycles. Some sealants are only partially cured during part manufacture. During subsequent part use, the operational temperatures activate the sealing process. After multiple thermal cycling, however, the sealant can be depleted and performance reduced.

Figure 15 is an illustration of the manufacturing process used to impregnate a 2-D CCC material with TEOS.

4.2.5.5 Inhibitors

Inhibitors are inorganic compounds that are added to a CCC substrate during fabrication and thereby impart oxidation resistance. Inhibitors are necessary to prolong composite life when the external coating is not effectively sealed. They also prevent catastrophic failure when the external coating fails. Most inhibition concepts restrict the access of oxygen to carbon and thereby reduce the oxidation rate. Since the matrix carbon in CCC materials is more rapidly oxidized than the fibers, the inhibition approach generally involves chemical additions to the matrix.

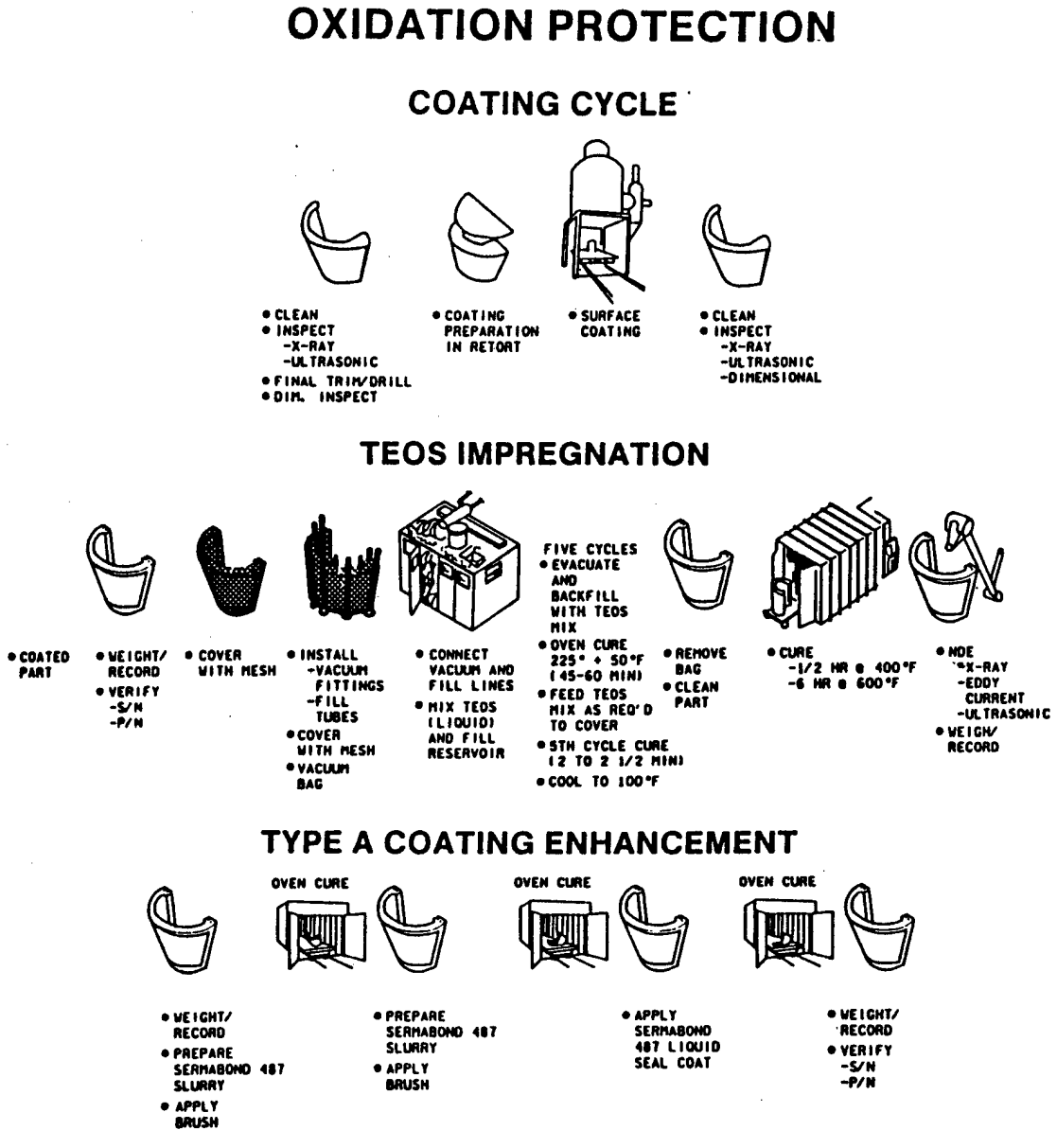


Figure 15. External and Internal Oxidation Protection of a 2-D CCC Material.

An effective inhibitor should satisfy as many of the following criteria as possible:

(a) chemical compatibility with the carbon substrate,
(b) newly-formed glasses should wet the carbon substrate,
(c) newly-formed glasses should be liquid between 538°C (1000°F) and 871°C (1600°F),
(d) newly-formed glasses should have a low moisture sensitivity,
(e) have a large volume increase upon oxidation,
(f) have a low thermal expansion, and
(g) have minimal effect on substrate mechanical properties.

Inhibitors are composed of glass-forming, oxygen-gettering elements and their compounds. The chemical compositions of inhibitors is generally company proprietary information. Nevertheless, a reading of the literature indicates that they are generally based on: (a) boron, (b) silicon, (c) zirconium, (d) lithium, (e) aluminum, and (f) their borides, carbides, silicides, and nitrides. The most effective particulate additions over a wide range of high temperatures have been based on boron. The element boron and its many compounds are refractory and thus can tolerate CCC processing temperatures and service conditions. Oxidation of the boron and boron compounds produces borate glasses, which appear to be uniquely suited for protecting carbon from high-temperature oxidation. The compound boric oxide has acceptable thermal and thermochemical stability in contact with carbon, and it can retain its identity at temperatures up to 1500°C (2732°F) under certain conditions. Boric oxide also has the surface tension, viscosity, and carbon wetting characteristics which enable an adherent, continuous, and self-healing glassy film oxidation barrier. Boron compounds are excellent oxygen getters because they readily oxidize. Even when present in small quantities, boric oxide reduces the rate of carbon oxidation by blocking chemically-active surface sites. The performance of an inhibitor at high temperature, however, is highly time dependent. With exposure time, the inhibitor content of a composite is reduced. For that reason it is necessary to use large weight percents of inhibitors for long-duration mission materials. Inhibitors may constitute between 30 and 40 weight percent of the CCC substrate.

Particulate inhibitors have several disadvantages. They increase the average ply thickness and thereby reduce the composite fiber volume fraction. Composite in-plane mechanical properties are consequently lowered. Particulate additives may also abrade the fibrous reinforcement with a reduction in mechanical properties.

Inhibitor particles, even in a finely divided state, are difficult to uniformly disperse in a liquid matrix. They tend to agglomerate or settle out of the carrier liquid matrix. The particles also have a tendency to collect on the outer layers of the reinforcement during matrix penetration of the porous part. Small particle sizes generally work the best. Forty microns diameter is about the maximum upper size particle that can be used.

Matrix inhibition can also be accomplished at the molecular level. Metal-organic compounds, which have been available since the 1960s, are added in solution form to a liquid resin during processing. Upon exposure to oxygen, they function in a manner similar to the particulate inhibitors.

4.2.5.6 Coated Fibers

Oxidation-protected carbon fibers have also been developed for use in CCC materials. Multifilament tows and yarns have been surface coated with a very thin layer of oxide, metal, carbide, nitride, or other refractory compounds. Coating methods have included (a) chemical vapor deposition, (b) electroplating, (c) physical vapor deposition (PVD), (d) electroplating, (e) liquid precursors, and (f) liquid metal transfer. Properties of the carbon fiber were influenced by the coating, depending mainly upon the (a) thickness, (b) composition, and (c) adherence to the substrate. Fiber tensile strength has been little affected by very thin coatings, but the axial elastic modulus was changed according to the simple rule-of-mixtures. Brittle coatings that strongly adhere to the fibers tended to reduce fiber strengths because cracks forming in the coatings at low strains extended into the substrate (fiber) and resulted in premature fracture. Very thin coatings helped to maintain the flexibility of the fiber. Hence, coating thicknesses are generally on the order of 0.1 to 0.2 micron. Adjacent fibers bonded together by a coating tended to lower composite axial tensile strength.

4.2.5.7 Performance

Oxidation-protected CCC materials are used in both (a) limited-life and (b) extended-life applications. Limited-life service environments are generally characterized by single or few thermal cycles, moderate to very high [above 1500°C (2732°F)] temperatures, and minutes-to-hours of exposure to oxidizing species. Single mission components like missile nosetips do not require oxidation protection because their flight times are short and some surface ablation can be tolerated. CCC materials that are multi-mission or encounter repetitive thermal cycling will typically require some form of oxidation protection. CCC brake discs, for example, contain a liquid paint-on coating on the exposed outer edges to limit oxidation during many

thousands of high-temperature air cycles. Extended-life CCC applications typically involve moderately high temperatures [600-1400°C (1112-2552°F)], numerous heating cycles, and many hundreds of service hours. All extended-life CCC components require oxidation protection. Two examples of extended-life oxidation-protected CCC applications are (a) the shuttle orbiter nosecap and (b) flaps and seals for gas turbine engines.

4.2.5.8 Chronology

The development of oxidation-protected CCC materials has been tremendously complex, filled with many disappointments and an occasional breakthrough. Fundamental problems are well understood, and present approaches are few, limiting, and costly. Several types of materials have been developed with outstanding performance in selected applications. The hypersonic Shuttle orbiter nosecap and wing leading edges are the most notable examples. Other application areas, like gas turbine engines and liquid propellant engines, require additional material improvements before widespread uses can be expected. Continued material development will be essential to realizing these anticipated high volume uses.

Table 12 lists an abbreviated chronology of oxidation-protected CCC materials. This table gives the development of these composite materials in terms of the first recorded achievement, year of accomplishment, and the performing organization.

4.2.5.8.1 *The 1960s*

First-generation oxidation-protected CCC materials were developed during the 1960s. Gas impermeable surface coatings were deposited onto the CCCs using a chemical vapor deposition (CVD) or pack cementation process. Silicon-carbide coatings were developed for short-time aerodynamically heated surfaces, and pyrolytic graphite was evaluated for rocket nozzle environments. These types of coatings provided a dramatic reduction in surface ablation during exposure. Research was also conducted on CVD co-deposited coatings, such as silicon carbide-zirconium carbide and pyrolytic graphite containing metallic carbide particles.

4.2.5.8.2 *The 1970s*

Second-generation oxidation-protected CCC materials became available in the early 1970s. It was demonstrated that most coatings had pin-size defects (holes), and oxidizing gases passing through these holes could vaporize the substrate carbon. The author can recall a CVD PG coated 2-D CCC after laboratory testing in a simulated liquid

TABLE 12
CHRONOLOGY OF OXIDATION-PROTECTED CCC AND HYBRID CARBON COMPOSITE MATERIALS

YEAR	HYBRID CARBON COMPOSITES	IMPORTANCE	ORGANIZATION
1962	2-D graphite (rayon-based) fabric/phenolic resin char containing particulate borates, silicates, oxides, phosphates, or combinations thereof	First-generation, oxidation-inhibited 2-D CCC materials	Chance Vought Corporation/USA
1963	2-D graphite (rayon-based) fabric/phenolic resin char CCC coated with silicon-rich silicon carbide	First-generation, oxidation-protected CCC material	Chance Vought Corporation/USA
1967	2-D graphite (rayon-based) yarn CVD coated with silicon carbide/resin char matrix CCC	First attempt to decrease oxidation of structural fibers in CCC materials	Carborundum Company/USA
1967	2-D graphite (rayon-based) fabric/carbon (PAN-based) film containing specialty fillers/phenolic resin char CCC	High-temperature, x-ray absorbing and insulative material for potential nuclear radiation uses	LTV Aerospace Corporation/USA
1968	Fibrous graphite (rayon-based) preform infiltrated with CVI silicon-carbide matrix	First graphite fiber-reinforced ceramic-matrix composite	The Marquardt Corporation/USA
1969/72	2-D graphite (rayon-based) fabric/resin char containing boron and boride particles	Very promising use of an oxygen scavenger/glass former for carbonaceous matrices	Carborundum Company/USA
1969	2-D graphite (rayon-based) fabric/phenolic resin char CCC CVD coated with codeposited zirconium carbide-pyrolytic graphite	Balanced property coating for CCC materials	AF Wright Laboratory/Materials Directorate/USA
1969	2-D graphite (rayon- or wool-based) felt/ CVI PG matrix CCC containing molecularly dispersed metallic or metallic carbide particulates	Uniform dispersion of ultra-small oxidation-inhibiting particles in an impermeable coating	BFGoodrich Aerospace/Supertemp/USA

TABLE 12 (Continued)
CHRONOLOGY OF OXIDATION-PROTECTED CCC AND HYBRID CARBON COMPOSITE MATERIALS

YEAR	HYBRID CARBON COMPOSITES	IMPORTANCE	ORGANIZATION
1973	Tetraethyl orthosilicate sealant used to fill microcracks in a silicon-carbide coated 2-D graphite (rayon-based) fabric/phenolic resin char CCC	Second-generation oxidation-inhibited CCC material	LTV Aerospace Corporation/USA
1978	3-D fine-weave orthogonal graphite (pitch-based) yarns with metallic or metallic carbide filaments in the z-direction/pitch coke matrix CCC	Candidate nosetip materials for particle-ladened, high-temperature air environments	Fiber Materials, Inc./USA
1980/84	Hybrid composites were fabricated by densifying porous 2-D CCCs with either titanium carbide or boron nitride	New tri-compositional composites with high intrinsic oxidation resistance	Universite de Bordeaux/Laboratoire de Chimie du Solide du CNRS/FRANCE
1980	3-D graphite (PAN-based) tow/pitch coke matrix CCC impregnated with rhenium metal	High-temperature particle erosion-resistant hybrid CCC materials	SPIRE Corporation/USA
1982	Columbian coated 2-D carbon (PAN-based) fabric/pitch coke CCCs	High-temperature metallic surface provided adequate oxidation resistance to substrate CCC in liquid propellant exhaust gases	Rockwell International Corporation/ Rocketdyne Division
1987	2-D carbon (PAN-based) fabric/phenolic char-CVI PG matrix CCC coated using preceramic polymers	Alternate high-performance oxidation-resistant coating for CCC materials	Rohr Industries, Inc./Refractory Technology Aerospace Components/USA
1987	2-D carbon (PAN-based) fabric/phenolic resin char with a lithium-containing borate glass sealant	Wide temperature range, reduced moisture-sensitive sealant for oxidation-inhibited CCCs	GA Technologies, Inc./USA
1988	2-D carbon (PAN-based) fabric/phenolic resin char containing molecularly dispersed inhibitors or oxygen scavengers	Oxidation inhibition of char matrices at the molecular level	Aerojet Solid Propulsion Company/USA
1988	3-D fibrous carbon (PAN-based) felt/coal tar pitch coke containing boron	Neutron-absorbing materials for high-temperature, plasma-facing components in fusion reactors	Hitachi Ltd./Hitachi Works/JAPAN University of Ibaraki/Faculty of Engineering/JAPAN

TABLE 12 (Concluded)

CHRONOLOGY OF OXIDATION- PROTECTED CCC AND HYBRID CARBON COMPOSITE MATERIALS

YEAR	HYBRID CARBON COMPOSITES	IMPORTANCE	ORGANIZATION
1989	2-D carbon (metal-boron compound containing PAN-based) tow-fabric/phenolic resin char CCC	Oxidation inhibition of carbon fibers at the molecular level	Hoechst Celanese Corporation/USA
1989	2-D graphite (pitch-based) fabric/pitch coke CCC coated with silicon nitride	Alternate high-performance oxidation-resistant coating for CCC materials	United Technologies Research Center/USA
1990	2-D carbon (PAN-based) fabric/phenolic resin char containing moisture-insensitive sealants	Alleviated a major deficiency of moisture-sensitive boron-containing sealants	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1990	2-D carbon (PAN-based) fiber/resin char CCC oxidation protected with a one-part coating	Improved coating for brake discs having lower cost and ease of application	Aircraft Braking Systems Corporation (ABS)/USA
1992	2-D carbon (PAN-based) stitched fabric/phenolic resin porous char containing a pulsed CVI silicon-carbide secondary matrix	Oxidation-inhibited 2-D CCC with uniform through-the-thickness protective carbide matrix	Kawasaki Heavy Industries/JAPAN Nagoya University/JAPAN
1992	Structural 2-D CCC materials were coated with multifunctional layers	Coatings provided thermal control, atomic oxygen protection, and transient high-temperature protection for space uses	Lockheed Missiles & Space Company, Inc./USA

propellant exhaust environment. The surface PG coating containing a major pinhole was intact, but a large amount of the underlying CCC had been oxidized. To accommodate this situation, it was necessary to develop new approaches for providing internal as well as external protection. Processes were developed for obtaining resin char or CVI matrices with dispersed metallic or metallic boride compounds. These compounds acted as "oxygen scavengers" as they were converted to metallic oxides at high temperatures and in the presence of oxidizing species. A more successful approach for internal oxidation protection involved the use of a preceramic or low-temperature melting oxide film to protect the carbonaceous phases.

4.2.5.8.3 *The 1980s*

Material developmental efforts during the 1980s involved further refinements of the basic internal-external schemes for providing oxidation protection. CVD coatings still focused on silicon-carbide and metallic-carbide coatings, but many other elements were introduced into the basic ceramic coating compositions. In the late 1980s considerable interest began to shift from silicon carbide compositions to silicon nitride coatings. The latter material appeared to have considerable potential for use, and certain properties were superior to the widely-used silicon carbide coatings. Having exhausted the investigation of candidate ceramic compositions, the industry's attention shifted to the development of multilayered coatings. The ceramic coatings were noted to have significantly higher thermal expansion coefficients compared to the substrate CCC. Following coating deposition at moderately high temperatures, the ceramic coating typically cracked during process cool-down because of the mismatch in expansion coefficients. Multilayered coatings showed some improvement because each of the layers was tailored to be closer to the adjacent material expansion coefficient. This successful development, however, was at the expense of increased composite complexity and higher processing costs. The industry then began to explore the potential of other coating compositions, and in the process discovered that high-temperature metallic-coated CCCs could replace all-metal components while exhibiting identical performance and significant weight savings. Columbium coatings were the first to be developed.

4.2.5.9.2 *The 1990s*

Progress in oxidation-protected CCC materials began to diminish. In the early 1990s the U.S. gas turbine engine materials developments began to be stretched out in time and reduced in scope. Two thousand hours of useful life had not been reached, and hence, new and novel approaches were needed. One of the interesting developments during these times concerned the use of preceramic polymers for forming carbide-containing

carbonaceous matrices. Polysilazane and other organo-ceramic polymeric compounds were synthesized for spinning into precursory ceramic fibers. These same types of precursory materials were also exploited for use as oxidation-resistant constituents of CCCs. Also during this time frame, repair coatings were developed for silicon carbon surfaced components.

Future developments in oxidation-protected CCC materials are expected to be controlled by two different factors. First, part service lives are typically long and beyond the intrinsic capabilities of current materials. Resources necessary to develop workable solutions will likely not be available because of a major downturn in worldwide defense funding. This resource vacuum will likely not be filled by commercial funding because oxidation-protected CCCs are used primarily in defense componentry. What is required, then, is a long-range and cost-effective plan to continue the development of applicable materials for both defense and civilian uses. Benefits could be enormous, but developmental costs and program focus have yet to be decided.

4.2.6 Hybrid Carbon Composites

Hybrid carbon composites contain a carbon constituent and a second major constituent of another chemical class. One of the most promising examples is a carbon fiber-reinforced ceramic composite wherein the fibers provide high structural properties, and the matrix provides specialized properties like oxidation resistance. The hybrid composites exhibit properties somewhere between the two major classes of materials used. For example, carbon fiber-reinforced ceramic (silicon carbide) matrix composites have high strength, high modulus and non-brittle mechanical behavior. Their thermal behavior is limited by the ceramic matrix material and the oxidation susceptibility of the carbon fibers. Silicon carbide- (and other ceramic fiber) reinforced carbon matrix composites have been fabricated, but their uses are limited by the oxidation susceptibility of the carbon matrix and the poor high-temperature structural properties of the silicon carbide fiber.

The development of hybrid carbon composites has progressed slowly due to: (a) lack of appropriate material concepts, (b) fabrication difficulties, and (c) the thermophysical incompatibilities of the constituent materials.

4.3 MATERIAL SCREENING AND EVALUATION

The measurement of properties and characteristics of new and improved CCC materials is an essential step in the total materials developmental cycle. A direct experimental approach has been successfully used to assess the relationship between the properties of a composite and the various constituent materials, fabrication parameters, and process variables that govern the preparation of that material. One can usually vary any of materials and process variables, test the resultant composite, and then determine the relationship.

Many materials and process variables influence the properties of CCC materials. Some of these factors include: (a) matrix type and volume, (b) reinforcement type, volume and orientation, (c) processing temperature, pressure and atmosphere, (d) heat treatment conditions, and (e) others. A detailed description of the materials composition, processing and quality of each test specimen should be determined in order to understand the test results. Most of the CCC properties published in the open literature are associated with an inadequate description of the test material.

The empirical testing approach, which has been widely used in the early years of CCC materials development, has several limitations. First, it is very difficult if not impossible to vary one materials and process parameter at a time to obtain a true relationship. Secondly, the Edisonian approach is time consuming. The remake of unacceptable test material can take months, thus greatly impacting any testing program schedule. Of greater importance is the high cost of CCC materials. This situation will generally limit the number of data points obtained. Lastly, the test specimen configurations and methodology have been adapted from other composite materials testing and they are not necessarily usable for CCC materials.

CCC testing is a complex task and few competent testing organizations exist.

4.3.1 Rationale and Considerations

Properties and characteristics of CCC materials are measured to:

(a) quantify material developmental progress,
(b) investigate phenomenological aspects,
(c) identify material attributes and limitations,
(d) obtain property inputs for prediction of materials performance, and
(e) obtain data for the design of prototype parts and for tradeoff studies.

The testing of CCC composites involves several important considerations:

(a) an understanding of the intended use and the way the data will be used,
(b) proper specimen design including a representative volume element or cross section and proper boundary conditions for the desired response,
(c) failure mode(s) must be correct,
(d) environmental conditions must be correct or simulated, and
(e) an understanding of the mechanics of composites as applied to the material being characterized and/or thermal response of the material.

4.3.2 Material Evaluation Approach

Microstructural, mechanical, thermal, and thermophysical properties are typically measured on new and improved CCC materials. The number of specimens employed and the temperature range of testing will vary greatly with the purpose of the materials evaluation. Newly-developed materials are first screened (evaluated) to obtain a small number of properties at or near room temperature. If the material advances with continued development, an engineering database will then be required. This more extensive database contains a larger number of data points and more environmental testing. A representative engineering database would typically contain such properties and characteristics as: tension, compression, shear, torsion, flexure, thermal expansion, thermal conductivity, specific heat, density, porosity, permeability, microstructure, and possibly others. All of these properties and characteristics are measured at room temperature, but a limited number of high-temperature properties may also be obtained. Three-to-five specimens per test condition are generally adequate. Directional properties are also measured to a limited extent. For design purposes, however, a statistical database is required. Large numbers of specimens are required to establish design properties and safety factors. Specialized tests are often conducted on newly-available materials depending upon the intended application. Frictional characteristics, for example, would be measured on CCC materials intended for aircraft brake disc applications. With the advent of oxidation-protected CCC materials, suitable laboratory devices were needed to measure (a) material oxidation rates and (b) residual mechanical properties. The simplest oxidation tests utilized laboratory air furnaces to perform isothermal and cyclic tests. Mass and volumetric measurements were made after defined time intervals. The furnace atmosphere was also monitored to identify gaseous species evolved during thermal exposures. This was accomplished by interfacing a mass spectrometer with a high-temperature inductively-heated furnace. Continuous mass changes during high-temperature air oxidation were also measured up to 1650°C (3002°F). These tests were performed with a state-of-the-art microbalance coupled with a molydisilicide resistively-heated furnace.

Thermogravimetric data were continuously recorded and plotted by interfacing the microbalance with a personal computer. Steady-state and cyclic heating of material specimens were also accomplished up to the temperature capabilities of the surface coating. Maximum temperature capabilities up to 2204°C (4000°F) have been developed with modified laboratory furnaces. Such furnaces are suitable for basic oxidation tests, heat treating, and mechanical property generation. Because oxidation testing of CCC materials is a relatively new technology, standardization has not been accomplished on testing equipment, methodology, and specimen design.

Quality assurance of CCC materials is an important topic because of the high costs and long time to replace defective materials. Various nondestructive inspection (NDI) and nondestructive evaluation (NDE) techniques have been employed to explore the properties and characteristics of materials, any associated interfaces, and components. No single nondestructive technique (NDT) stands out as a panacea. Each technique has its own strengths, shortcomings, and peculiarities depending upon the type of material under investigation and the type of flaws being sought out. Each technique should be considered in terms of its capability, adaptability to complex geometries, cost, and possible damage to the material during testing. All of the core NDE/NDI methodologies have been employed with CCC materials, including ultrasonic, acoustic, eddy current, radiographic, holographic, thermal or infrared thermography, magnetics, penetrants, fiber optics, visual and optical techniques. Techniques exist for identifying material nonuniformities, irregularities, flaws and defects, but much work is yet needed to quantify the effects of defects on composite properties. Materials are routinely inspected for: (a) broken fibers and bundles, (b) woven fiber irregularities, (c) matrix density variations, (d) cracks, (e) voids, (f) inclusions, (g) pore size and distribution, and (h) debonded regions. NDE has been applied primarily to component inspection, but it is being increasingly used to assure the uniformity and quality of test specimens. For the future, the NDE/NDI knowledge base will require integration of NDE techniques and data into other disciplines such as structural and thermal analysis, processing monitoring and control, and in-test and in-service monitoring.

4.3.3 Test Methods

Material test methods for CCC materials were largely derived from high-temperature graphite evaluation techniques, with some consideration of the "composite" microstructure and its highly directional properties. High-temperature measurements necessitated the development of new equipment particularly for CCC materials in cylindrical configurations. Each testing laboratory, however, has developed techniques which it feels provide acceptable properties. However, experience has shown that CCC properties are sensitive to variations in the

test method. It is not surprising that different results (on the same material) are reported by different testing laboratories. The situation is getting much better, however, as added testing experience is gained and an improved understanding is obtained on CCC materials behavior. In Europe, mechanical and thermal property test methods are being evaluated by various organizations. By 1996 the working group anticipates the establishment of new standards for the testing community.

4.3.4 High Temperature Testing

CCC material properties have been measured up to very high temperatures in various environments, including vacuum, air, inert gases, and others. Air environments have been of greatest interest, because many applications involve aerodynamic heating and very high temperatures. Test facilities and testing methodology have been gradually developed in the United States from the late 1970s through the 1980s. The maximum test measurement temperature varies with the type of test, but the following will indicate the general level of capabilities. For mechanical properties, maximum measurement temperatures were: (a) compression strength to 3038°C (5500°F), (b) torsional properties to 3038°C (5500°F), (c) flexural properties to 3038°C (5500°F), (d) tensile strength to 3038°C (5500°F), and (e) dynamic modulus to 2204°C (4000°F). For testing in air, maximum testing temperatures are on the order of: (a) 1760°C (3200°F) for tensile stress:strain, fatigue and creep/stress rupture, (b) 1538°C (2800°F) for compressive stress:strain, fatigue and creep/stress rupture, and (c) 1538°C (2800°F) for interlaminar shear strength using a double-notch shear specimen. Thermophysical property testing and their maximum measurement temperatures were: (a) thermal conductivity to 3038°C (5500°F), (b) thermal expansion to 3038°C (5500°F), and (c) heat capacity to 3038°C (5500°F).

4.3.5 Composite Properties

Based on properties, there are three general classes of CCC materials. They are: (a) low-modulus, low-strength, two-directionally reinforced (2-D) materials, (b) high-modulus, intermediate-to-high strength, 2-D materials, and (c) high-modulus, intermediate-to-high strength, three-directionally reinforced (3-D) materials. Composite properties are dictated primarily by the fiber type and textile architecture. Process variables are also important but to a lesser degree. Some of these variables include (a) matrix material type, (b) process and heat treatment temperature, (c) process pressure, and (d) number of densification cycles. In-plane properties are controlled largely by the reinforcement type, whereas the transverse (through-the-thickness) properties are influenced primarily by the matrix and to a lesser extent the fiber.

4.3.5.1 2-D Composites

The fabrication of CCC materials during the past three decades has been marked with great improvements in composite properties. Table 13 records the tremendous progress made in upgrading fabric-reinforced CCC properties since 1966. Composite densities were increased from 1.16 g/cm^3 (0.042 lb/in^3) to about 1.66 g/cm^3 (0.060 lb/in^3). In-plane composite tensile strengths were increased from 19 MPa (2.8 ksi) to 331 MPa (48 ksi), and in the process became useful for high-temperature structures. These composite advancements were due to two factors. First, added matrix densification of the composites through repeated impregnation/carbonization resulted in a better transfer of stresses into the reinforcement. Secondly, low-strength and low-modulus fibrous carbon fabrics were replaced with high-strength, intermediate-modulus fibrous carbon fabrics. For many applications, however, warp-aligned or 0°/90° fabric-reinforced laminates are not ideal due to the angle of induced stresses. For these cases a more balanced structural composite is required. Quasi-isotropic-reinforced composites are often used for these types of structures. As noted in Table 14, the 2-D fabric-reinforced CCC properties are a strong function of fiber orientation in relation to applied stress. In-plane (warp) tensile strengths of CCC materials decreased about 31-45 percent as the fibers were oriented in other directions and they carried only a fraction of the in-plane stress.

4.3.5.2 3-D Composites

3-D orthogonal-reinforced CCC materials have also been improved greatly during the 1970s. Table 15 presents the properties of 3-D fine-weave pierced fabric-reinforced CCCs, and Table 16 lists the properties of 3-D fine-weave orthogonal-reinforced CCCs. Dramatic increases in density and mechanical properties were achieved in transitioning from low- strength, rayon-based graphite fabric to high-strength, PAN-based carbon fabric and the use of HIPIC pitch matrices instead of lower carbon-yielding phenolic matrices. The development of cylindrical 3-D CCC materials was also a remarkable achievement because it enabled the use of these materials in rocket nozzle throats, exit cones, and other applications. Table 17 lists various materials properties in the three major planes, i.e., axial, hoop (circumferential), and radial (through-the-thickness). High-density CCCs were obtained with either CVI pyrocarbon, resin char or pitch-resin carbonaceous matrices. Continuous filament reinforced CCC materials provided the strongest and stiffness composites in the plane of reinforcement. Naturally, the apportionment of reinforcing fibers among the three major axes limits the total composite fibrous reinforcement content and also limits the mechanical properties available in any of the three major planes.

TABLE 13
PROPERTIES OF 2-D FABRIC-REINFORCED CCC MATERIALS

Properties	Test Direction	1966 (WCA Graphite PW Fabric/Phenolic Char)	1978 (WCA Graphite PW Fabric/Phenolic & Furfuryl Alcohol Char)	1982 (T-300HT Carbon 8HSW Fabric/ Phenolic Char)	1982 (T-300HT Carbon 8HSW Fabric/CVI Pyrolytic Carbon)
DENSITY, g/cm^3 (lb/in^3)		1.16 (0.042)	1.58 (0.057)	1.63 (0.059)	1.66 (0.060)
TENSILE STRENGTH, MPa (ksi)	warp	19 (2.8)	76 (11)	331 (48)	303 (44)
	fill	-	39 (5.6)	276 (40)	214 (31)
	x-ply	-	5.3 (0.77)	4.5 (0.65)	5.5 (0.80)
TENSILE MODULUS, GPa (Msi)	warp	2.8 (0.40)	15 (2.1)	117 (17)	110 (16)
	fill	-	-	103 (15)	90 (13)
	x-ply	-	-	3.1 (0.45)	-
TENSILE ULTIMATE STRAIN, %	warp	0.17	0.21	0.33	0.90
	fill	-	-	0.24	1.2
COMPRESSIVE STRENGTH, MPa (ksi)	warp	-	97 (14)	200 (29)	214 (31)
	fill	-	103 (15)	179 (26)	221 (32)
	x-ply	-	-	255 (37)	
COMPRESSIVE MODULUS, GPa (Msi)	warp	-	31 (4.5)	110 (16)	90 (13)
	fill	-	-	110 (16)	103 (15)
	x-ply	-	-	8.3 (1.2)	-
FLEXURAL STRENGTH, MPa (ksi)	warp	23 (3.3)	124 (18)	241 (35)	303 (44)
	fill	-	110 (16)	-	-
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)		-	10 (1.5)	9.0 (1.3)	9.7 (1.4)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	warp	2.9 (1.7)	8.7 (5.0)	45 (26)	40 (23)
	fill	-	-	43 (25)	-
	x-ply	1.2 (0.67)	3.6 (2.1)	4.7 (2.7)	4.8 (2.8)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	warp	5.0 (2.8)	-	1.3 (0.73)	1.2 (0.67)
	fill	-	-	1.4 (0.76)	-
	x-ply	-	-	5.9 (3.3)	6.3 (3.5)

Room temperature values; not for design purposes.

TABLE 14

FABRIC ORIENTATION EFFECTS ON 2-D CCC MATERIAL PROPERTIES

Properties	Test Direction	2-D CCC (T-300HT 8HSW Carbon Fabric/ Phenolic Char Matrix)		2-D CCC (HM Graphite 8HSW Fabric/CVI Pyrolytic Carbon Matrix)	
		Warp-Aligned	Quasi-Isotropic	Warp-Aligned	Quasi-Isotropic
DENSITY, g/cm^3 (lb/in^3)		1.63 (0.059)	1.63 (0.059)	1.55 (0.056)	1.55 (0.056)
TENSILE STRENGTH, MPa (ksi)	warp, 0°	330 (48)	228 (33)	476 (69)	262 (38)
TENSILE MODULUS, GPa (Msi)	warp, 0°	117 (17)	69 (10)	124 (18)	90 (13)
COMPRESSIVE STRENGTH, MPa (ksi)	warp, 0°	200 (29)	166 (24)	228 (33)	159 (23)
COMPRESSIVE MODULUS, GPa (Msi)	warp, 0°	110 (16)	63 (9.2)	117 (17)	76 (11)
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)		9.0 (1.3)	17 (2.4)	9.0 (1.3)	9.0 (1.3)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	warp, 0° x-ply, 90°	45 (26) 4.7 (2.7)	- -	42 (24) 4.8 (2.8)	40 (23) 4.8 (2.8)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	warp, 0° x-ply, 90°	1.3 (0.73) 5.9 (3.3)	- -	0.68 (0.38) 8.1 (4.5)	0.67 (0.37) 8.3 (4.6)

Room temperature values; not for design purposes.

TABLE 15
PROPERTIES OF 3-D FINE-WEAVE PIERCED FABRIC CCC MATERIALS

Properties	Test Direction	1971 3-D FWPF CCC (WCA Graphite PW Fabric & T-50 Graphite Yarn/Phenolic Char)	1974 3-D FWPF CCC (T-50 Graphite 8HSW Fabric & T-50 Yarn/Pitch Coke)	1976 3-D FWPF CCC (HM 3000 Carbon 8HSW Fabric & HM 1000 Carbon Yarn/Pitch Coke)
DENSITY, g/cm^3 (lb/in^3)		1.65 (0.060)	1.91 (0.069)	1.95 (0.070)
TENSILE STRENGTH, MPa (ksi)	X Z	35 (5.1) 103 (15)	165 (24) 131 (19)	228 (33) 172 (25)
TENSILE MODULUS, GPa (Msi)	X Z	11 (1.6) 41 (6.0)	90 (13) 76 (11)	83 (12) 69 (10)
TENSILE ULTIMATE STRAIN, %	X Z	0.83 0.25	0.25 0.19	0.25 0.19
COMPRESSIVE STRENGTH, MPa (ksi)	X Z	62 (9.0) 83 (12)	90 (13) 103 (15)	138 (20) 117 (17)
COMPRESSIVE MODULUS, GPa (Msi)	X Z	11 (1.6) 23 (3.3)	69 (10) 45 (6.5)	83 (12) 66 (9.5)
FLEXURAL STRENGTH, MPa (ksi)	X Z	35 (5.0) 52 (7.6)	200 (29) 131 (19)	- 172 (25)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	X Z	83 (48) 55 (32)	160 (93) 100 (58)	159 (92) 130 (75)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	X Z	3.1 (1.7) 1.1 (0.60)	1.2 (0.67) 1.2 (0.67)	1.1 (0.63) 1.2 (0.65)

X - Properties parallel to fabric axes.
Z - Properties perpendicular (transverse) to fabric axes.
Typical room temperature values; not for design purposes.

TABLE 16
PROPERTIES OF 3-D ORTHOGONAL CCC MATERIALS

Properties	Test Direction	1971 3-D 2-2-3 CCC (T-50 Graphite Yarn/Phenolic Char)	1974 3-D 2-2-3 FW CCC (T-50 Graphite Yarn/Pitch Coke)	1976 3-D 2-2-3 FW CCC HM 3000 & 1000 Carbon Tow/Pitch Coke)
DENSITY, g/cm^3 (lb/in^3)		1.60 (0.058)	1.88 (0.068)	1.91 (0.069)
TENSILE STRENGTH, MPa (ksi)	X Z	97 (14) -	172 (25) 282 (41)	207 (30) 324 (47)
TENSILE MODULUS, GPa (Msi)	X Z	56 (8.1) -	62 (9.0) 97 (14)	55 (8.0) 90 (13)
TENSILE ULTIMATE STRAIN, %	X Z	0.20 -	0.30 0.40	0.22 0.38
COMPRESSIVE STRENGTH, MPa (ksi)	X Z	69 (10) -	76 (11) 165 (24)	97 (14) 179 (26)
COMPRESSIVE MODULUS, GPa (Msi)	X Z	43 (6.2) -	55 (8) 159 (23)	55 (8.0) 97 (14)
FLEXURAL STRENGTH, MPa (ksi)	X Z	- 97 (14)	- 283 (41)	- 221 (32)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	X Z	86 (50) -	80 (46) 140 (81)	92 (53) 116 (67)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	X Z	0.9 (0.5) -	0.97 (0.54) 0.67 (1.2)	1.3 (0.70) 1.2 (0.67)

X - Properties perpendicular (transverse) to billet major axis (height).
Z - Properties parallel to billet major axis (height).
Typical room temperature values; not for design purposes.

TABLE 17
PROPERTIES OF 3-D CYLINDRICAL CCC MATERIALS

Properties	Test Direction	1975 Needled Graphite Felt/CVI Pyrolytic Graphite	1977 T-50 & WYB Graphite Yarns/ Phenolic & Furfuryl Alcohol Char	1985 T-300 Tow/Pitch Coke & Resin Char	1988 Needled Carbon Fiber Tape/CVI Pyrolytic Carbon
DENSITY, g/cm^3 (lb/in^3)		1.80 (0.065)	1.63 (0.059)	1.89 (0.068)	1.70 (0.061)
TENSILE STRENGTH, MPa (ksi)	axial	38 (5.5)	228 (33)	145 (21)	35 (5.0)
	hoop	36 (5.2)	165 (24)	110 (16)	50 (7.2)
	radial	10 (1.5)	2.8 (0.41)	138 (20)	18 (2.6)
TENSILE MODULUS, GPa (Msi)	axial	10 (1.5)	59 (8.5)	131 (19)	17 (2.4)
	hoop	5.5 (0.80)	97 (14)	-	20 (2.9)
TENSILE ULTIMATE STRAIN, %	axial	0.72	0.44	-	0.30
	hoop	0.65	0.25	0.70	0.35
COMPRESSIVE STRENGTH, MPa (ksi)	axial	69 (10)	103 (15)	76 (11)	69 (10)
	hoop	66 (9.5)	110 (16)	90 (13)	83 (12)
COMPRESSIVE MODULUS, GPa (Msi)	axial	7.6 (1.1)	48 (7)	110 (16)	12 (1.7)
	hoop	8.3 (1.2)	83 (12)	117 (17)	20 (2.9)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	axial	251 (145)	74 (43)	69 (40)	80 (46)
	hoop	209 (121)	-	69 (40)	-
	radial	176 (102)	38 (22)	48 (28)	52 (30)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	axial	5.2 (2.9)	1.0 (0.57)	1.4 (0.80)	2.7 (1.5)
	hoop	3.6 (2.0)	1.2 (0.67)	1.4 (0.77)	2.3 (1.3)
	radial	4.1 (2.3)	5.4 (3.0)	3.1 (1.7)	3.1 (1.7)

Room temperature values; not for design purposes.

4.3.5.3 Oxidation-Protected CCC Materials

The properties of CCC materials may be greatly altered by the presence of a ceramic coating, sealant, or particles used to achieve oxidation resistance. Few studies have been performed on the relationship of constituent materials to composite properties, but some data are available.

Mechanical properties of state-of-the-art oxidation-protected 2-D CCC materials are given in Tables 18 and 19. The composites include: (a) an all-carbon structural laminate, (b) a similar material containing particulate inhibitors, and (c) an oxidation-inhibited laminate with an outer coating of silicon carbide. In general the presence of oxidation-inhibiting constituents caused an increase in composite density. In-plane mechanical properties were reduced if particulates replaced some of the composite volume previously occupied by continuous filaments. In-plane tensile strengths were decreased by the addition of a ceramic coating, but in-plane compressive strengths were increased significantly. Oxidation-protected composites had lower in-plane moduli values than similar all-carbon materials.

Structural properties of CCC materials are affected by oxidation as noted in Figure 16. A five percent mass loss reduced the (already low) composite interlaminar shear strength by about 50 percent. At the same mass loss level, the in-plane composite strength was decreased about 40 percent. Tensile strength properties were little affected until the composite lost about four percent weight. At this point the carbonaceous fibers began to be attacked and produced a loss of strength.

4.3.5.4 Hybrid Carbon Composite Materials

The room-temperature properties of various hybrid carbon composite materials are given in Tables 20 and 21. Table 20 gives comparative properties of 2-D fabric-reinforced ceramic-matrix (pyrolytic carbon, graphitized coke or silicon carbide) composites. Table 21 reports additional data on various 2-D fabric-reinforced hybrid composites and an all-ceramic (silicon carbide) composite material.

In general CVI pyrolytic graphite or silicon carbide matrices result in rather brittle composites. The use of silicon-carbide fabric in lieu of carbon fabric results in a lower composite tensile strength and modulus.

TABLE 18
PROPERTIES OF OXIDATION-INHIBITED MATRIX CCC MATERIALS

Properties	Test Direction	2-D CCC (T-300HT Carbon 8HSW Fabric/Resin Char)	2-D CCC (T-300HT Carbon 8HSW Fabric/ Particulate Fillers/Resin Char)
DENSITY, g/cm^3 (lb/in^3)		1.55 (0.056)	1.76 (0.064)
TENSILE STRENGTH, MPa (ksi)	warp x-ply	400 (58) 1.4 (0.20)	317 (46) 2.8 (0.41)
TENSILE MODULUS, GPa (Msi)	warp	76 (11)	76 (11)
TENSILE ULTIMATE STRAIN, %	warp	0.78	0.58
COMPRESSIVE STRENGTH, MPa (ksi)	warp	193 (28)	186 (27)
COMPRESSIVE MODULUS, GPa (Msi)	warp	69 (10)	83 (12)
IN-PLANE SHEAR STRENGTH, MPa (ksi)	warp	30 (4.4)	64 (9.3)
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)	warp	12 (1.8)	12 (1.8)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	warp x-ply	21 (12) 5.7 (3.3)	14 (8.3) 4.3 (2.5)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	warp x-ply	1.7 (0.93) 5.9 (3.3)	1.7 (0.93) 3.6 (2.0)

warp - Properties parallel to warp direction of fabric.
x-ply - Properties perpendicular (transverse) to the warp-fill direction of fabric.
Room temperature values; not for design purposes.

TABLE 19
PROPERTIES OF OXIDATION-INHIBITED 2-D FABRIC-REINFORCED CCC MATERIALS

Properties	Test Direction	2-D CCC (T-300HT8 HSW/Phenolic Char/Carbon Filler/CVI Pyrolytic Carbon)	2-D OPCCC (T-300 HT 8HSW/Phenolic Char/Carbon Filler/ Oxidation Inhibitor/Pyrolytic Carbon)	2-D OPCCC (T-300HT 8HSW/Phenolic Char/Carbon Filler/ Oxidation Inhibitor/Pyrolytic Carbon/Silicon Carbide Coating)
DENSITY, g/cm^3 (lb/in^3)		1.69 (0.061)	1.78 (0.064)	2.20 (0.072)
TENSILE STRENGTH, MPa (ksi)	warp x-ply	345 (50) 8.3 (1.2)	324 (47) 9.7 (1.4)	207 (30) 24 (3.5)
TENSILE MODULUS, GPa (Msi)	warp	110 (16)	97 (14)	62 (9.0)
TENSILE ULTIMATE STRAIN, %	warp	0.47	0.61	0.34
COMPRESSIVE STRENGTH, MPa (ksi)	warp	207 (30)	228 (33)	455 (66)
COMPRESSIVE MODULUS, GPa (Msi)	warp	90 (13)	103 (15)	10 (10)
FLEXURAL STRENGTH, MPa (ksi)	warp	303 (44)	-	317 (46)
FLEXURAL MODULUS, GPa (Msi)	warp	-	-	62 (9.0)
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)	warp	19 (2.7)	21 (3.0)	-

0°, 90° oriented fabric constructions.
Room temperature values; not for design purposes.

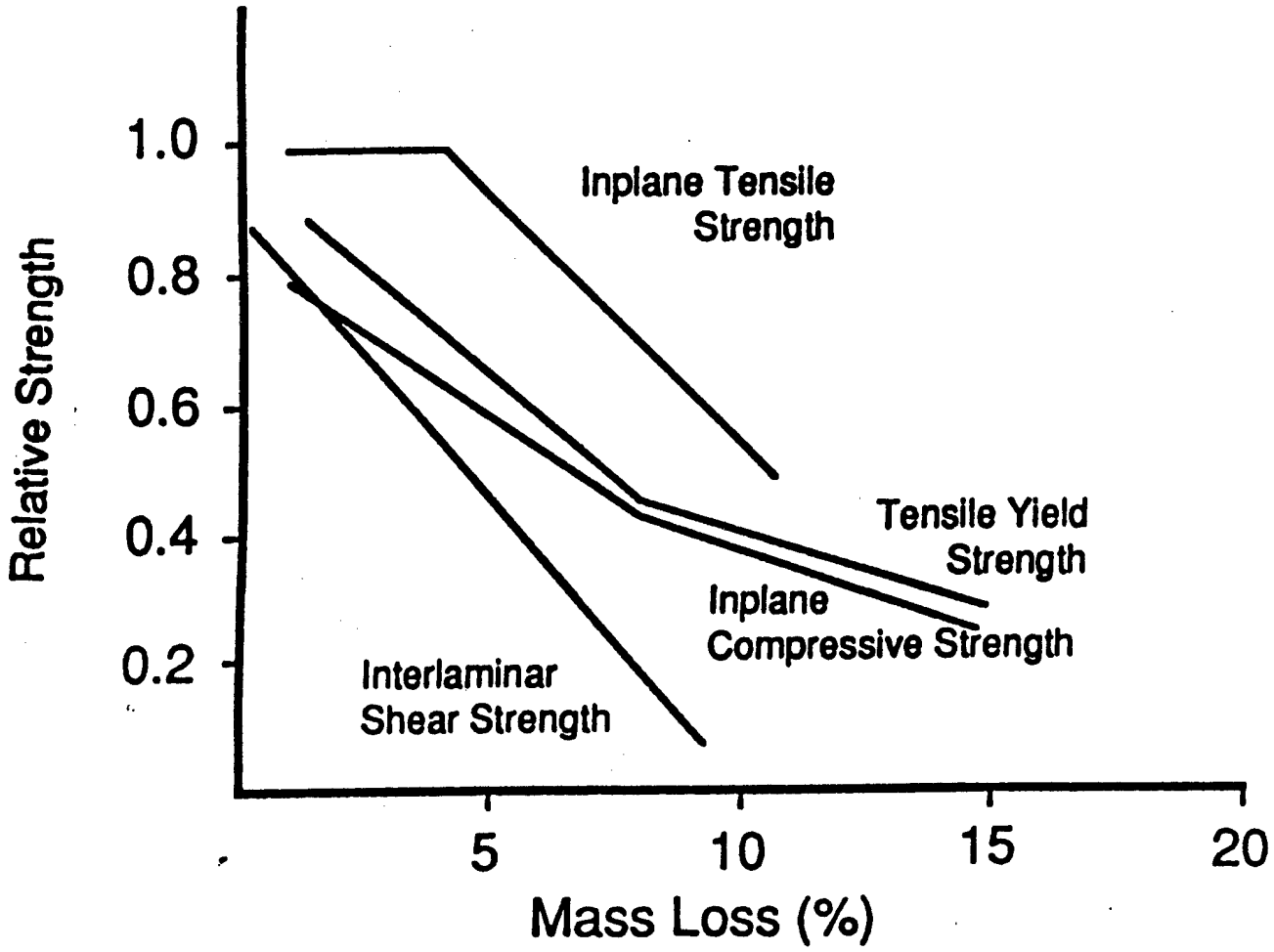


Figure 16. Influence of Oxidation on Mechanical Properties of a 2-D CCC Material.

TABLE 20

PROPERTIES OF 2-D COMPOSITE MATERIALS BASED ON CARBONACEOUS, CERAMIC, AND HYBRID MATRICES

Properties	Test Direction	2-D CCC (T-300HT Carbon 8HSW Fabric/ Phenolic Char/CVI Pyrolytic Carbon)	2-D C/SiC (T-300HT Carbon 8HSW Fabric/ Phenolic Char/CVI Silicon Carbide	2-D SiC/C (Silicon Carbide 8HSW Fabric/Pitch Coke)	2-D SiC/SiC (Silicon Carbide 8HSW Fabric/CVI Silicon Carbide)
DENSITY, g/cm^3 (lb/in^3)		1.69 (0.061)	2.10 (0.076)	2.01 (0.073)	2.50 (0.090)
TENSILE STRENGTH, MPa (ksi)	warp x-ply	345 (50) 8.3 (1.2)	352 (51) -	207 (30) -	193 (28) 10 (1.5)
TENSILE MODULUS, GPa (Msi)	warp	110 (16)	90 (13)	64 (9.3)	214 (31)
TENSILE ULTIMATE STRAIN, %	warp	0.47	-	0.37	0.22
COMPRESSIVE STRENGTH, MPa (ksi)	warp	207 (30)	579 (84)	228 (33)	800 (116)
COMPRESSIVE MODULUS, GPa (Msi)	warp	90 (30)	-	69 (10)	-
FLEXURAL STRENGTH, MPa (ksi)	warp	303 (44)	503 (73)	83 (12)	255 (37)
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)	warp	19 (2.7)	35 (5.0)	12 (1.7)	32 (4.6)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	warp	1.2 (0.67)	5.4 (3.0)	4.1 (2.3)	5.9 (3.3)

0°/90° fabric lay-up in composite.
Room temperature values; not for design purposes.

TABLE 21

COMPARATIVE PROPERTIES OF 2-D CARBONACEOUS, CERAMIC, AND HYBRID MATRIX COMPOSITE MATERIALS

Properties	Test Direction	2-D CCC (HM Graphite 8HSW Fabric/CVI Pyrolytic Carbon)	2-D Gr/SiC (Graphite PW Fabric/ CVI Silicon Carbide)	2-D SiC/SiC (Silicon Carbide PW Fabric/CVI Silicon Carbide)
DENSITY, g/cm^3 (lb/in^3)		1.55 (0.056)	2.02 (0.073)	2.50 (0.090)
TENSILE STRENGTH, MPa (ksi)	warp	262 (38)	317 (46)	193 (28)
TENSILE MODULUS, GPa (Msi)	warp	90 (13)	97 (14)	200 (29)
TENSILE ULTIMATE STRAIN, %	warp	0.45	0.99	0.46
COMPRESSIVE STRENGTH, MPa (ksi)	warp	159 (23)	510 (74)	772 (112)
COMPRESSIVE MODULUS, GPa (Msi)	warp	76 (11)	97 (14)	179 (26)
INTERLAMINAR SHEAR STRENGTH, MPa (ksi)		9.0 (1.3)	28 (4.0)	43 (6.2)
THERMAL CONDUCTIVITY, W/m·K (Btu/ft·h·°F)	warp x-ply	40 (23) 4.8 (2.8)	- -	19 (11) 9.5 (5.5)
THERMAL EXPANSION COEFFICIENT, RT to 1650°C (3002°F) ppm/°C (ppm/°F)	warp x-ply	0.67 (0.37) 8.3 (4.6)	3.6 (2.0) 10 (5.7)	3.6 (2.0) 9.2 (5.1)

2-D quasi-isotropic reinforcement orientation.
Room temperature values; not for design purposes.

4.3.6 Data Analysis

CCC analyses and data reduction are complicated by material anisotropy and the unique behavior of these materials. There is a general lack of fundamental behavior theory and an inability to accurately model CCC behavior.

The properties of CCC materials tend to be slightly more scattered than the properties of available homogeneous structural materials. Coefficients of variation above 10 percent are frequently noted for some of the material properties like strength and stiffness. Consequently large factors of safety are usually required to design safe CCC structures. Proper analysis of a design's safety can become very complex if the many relevant properties are taken to vary independently. The causes for property scatter are not well understood, including the underlying factors and the interrelationship between property variations. Increased knowledge of the structure:property relationships should assist in our understanding and control of CCC property scatter.

4.3.7 Engineering Databases

CCC materials in a "laboratory" stage of development are routinely evaluated for a limited number of general, physical, and mechanical properties. Both room and elevated temperature properties are measured, but data acquisition is kept to a minimum to contain costs. Properties not measured are typically estimated from more extensive databases on similar materials (if one exists). If not, computational technologies are invoked to predict properties or simple human judgment is used to provide a reasonable estimate. With continued development of a CCC material, the quality and uniformity generally improve. Unique properties or combinations of properties are identified, and potential application outlets become apparent. At this point in the materials development, an engineering database is usually generated on the material. Many engineering databases have been generated as noted in Table 22. Such databases are usually funded by the government or aerospace companies, and hence they are not available to the general public.

4.3.8 Chronology

Test methods for determining the properties and characteristics of CCC materials were originally based on monolithic metallic, graphitic, and to some extent organic matrix composite test methods. Many critical issues existed, such as specimen design, mechanics analysis of material response, etc. In addition testing problems were greatly increased by the need for high-temperature data.

TABLE 22
CHRONOLOGY OF U.S. CCC MATERIALS PROPERTY DATABASES

YEAR	PROPERTY DATABASES	IMPORTANCE	ORGANIZATION
1965	2-D graphite (rayon-based) fabric/phenolic char CCC	Enabled prototype design of the NERVA hot hydrogen nuclear propulsion exit cone	Westinghouse Electric Corporation/ Astronuclear Laboratory/USA
1967	2-D graphite (rayon-based) fabric/phenolic char CCC	Enabled prototype designs of entry and reentry vehicle components	LTV Aerospace Corporation/USA
1969/70	2-D tapewrapped graphite (rayon-based) fabric/phenolic char CCC	Enabled prototype designs of various solid propellant motor nozzle components	Southern Research Institute/USA
1971	Uncoated and silicon-carbide coated 2-D graphite (rayon-based) fabric/phenolic char CCC	Enabled prototype designs of thermal protection components for U.S. shuttle orbiter	LTV Aerospace & Defense Company/USA Battelle Columbus Laboratories/USA
1972	3-D orthogonal graphite (low-modulus, rayon-based) yarn/phenolic char matrix CCC	Enabled first-generation prototype designs of nosetips for ballistic missile reentry vehicle systems	Southern Research Institute/USA
1974	4-D and 7-D graphite (PAN-based) tow/HIPIC coal tar pitch coke CCCs	Enabled prototype designs of reentry vehicle nosetips and rocket nozzle throats	Southern Research Institute/USA
1974	3-D pierced fabric and 3-D orthogonal graphite (PAN-based) tow/HIPIC coal tar pitch coke CCCs	Permitted prototype shell and plug nosetip designs of strategic missile reentry vehicles	Southern Research Institute/USA
1975	3-D needled graphite (rayon-based) felt/CVI PG CCC	Permitted prototype designs of strategic missile reentry vehicle heatshields	Southern Research Institute/USA
1975	3-D cylindrical graphite (PAN-based) tow/resin char CCC	Enabled prototype designs of strategic missile reentry vehicle heatshields	Southern Research Institute/USA
1976	3-D orthogonal graphite (high-modulus, rayon-based) yarn/HIPIC pitch coke CCC	Enabled prototype designs of stronger and stiffer nosetips for ballistic missile reentry vehicle systems	Southern Research Institute/USA
1976	3-D orthogonal graphite (mesophase pitch-based) yarn/HIPIC pitch coke matrix CCC	Permitted prototype designs of stiffer nosetips for ballistic and antiballistic missiles	Southern Research Institute/USA
1978	2-D involute graphite (rayon-based) fabric/ pitch-resin carbon matrix CCC	Enabled accurate prototype designs of solid rocket motor nozzle exit cones	Southern Research Institute/USA

TABLE 22 (Continued)
CHRONOLOGY OF U.S. CCC MATERIALS PROPERTY DATABASES

YEAR	PROPERTY DATABASES	IMPORTANCE	ORGANIZATION
1978	4-D hexagonal, tetrahedral pyramidal and tetrahedral cubic graphite (high-modulus, rayon-based) yarn/HIPIC pitch coke CCCs	Permitted prototype designs of high bend stiffness nosetips for maneuvering reentry vehicles	Southern Research Institute/USA
1978	Uncoated and silicon-carbide coated 2-D carbon (PAN-based) fabric/phenolic char CCCs	Permitted prototype designs of thermal protection components for hypersonic flight vehicles and gas turbine engines	Vought Corporation/USA
1980	3-D orthogonal graphite (HM PAN-based) tow/HIPIC pitch coke matrix CCC with tantalum carbide fibers in the z-direction	Permitted prototype designs of particle erosion-resistant nosetips for ballistic missile reentry vehicles	Southern Research Institute/USA
1980	3-D orthogonal carbon (PAN-based) yarn/ HIPIC coal tar pitch coke CCC impregnated with rhenium metal	Enabled prototype designs of all-weather missile nosetips	Southern Research Institute/USA
1981	5-D graphite (PAN-based) tow/coal tar pitch coke CCC	Enabled prototype designs of solid rocket motor nozzle ITEs	Southern Research Institute/USA
1981	4-D hexagonal graphite (HM PAN-based) tow/pitch coke CCC containing tantalum carbide	Enabled prototype designs of particle erosion-resistant nosetips for missile reentry vehicles	Southern Research Institute/USA
1982	Cylindrical 3-D carbon (PAN-based) tow/ HIPIC and LOPIC pitch coke CCCs	Enabled prototype designs of solid rocket motor nozzle ITEs	Atlantic Research Corporation/USA
1982	2-D Graphite (PAN-based) 8HS fabric/ carbon powder-filled phenolic resin char-CVI carbon CCC	Permitted prototype designs of higher strength and higher stiffness structural CCCs for gas turbine engine components	Southern Research Institute/USA
1982	3-D pierced fabric (mesophase pitch-based) 8HS fabric-yarn/HIPIC coal tar pitch coke matrix CCC	Permitted prototype designs of stiffer and higher-density nosetips for ballistic missile reentry vehicles	Southern Research Institute/USA
1983	3-D contour autowoven carbon (PAN-based) tow/pitch coke-resin char matrix CCC	Enabled prototype designs of lighter-weight and higher-performance ITEs of solid rocket motor nozzles	Southern Research Institute/USA

TABLE 22 (Concluded)
CHRONOLOGY OF U.S. CCC MATERIALS PROPERTY DATABASES

YEAR	PROPERTY DATABASES	IMPORTANCE	ORGANIZATION
1984	3-D cylindrical carbon (PAN-based) tow/ phenolic char CCC impregnated with phenolic resin	Permitted prototype designs of insulative CCC thermal protection components	Southern Research Institute/USA
1984	4-D rigid-rod carbon (PAN-based) tow/carbon powder-filled coal tar pitch coke matrix CCC	Enabled prototype designs of ITEs for solid propellant rocket motor nozzles	Southern Research Institute/USA
1985	2-D plain woven graphite (HM PAN-based) fabric/CVI silicon-carbide matrix hybrid composite	Permitted prototype designs of liquid propulsion and aerodynamically-heated flight components	Southern Research Institute/USA
1986	Silicon-nitride coated 2-D carbon (PAN-based) fabric/phenolic char-CVI PG CCC	Enabled prototype designs of gas turbine engine components	Southern Research Institute/USA
1990	Uncoated and silicon-carbide coated 2-D carbon (PAN-based) fabric/oxidation-inhibited phenolic char-CVI PG CCCs	Enabled prototype designs of gas turbine engine components	Southern Research Institute/USA
1991	2-D graphite (mesophase pitch-based) unbalanced fabric/CVI pyrolytic graphite CCC	Enabled prototype design of space structures	BFGoodrich Aerospace/Super-Temp/USA

Tables 23 and 24 contain a chronology of the significant events pertaining to CCC property generation and nondestructive evaluation.

4.3.8.1 The 1960s

The first recorded properties of CCC materials were measured in the early 1960s. Graphite fabric-reinforced pyrolyzed phenolic char was removed from ablated reentry nosetips, and various physical and mechanical properties were measured. The quality of the data left much to be desired, but outstanding mechanical and impact properties of these porous CCC specimens were noted.

Physical, mechanical, and thermal properties of unidirectional and fabric-reinforced CCC materials were also obtained in the early 1960s. Later frictional characteristics were measured on low-density, 2-D CCC materials. From these data it became apparent that CCC offered potential for use in braking systems. 3-D CCC materials were tested at room temperature in the late 1960s. These experiences pointed out the increased complexity of 3-D material behavior, such as fiber bundle pullout, nonlinear stress-strain curves, etc. The need for high-temperature test methods was also apparent because the newly-available 3-D CCC materials appeared to have potential for use on missile nosetips.

4.3.8.2 The 1970s

The first engineering and design databases for a CCC material were generated during the late 1960s and the early 1970s. The materials involved were 3-D needled felt reinforced pyrolytic graphite and 2-D filament-wound pyrolytic graphite composites. Full-scale missile heatshields of these materials were evaluated with x-ray, ultrasonics, DXT, eddy current, infrared, and holography. This was the first extensive use of nondestructive inspection techniques, and it aided greatly in certifying the heatshields. Most CCC testing, however, centered on coated 2-D CCC materials being developed for the U.S. space shuttle. These tests provided considerable experience and guidance for the improvement of test specimen geometry and methodology. High strain rate properties of 3-D CCCs were measured for the first time. Their outstanding properties suggested that 3-D CCCs had potential for use in nuclear blast, impact, gunfire and other high strain rate environments. Fracture toughness values for 2-D CCC materials were also measured for the first time. The materials exhibited high toughness values, i.e., considerably greater than polycrystalline graphites.

TABLE 23
CHRONOLOGY OF CCC MATERIAL PROPERTY MEASUREMENTS

YEAR	PROPERTIES & TEST METHODS	IMPORTANCE	ORGANIZATION
1960	General and mechanical properties of simulated (pyrolyzed graphite fabric/ phenolic) CCCs were measured in a laboratory	Standard test methods and specimen geometries were not adequate for newly-available CCC materials	AF Wright Aeronautical Development Center/Materials Central/USA
1962	Mechanical properties of coated and uncoated 2-D CCCs were measured up to 1650°C (3002°F)	First engineering properties for designing CCC prototypes	Chance Vought Corporation/USA
1972	Mechanical properties of 2-D and 3-D CCC materials were measured at high strain rates	Structural material properties were higher at high strain rates (vs. conventional testing strain rates) thus suggesting high resistance to nuclear-induced blowoff stresses	Kaman Sciences Corporation/USA
1973	Mechanical properties of CCCs were altered by fast neutron irradiation effects	Nuclear radiation resistance of CCC materials may be adequate for uses in fission and fusion power reactors	General Dynamics/Convair Aerospace Division/USA
1974	Circumferential thermal expansion, tensile, and compressive properties of cylindrical CCC materials were measured up to 1650°C (3002°F)	Property database used to design a CCC missile heatshield	Southern Research Institute/USA
1974/78	Thermal, mechanical and high-temperature properties of uncoated n-D CCCs were measured up to 1650°C (3002°F)	Unique specimen geometries and testing procedures were needed for generating a database	Southern Research Institute/USA
1974/75	Longitudinal tensile, transverse tensile, and shear properties were measured for 1-D CCCs	Constituent properties were made available for mechanical analyses of 3-D CCCs	University of Wyoming/Composite Materials Research Group/USA
1975	Thermophysical properties of intermediate-density 3-D CCCs were measured up to very high temperatures	High-temperature materials properties were made available for design of missile nosetips	Purdue University/Thermophysical Properties Research Laboratory/USA
1975	Shear properties of 2-D CCCs were measured and related to materials and process conditions	Provided approaches for increasing a limiting property (interlaminar shear strength) of 2-D CCCs	Aerojet Solid Propulsion Company/USA

TABLE 23 (Continued)
CHRONOLOGY OF CCC MATERIAL PROPERTY MEASUREMENTS

YEAR	PROPERTIES & TEST METHODS	IMPORTANCE	ORGANIZATION
1977	Total hemispherical emittance of silicon-carbide coated 2-D CCC was measured from -173°C (-279°F) to 177°C (351°F) and after repeated thermal cycling	A critical thermophysical property of coated 2-D CCC material became available for shuttle thermal protection systems design	Massachusetts Institute of Technology/USA
1979	Specialized test methods were developed and uniaxial tension, compression, and shear properties were measured in all three coordinate directions of 3-D CCCs	Directional material properties were used for predicting modeling effects and irreversible changes in loaded CCCs were detected with acoustic emission and SEM fractography	University of Wyoming/Department of Mechanical Engineering/USA
1979	Single, central source was created for the collection, organization, storage, retrieval, analysis, and dissemination of U.S. CCC data	The computerized system incorporated about 900 individual process and property parameters associated with CCC materials	Battelle Columbus Laboratories/USA
1979/81	Porosity and permeability properties of uncoated 2-D and 3-D CCCs were measured at room and elevated temperatures	Data were needed for post-test billet failure analysis and for designing nozzle insulators	Southern Research Institute/USA
1980	Specific heat of CCC materials was measured in a laboratory	Thermophysical property data were used for prototype design	Purdue University/Thermophysical Properties Research Laboratory/USA
1980	Fatigue strengths of silicon-carbide coated 2-D carbon (PAN-based) fbric/phenolic char CCC were measured up to 100 million cycles	Fatigue life of the coated CCCs were limited by cracking of the surface coating	United Technologies/Pratt & Whitney Aircraft/USA
1981	New and modified property measurements techniques were evaluated and used for 2-D CCCs	Specimen design guidelines, test methods and laboratory tests were established for CCC nozzle materials	Atlantic Research Corporation/USA
1982	*In situ* thermal conductivity of carbon fiber and carbon matrix was measured in a 3-D CCC	Thermal conductivities of the constituents were changed by high-temperature processing	Purdue University/Thermophysical Properties Research Laboratory/USA

TABLE 23 (Continued)
CHRONOLOGY OF CCC MATERIAL PROPERTY MEASUREMENTS

YEAR	PROPERTIES & TEST METHODS	IMPORTANCE	ORGANIZATION
1982	Socket bend test method was developed and bending characteristics were measured for n-D and 3-D CCCs	Bend stiffness and failure mode data were used for design of prototype nosetips of maneuvering reentry vehicles	Southern Research Institute/USA
1983	Test method was developed for measuring properties of large diameter threaded joints between 3-D and 2-D CCCs	Useful for selection of thread forms and materials	Jortner Research & Engineering/USA
1983	Mechanical properties of coated and uncoated 2-D CCCs were measured after exposure to high temperature (600°C, 1112°F) air	Mechanical properties were altered by carbon matrix loss and fiber-matrix degradation	The Pennsylvania State University/ Department of Materials Science & Engineering/USA
1983	Hoop tensile and thermophysical properties of 3-D cylindrical carbon (PAN-based) tow/ HIPIC coal tar pitch coke CCC	New hydrostatic ring test was used to obtain critical design data	Southern Research Institute/USA
1983	Restrained thermal expansion properties of 2-D and 3-D CCCs were measured at temperatures up to 2538°C (4600°F)	Diametral growth data became available for design of CCC nozzle exit cones	Southern Research Institute/USA
1985	Compressive properties were measured for thin-walled structural CCCs	Key design properties became available for spacecraft components	Southern Research Institute/USA
1986	Mechanical properties of unique construction uncoated CCCs were measured using new specimen designs and testing methodologies	Structural properties of CCCs appeared to be adequate for highly-stressed parts of gas turbine engines	Illinois Institute of Technology/USA
1986/87	Shear strengths of 2-D CCCs were measured under pure interlaminar shear conditions	More accurate interlaminar shear strength data became available for design purposes	Jortner Research & Engineering, Inc./USA
1986	Thermal expansion and interlaminar mechanical properties of uncoated and coated 2-D carbon (PAN-based) fabric/ phenolic char CCC were measured after thermal cycling	Thermal cycling did not affect the interlaminar properties of these particular 2-D CCCs	NASA-Langley Research Center/USA

TABLE 23 (Concluded)
CHRONOLOGY OF CCC MATERIAL PROPERTY MEASUREMENTS

YEAR	PROPERTIES & TEST METHODS	IMPORTANCE	ORGANIZATION
1987/92	High cycle fatigue properties of oxidation-inhibited CCCs were measured up to one million cycles and high temperatures	Minimal property changes were encountered in a random fatigue environment	Rohr Industries, Inc./Refractory Technology Aerospace Components/USA
1987	A test method was developed for measuring transverse (cross-ply) tensile strengths of 2-D CCCs up to 2000°C (3632°F)	Quantitative high-temperature data was obtained on a limiting property of 2-D CCCs	Wright State University/Mechanical and Materials Engineering/USA
1990	Properties measured on uncoated and silicon-carbide coated 2-D carbon (PAN-based) fabric/oxidation-inhibited phenolic char-CVI PG CCCs	Enabled prototype designs of gas turbine engine components	Southern Research Institute/USA
1991	Properties measured on 2-D graphite (mesophase pitch-based) unbalanced fabric/CVI pyrolytic graphite CCC	Enabled prototype design of space structures	BFGoodrich Aerospace/Super-Temp/USA

TABLE 24
CHRONOLOGY OF CCC NONDESTRUCTIVE EVALUATION AND INSPECTION

YEAR	NDE/NDI EVENTS	IMPORTANCE	ORGANIZATION
1970	X-ray, ultrasonics, DXT, eddy current, infrared and holography techniques were used on 3-D graphite felt/CVI pyrolytic graphite matrix CCC Frusta	CCC heatshield quality was certified with the use of available NDI/NDE methods	Atomic Energy Commission/Sandia Laboratories/USA
1978/83	X-ray computed tomography (CT) was applied to the NDI/NDE of CCC rocket nozzle parts	First industrial CT for inspecting and evaluating large CCC parts	Advanced Research and Application Corporation/System Design/USA
1983/85	Computed x-ray tomographic NDI method demonstrated for 2-D and 3-D CCCs in coupon, ring, billet, and exit cone configurations	Reliable inspection method verified for small-to-very large solid rocket motor CCC components	Aerojet Strategic Propulsion Company/USA
1983	Acoustic emissions from 3-D CCC materials during compression was correlated with the stress state	Acoustical emission (with further development) was judged to be a usable quality control technique	Rockwell International Corporation/North American Aircraft Operations/USA
1984	Computer-aided tomography (CAT) applied to CCC materials to assess material anomalies, defects, and other property-altering inclusions	Extremely large amount of nonspecification materials data became apparent, but its significance was unknown	Prototype Development Associates (PDA)/ Engineering/USA
1984	State-of-the-art NDI/NDE methods used to identify defects in 2-D CCC exit cone materials	Dry plies, fabric wrinkles and low-density bands were identified as primary causes for reduced 2-D mechanical properties	Southern Research Institute/USA
1986	Digital eddy current impedance NDE test method was developed to measure fabric wrinkles and folds in 2-D involute CCCs	Eddy current scanning of CCC exit cones was useful in identifying strength-reducing composite anomalies	Boeing Aerospace Company/USA
1986	Conventional NDE/NDI techniques were used to quantify anomalies in rejected 2-D involute CCC exit cones	CCC failure strengths and modes were correlated with material anomalies (defects), but NDE/NDI was inadequate for prediction of anomalous material behavior	Southern Research Institute/USA

The mid-1970s was a time of increased CCC testing and the initiation of new test equipment development. 3-D CCC materials were sufficiently mature to warrant the generation of statistical design databases. 3-D orthogonal-reinforced CCCs and 3-D pierced fabric-reinforced CCC materials were extensively characterized for missile nosetip designs. Other n-D CCCs like 7-D CCCs were also characterized to a limited extent. Overseas the USSR published its first article on properties of research CCC materials. Germany published the frictional characteristics of 1-D CCC. France published electronic and thermal properties of CVD PG felt materials. The generation of properties of cylindrical CCC materials required new test equipment. The first high-temperature hydrostatic ring test device was built, checked out, and used to measure hoop tensile properties.

The number of organizations testing CCC materials began to increase. All of the major aerospace companies had a testing laboratory. Several U.S. universities began to use their expertise to measure mechanical and thermophysical properties of various CCCs. One independent research laboratory was also established to serve the testing needs of the defense community. The development of CCC materials, however, required an understanding of the materials and process relationships. The first published report relating the shear strength of 2-D CCCs to key materials and process variables employed to fabricate the test specimens. Thermostructural capability of 2-D and 3-D CCCs was a major concern at that time. Laboratory equipment was built to create a steep thermal gradient in a CCC specimen, but all levels of intense heating failed to fracture the material. From these data it was apparent that 3-D CCCs were a prime candidate for future missile nosetips. Properties were also generated on candidate rocket nozzle and space radioisotope power canisters for the purpose of guiding ongoing materials development.

In the late 1970s a design database was generated on 2-D CCCs for rocket nozzle exit cone designs. The first computerized CCC data storage and retrieval system was initiated in 1979. It was disbanded several years later due to lack of user financial support. 2-D CCCs continued to be of great interest to the aircraft brake industry. Many versions of the materials were fabricated and tested for frictional, wear, mechanical, thermophysical, and general characteristics. This work indicated a superiority of pyrolytic carbon matrices for brake disc applications. CCCs of increased complexity were fabricated in various developmental programs. 4-D composites, for example, had multiple axes of reinforcement and thus required special test matrices for their evaluation. Test equipment was upgraded during this period, and some unique test equipment was designed and assembled. For example, a high-temperature permeability method and equipment was developed to measure the flow of hot gases through CCC nozzle

parts. Such data were needed to design insulator backup articles and to help explain billet cracking during processing. Large- and full-scale parts were being manufactured, and their quality was of considerable concern. X-ray computed tomography was applied for the first time to rocket nozzle parts. A phenomenal amount of information was obtained by this NDE technique, much of which defied interpretation.

4.3.8.3 The 1980s

During the early years of the 1980s, all CCC test methods came under review. Specimen design, test procedures, adequacy of test equipment, simulation capabilities, etc. were evaluated in detail and recommendations made for upgrading. Test equipment continued to be improved. The high-temperature ring test method was modified to measure tensile stress:strain, compressive stress:strain, and thermal expansion in the circumferential direction of cylindrical materials. The high-temperature ring method was also modified to measure diametrical growth of CCCs under restrained loads somewhat similar to that encountered by nozzle throat materials during firing. Most of the CCC testing involved nozzle materials for the throat and exit cone regions. Fifteen-inch diameter 3-D CCC billets were extensively characterized to support material selection and design of nozzle throats and ITEs. Physical property acceptance methods were evaluated and upgraded for 2-D CCC involute exit cone materials. Laboratory test methods became more sophisticated. For the first time, the thermal conductivity of fiber and matrix in a 3-D CCC material was measured over a wide temperature range.

During the mid-1980s, intensive efforts were being devoted to the development of oxidation-resistant materials for potential uses in gas turbine engines, hypersonic flight vehicles, and liquid propellant engines. Existing test methods did not seem applicable for the multilayered composites, and many issues had to be resolved to obtain the needed properties and characteristics. The validity of testing coated specimens versus independent measurement of the coating and the substrate had to be resolved. Oxidative characteristics of the coated materials were also required as well as the composite properties after oxidation. Various high-temperature heating cycles were formulated to invoke the correct materials response in partially simulated environments. Most testing organizations developed their own particular thermal cycles, and little was done to standardize the testing.

In the mid 1980s test equipment and methods continued to be improved. For example, equipment was designed to conduct compression-compression biaxial tests on 3-D CCCs to obtain data indicative of nozzle ITE stress states with constraining and surrounding

structures. The potential use of CCCs in rotating and acoustic environments created a need for the measurement of dampening characteristics. In a comprehensive program it was demonstrated that CCC material had desirable high dampening characteristics during exposure to one million cycles in a random fatigue environment. Overseas, the testing of CCC materials greatly increased as materials matured in various development programs. Flat and ring test methods were developed in France for evaluating 2-D, 3-D, and 4-D materials in tension, compression, bending, and shear. 3-D CCC materials were also being evaluated in Russia, People's Republic of China, and several other countries. Frictional testing of 2-D CCC materials increased greatly in Europe and Asia as guidance was needed for the development of aircraft brake discs. With respect to quality assurance of CCC materials, the early to mid-1980s also witnessed the first use of computer-aided tomography (CAT) applied to CCC articles to identify anomalies, defects, and other property-altering inclusions. Other NDE methods were also evaluated for utility, including digital pulse echo (DPO) ultrasonics and digital eddy current impedance methods.

In the late 1980s the measurement of shear properties of CCC materials was identified as a major testing problem. Many different shear tests were being used, and there were no accepted standards for shear measurements. A modified direct shear test method was developed for 2-D CCC materials. This method allowed strength measurements under pure interlaminar shear and also under biaxial states involving cross-ply tension/compression. Thin CCC structures became of interest for spacecraft and turbine engine applications. This necessitated a re-evaluation of applicable test specimen geometries and methods to identify or develop acceptable measurement techniques. Overseas, France developed a unique test method for evaluating coated CCC materials in tension and compression and after thermal cycling. A solar furnace was used to produce test temperatures up to 1500°C (2732°F). CCC materials also became of interest to the nuclear power community. They were evaluated for first wall components of fusion reactor devices. Erosion, thermal shock resistance, and fracture toughness characteristics were measured. NDE for CCC quality assurance was greatly expanded in the late 1980s. Advanced methods were used to quantify anomalies in rejected CCC materials, and a correlation was developed between failure strengths-and-modes to anomalies (defects). Much additional work, however, is needed in this area.

4.3.8.4 The 1990s

In the early 1990s work continued on developing acceptable test methods for measuring the mechanical properties of thin composites and oxidation-resistant materials. Conventional ASTM test methods were found to be not usable for generation of

mechanical properties, especially for double-notch interlaminar tests in the fill direction of 2-D composites. Extensive test method modifications were subsequently made, and the first engineering database was established for lightweight, high stiffness, high tolerance 2-D CCC spacecraft structural materials. Additional work was performed on shear testing, and a modified short-beam shear test method was developed and verified for 2-D fabric-reinforced CCC materials. The new specimen design involved a sandwich construction that consisted of a CCC laminated core and thin high-strength graphite/epoxy facesheets bonded to the core. The facesheets were loaded in flexure, while the CCC core was loaded in transverse shear. Premature failures were avoided, such as delamination at the free edges, facesheet separation or peel from the core surface, or crushing at the load heads. Excellent correlation was obtained between test data and predicted results. In the area of CCC fracture, there was a significant increase in the design database. With respect to oxidation- resistant CCC materials, extensive screening was accomplished on new and improved materials. A comprehensive engineering database was completed on eight different 2-D CCC materials. Physical, mechanical, and thermal properties were reported on uninhibited and inhibited 2-D structural substrate materials at room and elevated temperatures. Overseas, research continued on the properties of newly developed materials. Some of the data was published in the open technical literature.

4.4 ENVIRONMENTAL TESTING

Environmental testing of new and upgraded CCC materials has been carried out as an evolutionary evaluation activity. The first stage of material evaluation was a screening activity as previously noted. A number of selected properties were measured, and a limited amount of environmental tests were also accomplished to identify promising materials for additional development. Materials having undesirable properties or a poor combination of properties were routinely rejected at this stage. Emphasis was then given to improving the uniformity, quality, and reproducibility of the material. Promising materials were subjected to more extensive property measurements and more sophisticated environmental testing. At this point two or more of the most promising developmental materials were selected for scale-up or manufacturing producibility runs. Material properties were fine tuned in accordance with the anticipated component, and more elaborate material evaluation activities were accomplished. Prototypes were evaluated in the best available ground-based test environments and, if successful, were followed by testing in actual service conditions. Needless to say, these types of full-scale article tests were very expensive. Some tests cost in the tens to hundreds of thousands of U.S. dollars.

Environmental testing should accomplish all of the following objectives:

(a) confirm that the material concept is suitable for the anticipated service conditions,
(b) identify any remaining material deficiencies,
(c) uncover any previously unrecognized failure modes,
(d) obtain materials properties and performance data from *in situ* or external instrumentation, and
(e) correlate actual with predicted properties and performance.

In addition, consideration should be given to all of the following factors:

(a) proper specimen or prototype design to obtain the correct boundary conditions,
(b) instrumentation that does not unduly disturb the localized material behavior,
(c) nondestructive inspection and evaluation of the test material to insure material quality and maximize the amount of performance information obtained,
(d) simulation of the most critical environmental parameters,
(e) failure modes identical to those encountered in real service environments,
(f) performance predictions prior to actual testing and followed up by correlations with actual test data, and
(g) use of the minimum cost facility to obtain all of the desired materials performance information.

Environmental simulation of the actual service environments is often impractical or impossible. Earth reentry probably represents the worst-case scenario. Key parameters include (a) environmental conditions, (b) size of part, (c) time (duration), and (d) combination of environments. In general, any one reentry environmental parameter can be produced if the size or time is not critical. Combined flight environmental conditions in the proper ratios cannot be simulated. The test engineer thus has no other choice but to evaluate the material in as many different and applicable facilities as possible. For reentry nosetip materials, the evaluation is quite extensive. Laboratory testing includes such facilities as: (a) windtunnels, (b) ballistic ranges, (c) rocket sleds, (d) nuclear effects simulators, (e) centrifuges, (f) air-stabilized arc jet heaters, (g) rocket motor exhausts, (h) space chambers, and (i) radar ranges. Partial simulation of the reentry environment is accomplished with sounding rockets and aircraft drop tests. Nuclear testing is accomplished in underground evaluation environments. Flight evaluation is carried out with various ground-launched boosters for short-to-long range flight evaluations. Flight evaluation involves reentry vehicle (RV) measurements including: (a) reentry optics, (b) ground optics, and (c) terminal reentry phase tracking and signature returns.

4.4.1 Friction and Wear

Utilization of CCC materials in various braking, bearing, power transmission, and similar uses depends greatly upon their friction and wear characteristics. These performance parameters were noted to be dependent upon the precise conditions of sliding imposed, and hence they are not fundamental material properties. Various parameters all played an important role, including the geometric shape and size of the contacting surfaces and the nature and roughness of the counterface material. Critical test parameters were: (a) relative sliding speed at the friction surface, (b) pressure on the friction surface, (c) kinetic energy per unit mass, (d) rate of energy dissipation, (e) ambient conditions, and (f) prior material history.

An inertial-type dynamometer has generally been used for frictional testing. The typical test specimen had a ring-on-ring configuration, with a small annular ring having an outer diameter of 5.54 cm (2.18 in), internal diameter of 3.48 cm (1.37 in), and a thickness of 0.64 cm (0.25 in). The specimen was mounted on a rotating shaft and subsequently pressed against a similar but stationary ring positioned on the same axis. More specifically, the CCC specimen rotor was connected to inertial plates on one side of the dynamometer. This section was rotated and its speed was variable. The weight of the inertial plates and the rotating velocity determined the energy level of the particular test. An energy level of about 1200 J/g (516 Btu/lb) was generally used which was typical of aircraft brake operating conditions. The other side of the dynamometer contained a CCC stator and a piston which forced the stator to rub against the rotor. Material evaluation was accomplished by rotating the inertial plates and CCC up to a predetermined speed, releasing the drive, and then applying constant brake pressure to decelerate the inertial plates. The initial rotational speeds generally varied from about 1,000 to 8,000 revolutions-per-minute (rpm), and the linear velocity of the friction surface was about 5 to 50 m/s (16 to 164 ft/s). The period of deceleration was about 8 to 10 seconds. This type of dynamometer test was conducted in a variety of atmospheres and conditions, including: (a) air, (b) nitrogen, (c) partial pressures of oxygen, (d) moisture levels, and (e) other environmental parameters of concern. After frictional testing, weight and linear measurements were made. Material weight loss was determined with an analytical balance. Specimen thickness changes were measured with a micrometer. Thickness changes were generally performed at about three different specimen locations and after 100, 200, and 250 stops (braking cycles). From the dynamometer testing, information was obtained on the: (a) loading conditions, (b) average friction coefficient, (c) time for the CCC disc to stop, (d) kinetic energy expended in stopping, and (e) temperature of the test material.

Full-scale CCC brake stators and rotors have been tested in the same general manner. A multi-disc brake assembly was mounted on a wheel with a tire, rotated at speeds between 1,000 and 8,000 rpm, constant interface pressure then applied, and the assembly decelerated to a stop. A predetermined number of stops were run for data acquisition and to calculate the anticipated wear life of the CCC brake system.

Frictional materials were also subjected to other environmental conditions, including: (a) impact tests, (b) water soak, (c) temperature cycling, (d) icing, (e) thermal shock, (f) salt spray, (g) high humidity, (h) oxidation, (i) vibration tests, and (j) hydraulic fluids.

4.4.2 Rocket Motor Exhaust

CCC materials have been extensively used in components of solid rocket motors. In such applications the composite materials were exposed to very severe environmental conditions including: (a) very high temperatures, (b) high heating rates, (c) chemical corrosion, (d) gas-dynamic shear stresses, (e) particulate erosion, and (f) other factors. Various ground-based test facilities have been developed for materials screening, performance evaluation, and final proof testing of components. These facilities were: (a) gas-stabilized electric arcs, (b) combustion-driven simulators, (c) small rocket motors, and (d) large rocket motors.

Small gas-stabilized electric arc plasma generators have typically been used to provide the first screening tests for candidate propulsion materials and to conduct specialized thermochemical and thermal tests on CCC materials. Tests were economical and fast, and they provided a basis for selecting materials used in follow-on developmental efforts. The simulated rocket exhaust gases were created by electrically heating an inert gas and then adding various gaseous compounds to achieve the desired gas chemistry. Flat-faced or hollow cylinder-type specimens were then immersed in the hot exhaust, subjected to steady-state heating, and maintained for several minutes or a shorter period of time. The specimens were typically noninstrumented, and only limited experimental data were obtained. Data acquistion generally included the average linear recession rate and depth of thermal penetration.

Combustion-driven facilities were also used to screen candidate CCC materials. The simulator rocket motor consisted of a: (a) combustion chamber, (b) propellant feed injector, (c) nozzle holder, and (d) nozzle test specimen. The combustion products and temperature of a solid propellant motor were properly duplicated by using the correct liquids, gases, and aluminized slurries. The test specimen resembled a small-scale rocket nozzle or a thick-walled cylinder having a small diameter (1.3 cm, 0.5 in) hole in the center. The test material was

evaluated by exhausting a 3204°C (5800°F) aluminized gas through the nozzle specimen at a velocity of about 1.59 km/s (5,200 ft/s). The test was continued for 60 seconds or until the chamber pressure decreased to 1.03 MPa (150 psia) due to specimen throat erosion. The total throat recession at any given time during testing was then calculated from the chamber pressure readings. Material data acquisition involved only instantaneous linear recession, as noted, and a calculation of the average erosion rate.

Small solid rocket motor simulators have historically been used to: (a) evaluate promising materials compositions and constructions, (b) provide databases for materials selection, and (c) obtain information for initial nozzle designs. Other more specialized uses have included: (a) gas impingement studies, (b) verification of thermal and thermostructural models, (c) correlation of ring and billet performance data, (d) assessment of the viability of subscale testing, and (f) evaluation of scaling effects. In a typical small rocket motor test, up to about 45.4 kg (100 lb) of solid propellant were used to generate the test environment. The test material was typically in the configuration of a nozzle throat having an internal diameter of about 1.3 to 7.6 cm (0.5 to 3.0 in). Either single or multiple specimens were tested during a single motor firing. Multiple specimens were in the form of rings (washers) which were placed adjacent to each other. Material exposure was for a period of about 30 to 45 seconds. Material data acquired from this type of testing included: (a) the average throat recession rate, (b) surface roughness, (c) throat asymmetry, and (d) in-depth thermal response.

Closer simulation of actual rocket motor environments has been achieved with large solid propellant rocket motor firings. One widely-used (reusable) test motor employed a 5,215 kg (11,500 lb) aluminized propellant charge to generate a flame temperature of about 3283°C (5941°F). The chamber pressure was about 5.51 MPa (800 psia), and the total burn time was about 70 seconds. Test materials were evaluated in the form of actual nozzle components, and most of the materials performance data were obtained during post-test analyses. Data generation typically included: (a) erosion profiles as a function of component position, (b) surface roughness and anomalies, (c) in-depth temperatures if instrumented, and (d) similar information.

The U.S. propulsion community has also used surplus rocket motors for materials and component testing. Air Force Minuteman third-stage motors have been routinely employed to evaluate CCC components such as 3-D CCC nozzle ITEs and CCC exit cones. The motors have utilized a propellant charge of about 3,175 kg (7,000 lb) to generate a flame temperature over 3116°C (5641°F) and a chamber pressure of about 2.8 to 4.1 MPa (400 to 600 psia).

4.4.3 Liquid Propellant Exhaust

Combustion test facilities have been used to evaluate candidate materials for liquid propellant engine components. The advantages of these ground-based simulators were: (a) correct exhaust chemistry, temperature and pressure conditions, (b) modest test costs, and (c) fast turnaround times. The test engine typically consisted of a combustion chamber, a propellant feed injector, a specimen nozzle holder, and the test specimen. Two types of propellants have been employed, including: (a) nitrogen tetraoxide and a mixture of 50:50 volume percent of hydrazine and unsymmetrical dimethylhydrazine, and (b) a more energetic chlorine trifluoride and hydrazine. The first propellant had a flame temperature of about 2927°C (5300°F) and a gas velocity of approximately 1.71 km/s (5.60 kft/s). The fluorinated propellant produced a flame temperature of about 3483°C (6300°F). The test specimen was a thick-walled cylinder containing an entrance section, a throat section, and an exit section. Hot exhaust gases created in the combustion chamber were passed under high pressure and through the nozzle specimen. An initial chamber pressure between 0.207 and 0.483 MPa (300 and 700 psia) was used, and as the throat eroded, the chamber pressure decreased. A test time of several hundred seconds was generally used, or it lasted until a predetermined chamber pressure was reached. Material data acquisition usually included: (a) total throat erosion, (b) throat asymmetry, if any, and (c) altered material surface features.

Small ground-based combustion devices have also been used to simulate ramjet propellant test conditions. The test arrangement included: (a) an oxygen/hydrogen torch igniter, (b) gaseous oxygen and nitrogen feed lines to simulate air flow, and (c) liquid fuel mixture of JP-4/toluene hydrocarbon fuels. Flame temperatures were about 1727-3141°C (2449-4440°F), and the initial gas velocities were approximately 1.17 km/s (3.85 kft/s). Chamber pressures were between 6.9 and 103 kPa (10 and 150 psia) to simulate either boost or cruise phase of the rocket ramjet engine. Material testing was generally accomplished in either of three modes, including: (a) steady-state conditions, (b) repetitive pulsing, and (c) multiple starts. Materials data obtained included: (a) total erosion as a function of specimen position, (b) throat asymmetry, if any, and (c) material surface characteristics.

4.4.4 Turbine Engine Exhaust

CCC materials intended for use in man-rated and expendable (limited-life) turbine engines have been screened in various laboratory devices and evaluated as subelements or full-scale components of actual engines.

Materials developers and turbine engine manufacturers have designed, built, and operated laboratory devices for measuring the oxidation of CCC materials under controlled conditions. All of the facilities were relatively simple and composed of a programmable high-temperature air furnace with rapid heating and cooling capabilities. Specific temperature-time cycles employed by the users have varied considerably, but in general they have been based on: (a) critical engine thermal conditions and (b) elevated temperatures needed to open and close composite surface coating cracks.

The general testing procedure has involved the preparation of small coated specimens having dimensions on the order of 7.6 cm (3.0 in) long, 0.25 cm (0.10 in) wide and 0.51 cm (0.20 in) thick. Specimens were conditioned prior to testing and then exposed in the air furnace in an "up" or "down" thermal cycle. For purposes of illustration the "up" cycle was conducted as follows. The coated specimen at room temperature was heated to 649°C (1200°F) over a period of 20 minutes. After exposure for 10 hours, the air temperature was increased to 816°C (1500°F) as quickly as possible. This test temperature was maintained for 10 hours and then quickly increased to 1093°C (2000°F). Following exposure for 2.5 hours, the air temperature was once again increased to a maximum of 1316°C (2400°F). After 2.5 hours at the maximum temperature, the air temperature was rapidly lowered to room temperature. At this point the specimen had been exposed to one full cycle. The cycle was repeated five times or until a total testing time of 150 hours was reached. An optional step was to measure moisture uptake at the end of a cycle by exposing the material to 90 percent relative humidity (RH) at 50°C (122°F) for two to three days. Materials data obtained in this manner were: (a) mass changes at predetermined times in the total cyclic heating test, (b) changes in surface characteristics like cracks or depleted sealants, (c) presence of oxidized products, and (d) other surface or internal changes.

Cyclic oxidation altered many of the properties of uncoated and protected CCC materials. To obtain a measure of the effect on mechanical properties, flexural specimens were tested prior to and after a predetermined number of exposure cycles. All tests were discontinued when five percent weight loss was incurred. Property changes were then correlated with the specimen weight loss.

Oxidation-protected CCC materials found promising in the oxidative screening tests and possessing adequate structural properties were then fabricated in the form of engine subelements or components. These parts were substituted in test engines for the existing metallic components and then tested. Various engine power settings were used, including idle, full power, and after burner conditions. The sequence of engine operation generally paralleled that of the

duty cycle of an operational turbine engine. At periodic intervals during the testing, the test parts were inspected visually or by nondestructive inspection techniques for any evidence of deterioration. At the end of the test program, the parts were removed from the engine and examined for: (a) dimensional and mass changes, (b) subsurface damage, and (c) altered properties.

4.4.5 Missile Reentry Flight

CCC materials have been widely used for the nosetips of strategic missile reentry systems. In these applications the composites have been exposed to extreme conditions of temperature, heating, pressure, and sometimes particulate erosion. The thermal, thermostructural, and ablation performance of these materials has been of paramount importance. Various test facilities have been developed for evaluation purposes, including: (a) air arc heaters, (b) combustion-driven devices (rocket engines), (c) ballistic ranges, and (d) arc wind tunnels.

Candidate thermal protection materials for missile reentry flights are first screened in a small, air-stabilized electric arc heater. A 500 kW (528 Btu/s) arc heater has been routinely used to generate the proper gas enthalpy, gas chemistry, heating rate, and stagnation pressure. The test material was machined or fabricated into a small diameter (1.9 cm, 0.75 in) specimen having a flat-faced or hemispherical-faced configuration, and exposed to the hot subsonic velocity, arc-heated gas stream. The specimen cold-wall heating rate was 136 to 407 cal/cm^2-s (500 to 1,500 Btu/ft^2-s), and the test duration was about two minutes. Material performance data obtained in this manner included: (a) total weight loss, (b) total linear recession, (c) backface temperature if thermocoupled, and (d) surface characteristics. The steady-state linear and mass ablation rates were then calculated from these data. Materials which survived the thermal shock conditions and exhibited low ablation were then selected for more comprehensive ablation testing.

The next level of ablation screening typically involved a 10 MW (9.5 kBtu/s) air arc heater. Test conditions were: (a) up to 814 cal/cm^2-s (3,000 Btu/ft^2-s) heating rates, (b) steady-state heating for several minutes, and (c) subsonic or supersonic jet flow. Nosetip specimens were on the order of 7.6 cm (3.0 in) diameter, and heatshield specimens were flat-faced and inclined at a small angle to the hot gas flow. Data acquisition was essentially the same as previously described.

High-powered air arc heaters were used for final ablation evaluation of candidate nosetip and heatshield materials. These facilities operated at power levels up to 60 MW (57 kBtu/s), cold-wall heating rates up to 4,070 cal/cm^2-s (15,000 Btu/ft^2-s) and impact pressures up

to 21.3 MPa (210 atm). Nosetip specimen geometries were either a sphere-cone with a small nose radius or a sphere-cylinder configuration. Models were generally mounted on a sting, rotated into the gas flow for a prescribed period of time, and then rotated out of the gas stream and cooled. Testing was accomplished in one of three different modes, including: (a) ramp, (b) steady-state, or (c) combination of ramp followed by steady-state exposure. The models were held stationary or rotated during ablation exposure. Tests conducted in the ramp mode provided data on the boundary layer transition characteristics (induced surface roughness) of the material. Tests accomplished in the steady-state mode provided information on material recession at constant stagnation pressure. Additional data obtained from these tests were model shape change as a function of time and internal temperatures if instrumented.

Missile thermal protection materials reentering the Earth's atmosphere at hypersonic velocities may encounter particulate erosion due to the presence of: (a) ice crystals, (b) dust particles, and (c) rain droplets. These environmental effects are particularly destructive due to the very high impact energies of the particles. Erosion tests were generally carried out in: (a) laboratory single particle facilities, (b) hypervelocity ballistic ranges, (c) combined ablation-erosion test facilities, (d) rocket sleds, and (e) sounding rockets.

The simplest particle erosion test has involved impacting a single plastic or ceramic bead (1,000- micron dia) with the test material. Exploding foils were used to accelerate the bead to velocities of 2.59 to 5.33 km/s (8.5 to 17.5 kft/s), and the bead impacted a small, flat-faced specimen at 90° to its surface. Both room and elevated temperature tests were performed. The specimen was then examined after impact to obtain the size and profile of the impact crater, total mass loss, and depth of the degraded surface region. These data were used to rank the various test materials and to provide data inputs for erosion and erosion/ablation computer codes.

Particle erosion testing has also been performed in various hypervelocity ballistic ranges which employ small test models flying at reentry speeds and through particulate environments of interest. The test models were evaluated in a free-flight mode, where the flight path was unconstrained and the model was destroyed at the end of the flight. Models were also tested in a track mode, where the flight path was constrained and the model recovered for post-test analyses. The facilities consisted of four major components, including: (a) a gun launcher to provide model velocities up to 7.32 km/s (24.0 kft/s), (b) a test chamber in which the model travels, (c) a track if needed for model guidance and control, and (d) a model recovery tube. The particulate material was suspended or free fell in the test chamber. The type of particulate material used was: (a) snowfields consisting of dendritic-crystal snowflakes or cirrus ice, (b) dustfields composed of spherical particles of various compositions and sizes, (c) water

droplet clouds consisting of particles less than 100 microns (0.00394 in) in diameter, and (d) rainfields composed of approximately 1-mm (0.0394-in) raindrops. Single- or multiple-impact water droplets have also been created with monodispersion generators. X-ray shadowgraphy and laser stero photography were used to measure model surface roughness, recession, and shape stability during flight. Post-test measurements on recovered models have also provided opportunities to examine the depth and nature of surface impacts and confirm dimensional changes induced by erosion.

Rain erosion tests have also been conducted with the aid of rocket sleds. Material specimens were typically mounted on a wedge or cone that was attached to the sled. The sled in turn was attached to a monorail and driven to high velocities with a solid propellant rocket motor. The test specimen was approximately 3.18 cm (1.25 in) in length, 3.18 cm (1.25 in) in width and 1.26 cm (0.5 in) in thickness. It was propelled through 610 m (2,000 ft) of man-made rain which had a mean drop size of 1.4 mm (0.055 in) and a rainfall rate of 3 g/m^3 (0.002 lb/ft^3). The test materials were recovered after exposure to the rainfield and post-test measurements made. Data obtained were photographs of the specimen surfaces and linear measurements of erosion as a function of position.

Sounding rockets have also been used for material erosion testing, but only limited materials evaluation has been carried out. The sounding rocket test environment simulates pertinent flight parameters such as Mach number, Reynolds number, pressure, and gas enthalpy; but of greater importance, it utilized actual atmospheric particulate matter. Several of the disadvantages of sounding rockets were: (a) expensive testing, (b) only limited amount of material could be evaluated, (c) material instrumentation was limited, (d) specimens were usually not recovered, and (e) uncertainities about the actual atmospheric conditions. Local weather conditions were closely monitored, and when the appropriate rain conditions existed, the sounding rocket was launched with the test material abroad. Materials performing well in all of the previous ablation and ablation-erosion tests were then instrumented and flown on actual missile entry trajectories to verify their performance and confirm the utility of performance prediction codes.

Reentry vehicle materials have also been thermostructurally tested in ground-based test facilities to verify their capability to withstand severe thermal gradients during entry heating. Various combustion-driven facilities have been used for this purpose. The advantages of these combustion facilities were: (a) large flowfields for evaluation of large-size components, (b) moderate to very high heating rates, and (c) ability to instrument and photograph the material

during testing. Gas chemistry, of course, was composed of propellant exhaust products and not the desired entry air environment. One of the U.S. test facilities employed for nosetip and heatshield thermostructural testing involved a fluorine-hydrogen rocket motor. This facility produced a stagnation point heating rate of 2,984 cal/cm^2-s (11,000 Btu/ft^2-s), a stagnation pressure up to 5.1 MPa (50 atm), and a heating time of about five seconds. Very high CCC model surface temperatures were reached, and very severe thermal gradients were produced in the material. Tested specimens were recovered for post-test analyses. Data included: (a) linear and mass ablation, (b) nosetip shape change, and (c) any evidence of substrate cracking due to thermally-induced stresses.

4.4.6 Aerospace Hypersonic Flight

Flight vehicles traveling at hypersonic velocities in the atmosphere have been subjected to (a) large temperature changes, (b) variable heating rates, (c) low gas pressures, (d) partial pressures of oxygen, (e) stress, (f) vibration, (g) acoustic noise, (h) particulate matter, and (i) other environmental parameters. All of these parameters have ranged over wide values, but for the purpose of illustration, the environmental conditions will be presented for the manned U.S. space shuttle orbiter. The peak convective heating rate was 16.3 cal/cm^2-s (60 Btu/ft^2-s), and the peak radiative heating rate was less than 0.54 cal/cm^2-s (2 Btu/ft^2-s). The ambient pressure ranged from zero in space to a peak dynamic pressure of about 1.38 MPa (200 lb/ft^2). The total heating time was about 1,200 seconds for each mission, and, the maximum temperature encountered was about 1538°C (2800°F). The design life was based on 100 missions.

Nosecap, leading edge, and adjacent thermal shielding materials have experienced the highest temperatures and heating rates of aerospace hypersonic flight vehicles. These materials have been routinely evaluated in large arc jet facilities, which simulated the gas enthalpy, heating rate, and pressure associated with flight conditions of interest. The test specimens were typically a subscale configuration of the end item or a flatfaced configuration resembling a heat shield. Specimens were typically instrumented and photographed during test to obtain the desired thermal and dimensional data.

Thermomechanical response of CCC materials intended for atmospheric hypersonic flight vehicles have been evaluated with either simple specimen geometries or subscale models. Structural materials properties were obtained by radiantly heating specimens in a chamber and subjecting them to various loads, loading cycles, or programmed heating cycles. Both quartz lamps and electrically-heated graphite elements have been used to furnish the radiant heat. Tests were conducted in either a vacuum, or at partial pressures of oxygen, to assess the

influence of oxidation on the mechanical properties of the test material. Specimens were subjected to post-test analyses to quantify oxidative effects.

Thermal testing of CCC materials has been conducted in the laboratory using similar procedures. The test specimen was generally a subscale version of the actual designed flight component, such as a CCC hot structure of a hypersonic gliding body. For this type of article, the vehicle forebody was heated to 1371°C (2500°F) using banks of radiant quartz lamps. The rate of heating was about 5.6°C/s (8.4°F/s). A vertical shear force of 107 N (24 klbf) was applied to the nosecap which was maintained at a stabilized temperature of 816°C (1500°F). The test article was thermally cycled many times, and video footage was taken of all the runs. Test data were acquired using high-temperature strain gages, high-temperature extensometers, conventional strain gages, and thermocouples.

Thermal testing of the U.S. space shuttle orbiter nosecap and wing leading edges was conducted in a similar fashion. Full-scale assemblies were tested in a 5 MW (4.7 kBtu/s) radiant heat test facility which was a thermal/vacuum altitude chamber containing carbon resistance heaters that were backed with a water-cooled shroud and test article cooling shrouds. The test article was suspended from an overhead rail system, which allowed positioning of the test part in the heater and subsequent movement into the cooling shrouds. The carbon resistance heaters were arranged in banks, and the energy output was controlled by an electronic computer feedback system employing fiber optic thermal sensors. Test articles were instrumented with about 200 sensors, including thermocouples, fiber optics, radiometers, and pressure sensors. All data obtained during testing were recorded on magnetic tape and in real time. Data acquisition included: (a) temperature-time profiles, (b) strain measurements, and (c) other key datapoints.

CCC materials used on aerodynamic surfaces may experience foreign object impact from a variety of threats, such as handling and service damage, launch, orbital debris, meteoroid impact, and runway debris from landing. The effects of impact damage on CCC materials have been studied with the use of (a) steel ball drop tests, (b) rain and ice impacts, (c) hypervelocity nylon projectiles, and (d) low velocity aluminum projectiles. The damage threshold value for these materials was calculated using the basic equation for kinetic energy and the normal velocity component for an oblique impact. Damage threshold values were reported in units of J/m^2 ($ft{\cdot}lbf/ft^2$).

The dynamic response of CCC flight materials was also of concern, and hence several different facilities have been built and used. They included: (a) shaker-table facilities, (b) acoustic sound chambers, and (c) progressive acoustic wave facilities. A typical shaker-table

test involved exposing panels to 10-20 g levels of random vibration. Acoustic tests involved sound pressures of over 160 decibels (db).

Other environmental tests have also been part of the overall evaluation plans. Tests generally included were: (a) material water retention, (b) effects of atmospheric contamination, and (c) lightning strike.

4.4.7 Planetary Entry Flight

Scientific probes have been designed for hypersonic flight in various planetary atmospheres, including Jupiter, Saturn, and Titan. The exterior structures of these probes are expected to experience very high total heat loads, high thermal fluxes, low-to-high dynamic pressures, and possibly meteoroid hazards. Unlike Earth entry, the planetary probes will likely encounter very high radiative heating fluxes due to: (a) the chemistry of the atmosphere, (b) the density of the atmosphere, and (c) the ultrahigh speed of the vehicle. Ground-test facilities used to evaluate CCC materials for these environments have been intense radiative and convective heating devices.

Specialized high power electric arc wind tunnels were used to evaluate materials, except for certain modifications. The gas chemistry was altered to better simulate the planetary atmosphere, and the model heating was augmented with laser radiative heating.

Another test facility that has been used successfully for producing intense radiative heating was the French solar furnace located in the Pyrenees Mountains. The solar furnace produced a 1,000 kW (1,055 Btu/s) beam over an area of 1 m (0.33 ft). The peak flux was 1,600 W/cm^2 (9.79 Btu/in^2-s) with one-half of the energy concentrated in an area having a diameter of 0.25 m (0.82 ft). Testing was carried out at ambient conditions or inside a 1 m (3.28 ft) diameter vacuum chamber. Testing involved: (a) measurement of temperature levels and thermal gradients, and (b) solar absorptance as a function of varying flux intensity and material composition and surface treatment. Sample temperatures were measured by rear surface contact with tungsten-rhenium alloy thermocouples, and front surface temperatures were recorded with optical pyrometers.

4.4.8 Space

The space environment is composed of various demanding conditions including: (a) a wide range of temperatures, (b) vacuum, (c) atomic and molecular species including atomic oxygen, (d) electron and charged particle plasmas, (e) electromagnetic and charge particle

radiation, (f) micrometeorite, and (g) space debris. In addition defense materials may be exposed to the destructive effects of: (a) intense laser beams, (b) various x-ray energies, and (c) hyper-velocity projectiles.

To gain a more quantitative understanding of the space environment, a description will be provided of the conditions experienced by the U.S. Long Duration Exposure Facility (LDEF). This space laboratory spent 69 months in low-Earth orbit, traveled over 741 million miles, and orbited the Earth about 32,000 times. Test materials on the forward facing side of LDEF were exposed to: (a) a high vacuum of 10^{-6} to 10^{-7} torr (0.0193 to 0.00193 psi), (b) 4,500 to 15,500 equivalent sun-hours of ultraviolet radiation, (c) electron and proton radiation of about 2.5×10^5 rads surface fluence, (d) atomic oxygen on the order of 10^3 to 9×10^{21} atoms/cm^2, (e) over 36,000 meteoroid and debris particle impacts having diameters of about 0.1 to 2.0 mm (0.0039 to 0.079 in), (f) cosmic radiation of about 6 rads, and (g) over 34,000 thermal cycles at temperatures ranging from about -1° to 88°C (-30° to 190°F).

4.4.8.1 Vacuum

Materials exposed to hard vacuum conditions of space have released absorbed gases, adsorbed species, and other volatile products. Depending upon spacecraft design, the volatile products were swept away in the vast depths of space or they condensed on and contaminated cryogenically-cooled optical systems or thermal control surfaces. It was therefore necessary to measure the outgassing of materials in a vacuum. The ASTM 595 test method was used for screening materials, but some modifications were made as noted in the following description. Small test specimens about 1-2 cm (0.4-0.8 in) were first vacuum baked for one hour and weighed. These pretreated specimens were then conditioned at 50 or 95 percent relative humidity. The specimens were subsequently heated to 400°C (752°F) for two hours in a vacuum, cooled to -50°C (-58°F), and the cycle repeated. Specimen weight was recorded after each temperature excursion and the total mass loss (TML) calculated. The collected volatile condensable materials (CVCM) were also determined by placing a cryogenically-cooled collector surface above the heated specimen and weighing before and after the heating cycle. As a test option the collector surface was replaced with a quartz crystal microbalance maintained at about -196°C (-321°F) and the outgassing rates determined at different temperatures. Further modifications of the vacuum chamber have also been accomplished to permit identification of the chemical composition of the outgassed species.

4.4.8.2 Temperature

The benign space environment involves a maximum temperature range from -273°C (-460°C) to about 149°C (300°F), although measured temperatures have not been that severe. These temperatures, nevertheless, may (a) alter certain mechanical and thermophysical properties, (b) change the surface, and (c) induce microcracking. Conventional testing equipment contained in a vacuum chamber has been routinely used to measure properties of interest. Perhaps the thermophysical property of greatest interest has been the coefficient of thermal expansion. Thermal expansion properties in the three principal axes of the material have been measured using an optical comparator technique. Small rectangular specimens were first thermally cycled over a predetermined temperature range and for about 10 times. The specimens were next vacuum dried at 104°C (220°F) until constant weight was obtained. The test specimens were then heated under vacuum to the maximum test temperature and until no strain changes were detected using a laser optical comparator. The materials were lastly cycled over the temperature range of interest and strain readings taken at 25°C (45°F).

Very high transient temperatures may be encountered by defense spacecraft materials exposed to laser or nuclear radiation. The effects of laser radiation on CCC materials have been measured in the laboratory. Test devices have typically employed laser irradiance of 1-1000 W/cm^2 (3.2-3,200 $kBtu/hr \cdot ft^2$). Both continuous wave (CW) and repetitive pulsed (RP) lasers have been used. Material exposures have been conducted in vacuum, vacuum plus solar heating, and partial vacuum conditions. Test specimens were generally flat in configuration and small, i.e. about 5 by 10 cm (2.0 by 3.9 in). Material performance data obtained in these tests have been (a) time to reach steady-state thermal conditions, (b) ablation rates, if any, (c) burnthrough time, if any, (d) indepth material response, if thermocoupled, (e) strain measurements, if instrumented, and (f) surface and subsurface damage using post-test observations and measurements.

4.4.8.3 Thermal Cycling

Spacecraft materials change temperature as they orbit into and out of the sun's rays. Repetitive temperature cycling of the materials takes place, which may alter properties including strength, thermal conductivity, and thermal expansion. Various test facilities have been developed and used for conducting vacuum thermal cycling of CCC materials. Because of the long time needed to thermally cycle a material design life (10 to 20 yr), accelerated thermal cycling chambers have been built for simulating one year of orbit in about 20 days. A typical accelerated heating/cooling facility had the capability of going from one temperature extreme to

the other in just over one minute, with no temperature dwells at either extremes. In this test small preconditioned specimens were used. After the appropriate number of thermal cycles, the specimens were tested for residual properties. Conventional surface photography could not be used to detect and measure the number of microcracks because CCC materials are usually full of microcracks and fiber-matrix debonded areas. Nevertheless, microcracking was measured with the aid of an acoustic monitor.

4.4.8.4 Atomic Oxygen

Material degradation is one of the most serious problems for organic and carbonaceous materials operating in the ram positions of low-Earth orbits (LEO). There is a strong correlation between material degradation and density of atomic oxygen. Thickness losses of more than one micron per day have been observed for exposures in the ram position, especially for amorphous carbon films.

Atomic oxygen is the predominant and most reactive gaseous specie at LEOs of 200 to 600 km (124 to 373 miles). It forms in the ionosphere through the dissociation of molecular oxygen by ultraviolet radiation in the 100-200-nm wavelengths. The neutral atomic oxygen has a kinetic energy level of about five electron volts (eV), and it is very reactive with CCC materials. Specialized test facilities have been built to generate atomic oxygen environments, but most facilities form a mix of atomic oxygen and ionic oxygen. Some of the methods employed have been (a) radio frequency (rf) heating, (b) direct current (dc) arc dissociation of oxygen and carrier gas, and (c) continuous wave or pulsed laser heating of oxygen-containing gases. The desired atomic oxygen fluences were about 10^{22} to 10^{24} atoms/cm^2 and a flux in the range of 5×10^{16} atoms/s-cm^2. Material testing involved small disc specimens having a diameter of about 2.5 cm (1.0 in) and exposing them to line-of-sight bombardment with an atomic oxygen beam for a predetermined period of time. The materials response data obtained from this type of test included (a) mass loss as a function of exposure time and (b) measurement of altered surface characteristics.

4.4.8.5 Radiation

The space environment contains various types of natural radiation including: (a) ultraviolet light, (b) charged atomic and molecular ions, and (c) electrons. Electron densities have been of concern because they may induce surface charging of dielectric materials. However, CCC materials are electrically conductive and dissipate any surface charge. On the

other hand, oxidation-protection CCC materials typically contain a nonelectrically conductive coating.

Electron radiation exposures have been carried out in a clean, turbopumped vacuum exposure chamber having a pressure of about 2×10^{-7} torr (0.0039 psi). Multiple specimens were simultaneously irradiated with 1 MeV electrons at a rate of 5×10^{7} rads/h. Post-test measurements conducted on the irradiated materials included: (a) definition of altered surface characteristics, (b) changed thermophysical properties, and (c) coating spall, if any.

4.4.8.6 Micrometeorite & Space Debris

The space environment contains a large amount of particulate matter (micrometeorites) and an ever-increasing amount of space debris. Micrometeorites typically have diameters of several millimeters or less which is sufficient to slowly erode impacted surfaces. Space debris is much larger in mass and size, and any encounter with such material at hypervelocities may be catastrophic.

Space impact testing has been carried out with (a) laboratory gas guns, (b) laboratory electromagnetic accelerators, and (c) actual exposures on space laboratories like LDEF. Staged compressed light gas guns have been developed for accelerating milligram to gram projectiles into a test target at velocities up to about 10 km/s (33 kft/s). Electromagnetic accelerators generated a plasma of ultra-small particles with an exploding metallic foil, and the particles were driven into the test specimen contained in a vacuum chamber. Material performance data acquired in these tests have included: (a) size of surface pitting and cratering and (b) subsurface damage.

4.4.9 Nuclear Radiation

Nuclear power generators and nuclear explosions create hostile environmental conditions including (a) x-rays, (b) neutrons, (c) gamma rays, and (d) optical flashes. Interaction of these energetic environmental parameters with CCC materials may produce (a) extremely high surface temperatures, (b) steep thermal gradients, (c) mechanical shock, and (d) altered material microstructure and properties. CCC materials, unlike many other materials, exhibit many properties that lend themselves to uses in nuclear applications. They absorb or transmit high fluences of x-rays, depending upon the radiation energy levels. Energy absorbed by the materials are converted to heat, which is easily accommodated as a result of the composite's high specific heat, high sublimation temperature, and high thermal properties at elevated temperatures. The materials are also highly resistant to mechanical shock due to an air blast wave or surface region

blow-off. The composites easily withstand intense optical flashes created by atmospheric blast conditions.

Atmospheric nuclear explosions create an intense, transient optical energy wave known as "nuclear flash." Thermal fluxes may be on the order of 400 kcal/cm^2/s (1,474 kBtu/ ft^2-s), which may generate surface temperatures over 1000°C (1832°F). Nuclear flashes have been simulated in the laboratory with various radiation devices including: (a) quartz lamp banks, (b) arc imaging furnaces, (c) solar furnaces, and (d) visual-wavelength lasers. Small test specimens were typically used, and the test data acquired were usually (a) surface recession, if any, and (b) in-depth material temperatures.

Simulated x-ray radiation and uniaxial-strain shock loading facilities have been used to evaluate CCC structural and shielding materials. High-intensity electron beams were directed on small flat-faced specimens to simulate x-ray heating effects. The amount of surface mass loss was recorded, and the ablated surface features were measured by post-test analyses. High-speed flat or curved-surface flyer plates were used to simulate the dynamic mechanical response of CCC materials arising from surface x-ray deposition and the attendant blow-off impulse (surface loading). For shock loading, a stress pulse was produced in a flat or cylindrical CCC specimen by using a gas gun or a magnetically-driven flyer plate to impact the specimen. An explosive has also been used to induce loading in a material. The Hugoniot characteristics of the material at low stress levels were obtained from three types of plate impact experimental methods performed with a gas gun. By varying the experimental configuration and instrumentation, the compressive loading, unloading, and spall strength data were experimentally measured. Attenuation experiments were also performed with an exploding foil which accelerated a thin flyer plate (flat or curved surface) into the target specimen. Dynamic material response data obtained included (a) material equation-of-state, (b) material spall strength or dynamic tensile strength, (c) impact velocity for spallation, and (d) shock attenuation. Mechanical properties of the materials were also measured at high strain rates, and the information was used for prediction of material performance. CCC materials found promising in above-ground tests were then further evaluated in underground nuclear experiments. Flat or other geometrical specimens were exposed simultaneously to different levels of x-ray energy. Some of the specimens were instrumented on the backface to measure induced strains due to surface blow-off. The exposure stations in the underground nuclear test were selected on the basis of one specimen surviving the test and the second specimen exceeding the fail-safe level of irradiation. After x-ray exposure, the specimens were retrieved and examined for radiation-induced surface losses, altered surface properties, cracks, and other damage features.

The effects of neutron radiation on CCC materials have been investigated in various materials testing reactors. These testing devices typically contained enriched uranium and were light water moderated and cooled. In the U.S. a considerable amount of testing has taken place in Department of Energy reactors. The Materials Open Test Assembly (MOTA) capsule of the Fast Flux Test Facility (FFTF) has been routinely used to expose small specimens. The peak damage dose was approximately 10-12 displacements per atom (dpa) or 1.5 to 1.8 x 10^{26} n/m^2 at an irradiation temperature of about 400°C (752°F). The neutron energy level was over 50 MeV. Similar experiments have also been carried out in the High Flux Isotope Reactor (HFIR). The materials were exposed to an accumulated fluence of 0.7 to 1.8 dpa (1.1 to 2.7 x 10^{25} n/m^2), radiation energy level over 50 keV, and at a temperature of about 600°C (1202°F). Post-irradiation measurements were then conducted on the specimens to determine any changes in (a) microstructure, (b) dimensions, (c) bulk density, (d) strength, (e) modulus, (f) Poisson's ratio, (g) fracture energy, (h) thermal conductivity, and (i) thermal expansion coefficient.

Gamma ray irradiation has been accomplished with cobalt-60 radiation sources. Test specimens were typically packed in a hollow aluminum can and lowered into a radioactive pipe. Irradiation was typically carried out in an air atmosphere and at room temperature. Specimens were exposed for the period of time necessary to obtained the desired radiation level (roentgen per hour), removed from the radiation source, and examined for microstructural changes.

4.4.10 Biomedical

CCC materials offer great potential for uses in various medical applications because they can withstand the harsh internal physiological environments of mammals. The intrinsic characteristics of these materials, which lend themselves to such biocomponents, include (a) biostability, (b) bioinert, (c) biocompatibility with blood, body fluids and tissue, (d) mechanical (tailored stiffness and stiffness) compatibility with bones, and (e) nontoxic wear products.

Laboratory testing of these material has generally involved (a) special considerations of biocompatibility with adjacent materials, and (b) structural properties. Typical testing has included sterilization by autoclaving, ethylene oxide, or gamma radiation treatments. A representative autoclaving cycle has involved 56°C (132°F) in steam for 15 minutes per cycle and up to 100 cycles. Gamma irradiation generally involved 2 to 4 millirads (Mrad) for four hours. Materials were then evaluated for longtime chemical stability by placing them in boiling saline solution (0.9 percent sodium chloride) for up to one year. To further guard against harmful effects, additional *in vitro* and *in vivo* assays were conducted. Materials passing all of these

screening tests were then implanted in animals for up to one year. Chronic toxicity and carcinogenicity tests were also conducted to further investigate any possible dangerous effects. These tests have included: (a) acute systemic toxicity in which solvent extracts are injected in mice; a duration of one week, (b) cytotoxicity tests for cytopathology in mouse fibroblast tissue culture; a duration of two weeks, (c) intracutaneous toxicity tests for local irritation in rabbit skin after injection of extracts; a period of two weeks, (d) hemolysis tests to establish blood compatibility of extract by evaluating released hemoglobin; a duration of one week, (e) AMES assay for potential mutagens with extract *in vitro*; a period of one month, (f) unscheduled DNA synthesis tests to indicate changes in cell DNA under the influence of extract; a period of one month; (g) long-term biocompatibility to evaluate carcinogenicity material implants in the intramedulary canal of rabbits; a duration of two years, and (h) long-term implantation study of material implanted in dogs or other animals; a duration of up to three years.

Specialized mechanical tests were routinely performed on biomedical CCC materials because most uses involve structural considerations. These tests generally included: (a) flexure and torsional loading under static and dynamic conditions, (b) fatigue characteristics at loads up to 10^8 cycles, (c) tribological characteristics using a ring-on-disc and ball-in-socket arrangements, (d) in-plane and out-of-plane moduli and strengths, and (e) notched and unnotched impact strengths. Wear particles originating from the friction and wear tests were also evaluated for biocompatibility.

4.4.11 Industrial

CCC materials have been used in a limited number of highly-specialized industrial applications including: (a) high-temperature furnace components and insulation, (b) high-temperature mechanical fasteners, (c) tooling parts and dies, (d) molten glass transfer components, (e) electronic crystal growing substrates, and (f) other uses. Just about any existing application for polycrystalline graphite could be a potential outlet for CCC materials provided (a) higher performance and improved properties are needed, and (b) higher initial material costs are not prohibitive.

Each of the potential industrial applications has its own set of requirements; thus the materials testing is tailored to the application. No attempt will be made to describe the varied tests for each application outlet.

4.4.12 Chronology

CCC materials screening and evaluation activities since the 1960s are listed in Table 25. These events generally refer to the first generation of materials properties and characteristics which were conducted with laboratory-scale test facilities. Later in the materials developmental cycle, larger and more elaborate test facilities were used for proof testing of CCC components.

4.4.12.1 The 1960s

First-generation CCC materials appeared to have the necessary properties to withstand ultrahigh temperatures associated with rocket propulsion and missile reentry. It was only logical then that the first materials screening efforts involved rocket propulsion exhaust and very high temperature air flows. In the early 1960s porous CCC and phenolic-impregnated CCC materials were evaluated in simulated liquid propellant exhaust environments. Low erosion rates were demonstrated even though the material was only of moderate density. During this same period, the first simulated reentry heating evaluation of 2-D CCC materials took place in small air-stabilized electric arc facilities. It was noted that the 2-D CCC materials were highly resistant to thermal shock and thermally-induced strains, but their ablation rates were higher than aerospace polycrystalline graphites. Since missile systems designers expressed little interest in the newly-available CCC materials, further attention was directed to upgrading certain materials properties and screening the materials for potential use in solid propellant environments.

During the mid-1960s, metallic carbide-coated and pyrolytic graphite-coated CCC materials were exposed for the first time to simulated solid propellant exhaust and found to be very promising. The carbide and pyrolytic graphite coatings were very resistant to hot exhaust flows, and the substrate CCC materials appeared to provide adequate support for the coatings. One of the most interesting things noted in these screening tests was the differential erosion rate between the surface coating and the substrate. One pyrolytic graphite-coated specimens had a pinhole and, during the test, oxidizing gas penetrated into the CCC substrate. A considerable amount of CCC material was vaporized, but the original configuration of the coating was maintained even though it was unsupported in the area of the substrate hole.

In the late 1960s, the first simulation reentry heating tests were conducted on intermediate density, 3-D CCC materials. Material evaluations were performed in air-stabilized electric arc facilities and in a hot-air wave superheater. Reasonable ablation rates

TABLE 25
CHRONOLOGY OF CCC MATERIAL ENVIRONMENTAL TESTING

YEAR	TESTING EVENTS	IMPORTANCE	ORGANIZATION
1962	Ablation rates and in-depth temperatures of 2-D CCCs were measured during exposure to arc heated air	CCC linear recession rates were only a fraction of conventional ablative graphite fabric/phenolic composites but higher than polycrystalline graphite materials; with further improvement, would have high potential for use on missile reentry vehicle nosetips	Avco Corporation/Research & Advanced Development Division/USA
1964	Ciurcumferential ablation rates of 2-D CCC cylindrical specimens were measured in a solid propellant motor and a liquid propellant engine simulators	Erosion (ablation) rates were only a fraction of conventional ablative plastic composites and thus CCCs had high potential for future motor and engine uses	Philco-Ford Corporation/Aeronutronic Division/USA
1966	Unique, progressive and noncatastrophic failure mode of 2-D CCCs were noted during flexural testing	Material behavior inferred that CCCs had high fracture toughness	Avco Corporation/Space Systems Division/USA
1966	Frictional characteristics of low-density, 2-D CCCs were measured	Low wear rate of CCCs indicated future uses in brakes and clutches	Carborundum Company/USA
1966	Frictional characteristics of low-density, 2-D CCCs were evaluated on a laboratory dynamometer	First demonstration of outstanding high-temperature coefficient of friction and potential for future aircraft brake discs	Goodyear Aerospace Corporation/USA
1967	High-speed flat flyer impact tests of 3-D CCCs produced minimal surface material removal and little structural damage to substrates	Impulse resistance was three times higher than graphite materials which suggested potential uses in intense x-ray environments	Avco Corporation/Space Systems Division/ USA
1967	Shape stability and low ablation rate of intermediate-density, 3-D CCC demonstrated in high-temperature, high-pressure (110 atm) air wave superheater	Shape stable nosetip specimens suggested future uses on accurate missile reentry systems	Cornell Aeronautical Laboratory/USA

TABLE 25 (Continued)
CHRONOLOGY OF CCC MATERIAL ENVIRONMENTAL TESTING

YEAR	TESTING EVENTS	IMPORTANCE	ORGANIZATION
1968	Circumferential erosion rates of 2-D CCC cylindrical specimens were measured in fluorinated liquid propellant exhaust products	High dimensional stability and thermal resistance suggested future applications in high energy space propulsion systems	The Marquardt Company/USA
1969	Circumferential erosion rates of CVD PG coated 2-D CCC thrust chambers were measured in hot exhaust products of a liquid propellant engine	High erosion resistance and structural integrity indicated possible uses as replacement materials for ablators and refractory metals	The Marquardt Company/USA
1970	High-speed bullet impact tests on 2-D carbon fabric/phenolic char CCC produced highly localized damage	First demonstration of CCC materials potential for armor applications	Naval Air Warfare Center/USA
1971	Ablation rates and substrate temperatures of silicon-carbide coated 2-D CCCs were measured in an air arc wind tunnel	High dimensional stability and thermostructural capability in very high temperature air suggested potential uses on future man-rated earth reentry capsules	Avco Corporation/Systems Division/USA
1971	Thermal shock and thermostructural characteristics of 3-D CCC nosetip specimens were measured at 11,000 Btu/ft^2-sec for 5 sec in fluorinated propellant exhaust gases	Exceptional resistance of 3-D CCCs to thermally-induced stresses inferred potential uses in future missile reentry vehicle nosetips	Philco-Ford Corporation/Aeronutronic Division/USA
1972	Minimal CCC surface loss and high structural survivability was demonstrated in an underground nuclear experiment	First demonstration of high intrinsic resistance of CCCs to intense x-ray environments	Air Force Materials Laboratory/USA
1972	Fracture toughness values were measured for 3-D needled graphite (rayon-based) felt/CVI PG matrix and 2-D filament-wound graphite yarn/CVI PG matrix CCCs	Greatly increased fracture toughness (reduced crack initiation and propagation) was demonstrated compared to conventional graphites	Atomic Energy Commission/Sandia Laboratories/USA

TABLE 25 (Continued)
CHRONOLOGY OF CCC MATERIAL ENVIRONMENTAL TESTING

YEAR	TESTING EVENTS	IMPORTANCE	ORGANIZATION
1972	Over 100 different CCC materials from 14 different manufacturers were evaluated with 130 full-size brake dynamometer tests	State-of-the-art CCCs were evaluated for potential aircraft braking systems	Goodyear Aerospace Corporation/USA
1973	Very high temperature electron beam heating tests were conducted on uncoated 2-D CCCs	Low ablation and surface integrity of CCCs during simulated x-ray deposition suggested future uses in nuclear radiation environments	Kaman Sciences Corporation/USA
1974	Supersonic single and multiple-particle erosion tests of 2-D and 3-D CCC materials were conducted in ice and rain environments	High erosion resistance to supersonic velocity particles suggested potential uses for all weather missile reentry vehicle nosetips	Avco Corporation/Systems Division/USA
1975	Surface roughness of 3-D CCCs was quantified during a ramp heating test method in a 50 MW air arc heater	Shape stability of nosetip materials suggested great potential for uses on strategic missile entry systems	Air Force Flight Dynamics Laboratory/USA
1975	Thermostructural response of 2-D and 3-D CCC specimens was investigated with a new laboratory device	Apparatus power levels (induced thermal gradients in CCCs) were insufficient to cause thermostructural fracture/failure of 2-D CCCs, but all graphite specimens were cracked	Southern Research Institute/USA
1977	Biocompatibility tests were conducted on various CCC materials	High biochemical resistance and structural properties of CCC materials suggested future uses as human bone replacements	Schunk Koblenstofftechnif GmbH/ GERMANY
1978/90	CCC materials property changes were measured after long-duration exposure to near-earth orbital environments	Minimal material loss was recorded for uncoated CCC materials, but oxidation-resistant coatings were recommended for low earth orbit CCCmaterials	McDonnell Douglas Astronautics Company/USA
1980	Ablation/erosion rates of 2-D and 3-D CCC nosetip specimens were measured in a particle containing, arc-heated air flow	Low thermal/particle erosion of CCC materials suggested future uses as all-weather missile reentry nosetips	Arnold Engineering Development Center/ Air Force Systems Command/USA

TABLE 25 (Continued)
CHRONOLOGY OF CCC MATERIAL ENVIRONMENTAL TESTING

YEAR	TESTING EVENTS	IMPORTANCE	ORGANIZATION
1980	High-temperature, long-duration oxidation tests were conducted on coated 2-D CCCs in a laboratory	Substrate weight loss was correlated with the degree of cracking in the surface coating	United Technologies/Pratt & Whitney Aircraft/USA
1980	Thermal cycling of silicon-carbide coated 2-D graphite (rayon-based) fabric/phenolic char flap liners was accomplished in hot exhaust product environments	High dimensional and thermal stability characteristics of oxidation-resistant CCCs indicated potential applications in man-rated gas turbine engines	United Technologies/Pratt & Whitney Aircraft/USA
1981	Erosion rate and throat asymmetries were measured for 150 CCC candidate materials in solid propellant motor exhaust gases	Low erosion and no materials failures were noted for throat diameters of 0.25 to 14.0 in; pressures from 500 to 1400 psi and burn times from 15 to over 150 sec	Various propulsion companies/USA
1981	Hypersonic, single-particle erosion tests were conducted on various CCC materials	Limited surface material loss from high-speed particle impact was demonstrated and provided data for computer-aided erosion predictions	Systems, Science and Software (S^3)/USA
1982	High-speed spin testing of silicon-carbide coated 2-D CCC rotors was accomplished at temperatures up to 1927°C (3500°F)	Coated CCC materials exhibited high dimensional stability, high stiffness and structural integrity, and thus had potential for uses in highly-stressed, rotating turbine engine parts	Williams International/USA
1984/89	Continuous-wave and repetitive pulsed laser energy irradiations were performed on various uncoated and coated CCCs	Very high intrinsic resistance to laser irradiation and associated heating of uncoated CCCs indicated potential uses as survivable space structures	Air Force Wright Aeronautical Laboratories/Materials Directorate/USA
1987	Transverse (across-ply) tensile strength properties of CCCs were measured up to 2000°C (3632°F)	Quantitative data was obtained on a limiting 2-D CCC property	Wright State University/Mechanical and Materials Engineering Department/USA

TABLE 25 (Concluded)
CHRONOLOGY OF CCC MATERIAL ENVIRONMENTAL TESTING

YEAR	TESTING EVENTS	IMPORTANCE	ORGANIZATION
1988	Static and mechanical properties of thermally-cycled, coated CCCs were measured up to 1500°C (2732°F)	Design properties of coated 2-D CCCs were obtained to support the "Hermes" advanced spaceplane nosecap and leading edge demonstrator	Aerospatiale/Aquitaine/FRANCE CIEMAT Solar Energy Platform/Almeria/ SPAIN
1988	High strain-rate CCC characteristics (planar impact, Hugoniot, transmitted wave, attenuated wave reduction and spallation) were measured for 2-D CCCs	2-D CCCs possessed outstanding resistance to mechanical shock loading	Ktech Corporation/USA

were recorded for the newly-available 3-D materials, even though very high stagnation pressure (up to 11.1 MPa, 110 atm) air flow was employed. These tests did much to reaffirm that 3-D CCC materials, with further development, would ultimately be the solution for the critical heating problem of ballistic reentry missiles. But not all CCC testing was aerospace related. One of the first pioneering industrial uses for CCC materials was as a nonlubricated, high-temperature bearing. Laboratory tests indicated a strong relationship between materials, frictional, and wear characteristics. Follow-on work centered on hybrid CCC compositions utilizing metallic or ceramic compounds.

4.4.12.2 The 1970s

Many new materials concepts were originated in the early 1970s. The new materials compositions and constructions originating from these concepts required screening. Hence, screening facilities were developed by all of the major aerospace companies and many of the materials developers.

Perhaps the most important materials created during the early 1970s were high-density 3-D orthogonal and 3-D pierced fabric-reinforced nosetip materials. Both of the material types were extensively tested in small to large air arc heaters, ballistic ranges, and other test facilities. Increased material density led to a lower ablation rate and, of great importance, provided improved nosetip shape stability. Many other forms of 3-D orthogonal CCC materials and the first n-directionally-reinforced CCCs were fabricated and screened. Higher-pressure air arc heaters became available, and additional screening tests were performed up to about 16.2 MPa (160 atm). Because of the low ablation rates of 3-D CCC materials, new nosetip designs became possible. The conventional shell configuration gave way to a new plug arrangement. Such nosetip configurations were evaluated at exceptionally high gas temperatures and heating rates and found to be very resistant to thermal and thermostructural degradative effects. CCC materials were evaluated for the first time at various x-ray fluences in underground nuclear experiments. The materials exhibited remarkable stability in such environments, thus inferring possible future applications for nuclear-resistant thermal protection components, structures, and shielding. Gunfire tests conducted on 3-D CCC materials were performed, and damage was shown to be confined to a very small area around the bullet hole. This type of behavior was quite unlike that of polycrystalline graphite which fractured into many pieces under similar test conditions. In the nozzle area, 3-D CCC materials were evaluated for the first time in simulated solid propellant exhaust. Tests conducted at 3.45 to 13.8 MPa (500 to 2000 psi) indicated that the materials were suitable for use at representative pressures of solid propellant motors. Three-directional CCC materials, with reinforcement in cylindrical coordinates, were

fabricated and tested. The rocket exhaust tests indicated that this form of reinforcement was preferred over previously-used 2-D fibrous reinforcements. Three-directional CCC materials were also evaluated in very energetic propellant exhaust gases derived from fluorinated propellants. The materials were shown to be compatible with such gases, and hence it was apparent that they had potential uses in the thrust chambers of liquid propellant systems. Three-directional CCC materials were also subjected to repetitive-pulse and multiple-start conditions. Excellent thermal shock resistance was demonstrated, thereby indicating outstanding potential for use in future rocket ramjet components. Silicon carbide-coated 2-D CCC materials were evaluated in a variety of simulated reentry heating conditions. It was noted that the composite coating provided excellent dimensional stability and protected the underlying CCC substrate from oxidative effects. In addition the reuse capability of carbide-coated CCC materials was demonstrated by exposing test specimens to 15 simulated reentry heating cycles. Outstanding tribological characteristics of CCC materials were demonstrated in various friction and wear tests. These promising results suggested great potential for use in high mass braking applications, like aircraft brakes. Over 100 different types of CCC materials were evaluated using dynamometer tests, and the higher-density composites were shown to have acceptable properties for aircraft braking systems. Full-scale CCC brake discs were fabricated and laboratory tested. The 2-D reinforced CCC materials were then successfully used on a fighter and bomber aircraft.

Significant materials screening and evaluation activities continued into the mid-1970s. The most important event was a successful intercontinental ballistic missile (ICBM) flight of a 3-D CCC nosetip material. While the nosetip survived the critical reentry environmental conditions, it became apparent that higher-density materials would be required for improved ablation resistance. Nosetip shape stability was also identified as a critical parameter since it greatly influenced vehicle accuracy. Extensive simulated reentry heating tests revealed that coarsely-woven 3-D CCC materials developed rough ablative surfaces, caused laminar flow to become turbulent, and in turn produced significantly higher ablation rates. Fine-woven CCC billets containing small-diameter fiber bundles and close bundle-to-bundle spacing were fabricated and demonstrated to be ideal. The most useful test proved to be ramp heating in which the test nosetip material was programmed toward the arc jet nozzle to replicate early reentry heating. Materials having minimal surface roughness delayed turbulent boundary layer heating, reduced total heating, and enabled better nosetip shape retention. Reentry flights through particulate-laden atmospheres, however, were also a distinct possibility. There was therefore a need to develop an "all-weather" nosetip material capable of surviving the destructive erosion effects of particles impacting a material surface at hypervelocities. Numerous ground-based tests were carried out using ablation-erosion facilities, rocket sleds, and ballistic ranges. Meanwhile, CCC materials

technology had been scaled up to the production of full-size missile heatshields. Several types of materials were proof tested in a large rocket engine test facility. By the mid-1970s it became apparent that specialized experimentation would be needed to support the development of predictive performance codes. This represented a dramatic departure from the ongoing "Edisonian" approach, and it provided a basis for ultimately predicting performance and verifying it by ground-based and operational testing.

Materials evaluation activities during the late 1970s were focused on evaluating new and improved materials for rocket nozzle throats and erosion-resistant nosetips. The testing of candidate nozzle materials took on a sense of urgency when it was demonstrated that pyrolytic graphite throats were rather unreliable, and only limited prospects existed for scaling the material to larger-size components. On the other hand there were over 40 different candidate CCC materials that offered promise for use in the throats of large solid propellant motors. With further evaluation the prime candidate materials were narrowed to (a) 3-D orthogonal, (b) 3-D pierced fabric, and (c) 4-D constructions. In the missile nosetip area, more extensive erosion testing took place with single-particle, multiple-particle, and ablation erosion test facilities. CCC materials containing refractory compounds were found to have superior erosion resistance compared to materials without these constituents. One of the most interesting materials evaluation activities underway in the late 1970s concerned the use of structural CCCs for biomedical applications. CCC parts were fabricated for various bone replacements and parts needed for the healing of bones. These parts included (a) hip joints, (b) knee joints, (c) bone plates, and (d) screws. Excellent compatibility of CCC with body tissues and fluids was demonstrated in this pioneering work of German and French engineers and scientists. Another interesting CCC materials screening activity concerned the high-speed impact testing of such composites. Two-directional or 3-D CCC materials, which were used as the outer shell of each fuel capsule of the power generator container, were accelerated into a concrete wall. The impact resistance and survival of the CCC materials were measured in terms of material deformation, fracture characteristics, and survivability criteria. The protective CCC containers were also subjected to simulated reentry heating to insure containment of the radioactive fuel element in the event of a spacecraft disaster.

4.4.12.3 The 1980s

In the early 1980s the utilization of 3-D CCCs for rocket motor nozzles became a certainty. Over 150 CCC nozzle components were tested in throat sizes ranging from 0.64 cm (0.25 in) to 356 cm (14.0 in), chamber pressures from 3.45 MPa (500 psi) to 9.65 MPa (1400 psi), and firing times ranging from 15 to over 150 seconds. In the area of frictional

materials, braking applications spread from aircraft systems to high-performance race cars. Two-directional CCC rotors and pads were successfully evaluated on laboratory dynamometers, and full-scale parts were road tested on applicable race tracks. The utilization of CCC materials in small expendable gas turbine engines also became of interest, and high speed testing of coated and uncoated specimens took place. Disc specimens were spun to over 100,000 revolutions per minute (rpm) without material failure. Silicon carbide-coated CCC test specimens were also evaluated at high rotational speeds and temperatures on the order of 1927°C (3500°F). The success of these tests suggested that oxidation-protected CCCs have possible use in rotating parts of turbine engines.

The majority of CCC testing during the mid-to-late 1980s involved the evaluation of oxidation-protected CCC materials intended for gas turbine engines. Many new coating materials and processes became available and were tested in laboratory air oxidation furnace facilities. Numerous testing cycles were developed to elucidate materials behavior at elevated temperatures of interest. Testing extended to full scale components in both man-rated and expendable gas turbine engines. The most promising test results were obtained on stationary, noncritical parts of turbine engines like flaps, seals, and other similar components. Hundreds of hours of operation were demonstrated, but sealants used in the protected CCCs were noted to be moisture sensitive. The engine tests also confirmed that oxidation-protected CCC substrates would be necessary for operational lives of 2,000 hours. Particulate and molecular inhibitors were developed to meet this challenge. One particular material system demonstrated excellent potential for use. A CVD silicon carbide-coated 2-D CCC substrate containing particulate inhibitors and a glassy sealant survived over 1,200 hours in cyclic oxidative tests at temperatures up to a maximum of 1400°C (2552°F). Overseas, coated CCC materials were being evaluated for application to the Russian Buran space shuttle orbiter. Details of the testing program were not disclosed which was typical of the former USSR publications on aerospace materials in that time frame.

4.4.12.4 The 1990s

During the early years of the 1990s, test and evaluation activities centered on protected CCC materials for supersonic and hypersonic flight vehicles and neutron-stable materials for nuclear fusion power reactor components. Mission simulation evaluations were conducted on oxidation-protected CCC panels. Over 200 hours of service life were demonstrated at temperatures up to about 1371°C (2500°F). For hypersonic atmospheric flight vehicles of the NASP or SSTO type, coated CCC thermal protection tiles were successfully evaluated for use. A full-scale coated CCC body flap was also fabricated and tested. Overseas,

both the French and Japanese successfully tested shuttle component materials in various ground-based facilities. Such materials are expected to be used for the nosecap, leading edges, and fins of these spaceplane technology demonstrators. Also in the early 1990s high-purity CCC materials were fabricated and tested in various neutron and nuclear environments. Neutron-dimensional changes were recorded and correlated with the fiber type, architecture, and graphitization temperature. Additional tests conducted overseas confirmed the potential utility of CCC materials as a replacement for high-purity (nuclear-grade) graphites. Most of the evaluation activities in the early 1990s, however, were concerned with measuring the properties and characteristics of CCCs for thermal management and space applications. Lightweight and high-modulus CCC hollow tubes were tested at high strain loads and at very high temperatures. Test results revealed that these materials were suitable for "survivable space structures" even at very high temperatures. CCC materials containing mesophase pitch-based carbon fibers were also evaluated for thermal conduction and found to be suitable for various thermal management applications. Both 2-D and 3-D CCC panels simulating space radiators were fabricated and tested successfully. Further testing of CCC materials will be undertaken to guide ongoing materials developments aimed at the friction and wear, electronic, thermal management, industrial, propulsion, and other application fields.

4.5 MODELING

Analytical modeling of CCC materials and their environmental response has involved either a pure mathematical treatment of an ideal material behavior or an empirical or correlative technique addressing real materials. While both predictive and correlative techniques have been used, correlative models have proven to be the most useful.

Analytical modeling capabilities have been developed to predict materials properties and performance, guide materials development, and assist in failure analyses. Mathematical models of materials behavior have been useful on three different levels. First, quantitative material synthesis has provided a definition of the material configuration needed to yield the desired performance characteristics. In addition the properties of new conceptual material have been predicted knowing applicable constituent properties. Secondly, the relative behavior of similar composites has been predicted from a database on one composite material. This approach is an enormously cost-effective method for optimizing or refining a given material composite without the need for timely and costly fabrication and testing. Thirdly, the mathematical models have been used to predict a larger database from a smaller database. They have also been used to match limited experimental data for some properties and some temperatures. Quantitative material synthesis has

been the most useful of the three modeling approaches described. Comparative evaluations have been employed to focus materials developmental efforts in areas of greatest interest and potential. Models for data enhancement have been a valuable adjunct to providing a larger database for systems designers.

4.5.1 Objectives

One objective of analytical modeling is to provide a cost-effective method for enhancing the efficiency of the materials development cycle. The initial step in the material modeling process is the selection of an appropriate analytical code. Definition of the appropriate modeling parameters must then be determined in order to create the best possible material representation. The required modeling parameters are analytical-code dependent. They may include such factors as (a) fiber and matrix properties, (b) degree of matrix cracking, (c) fiber sheath content, and (d) sometimes other parameters. In addition the properties of the original constituents generally change during processing. Hence the process history becomes a major influence upon the final *in situ* constituent properties.

Analytical modeling has also been applied to CCC processing. The objective of the modeling was to relate process parameters to composite properties and performance. This analytical model was composed of two basic parts, namely the environmental model and the mechanical model. The process environmental model analyzed the process thermochemistry, heat transfer, and flow field for the liquid and gases in all regions of the processing locale. Its primary purpose was to furnish the material temperature and pressure boundary conditions for the mechanical model. The mechanical model then predicted the process stresses, strains and displacements in the material, followed by a failure analysis to determine the nature and extent of any damage which might have occurred. This method was repeated for incrementally-applied loading until the entire process was modeled. The models were then validated using experimental data from specially-fabricated test specimens. The final composite properties which are predicted and measured include all of the important thermal, thermoelastic, and strength properties.

4.5.2 Evolution

In the early years of CCC materials development, empirical approaches were typically used to obtain new and improved composites. Attempts to use existing models for the prediction of material properties and performance were not too successful because of (a) lack of many needed constituent properties and (b) the need to upgrade the models to account for the unique behavior of CCC materials. Most of the early modeling activities were devoted to

predictions of thermochemical ablation and thermostructural response which was in support of the development of missile nosetips, heatshields, and rocket nozzles. Performance predictions were then correlated with laboratory or ground-based facility test results to determine their degree of utility and accuracy. For example the ablation and shape stability of 3-D CCC nosetip materials were predicted with various codes, and then the actual materials performance was experimentally determined in a high-temperature air arc heater. Material performance predictions were improved by coupling code calculations with experimentation. Ultimately the material matured to the point of requiring full-scale part testing in ground-based facilities or actual article testing in service environments. Instrumentation of these full-scale articles to obtain data was generally limited because the presence of instrumentation often altered the local material response characteristics or caused localized failure.

In subsequent years the models were improved and used to assist in component failure analysis. One important example of this work involved the modeling and analysis of a large 3-D CCC nozzle billet that cracked during processing. Composite hoop fiber stresses during processing were predicted, and it was found that the process stresses had exceeded the intrinsic hoop tensile strength of the material. Subsequent analyses were performed on the effect of weave architecture, weave variation with radius, billet geometry, and fiber type. The results of the modeling defined guidelines for specifying billet geometry and weave geometry variation with radius to minimize process-induced stresses and thus maximize the probability of billet survival during processing. The new analytical capability was subsequently used to manufacture additional thick-walled CCC billets without material failure.

In the third major evolutionary phase of analytical modeling, an expert system computer code was developed to aid designers and fabricators in selecting optimum material constituents, architecture, and processes for a defined set of CCC requirements. The code enabled the user to enter constraints and goals through an interactive interface and thereby rank candidate materials in order of preference from a manufacturability viewpoint. Both algorithmic and heuristic rules were used to determine acceptable sets of materials and process parameters that would generate a minimum number of candidate material classes. The user then instructed the code to predict the thermomechanical elastic and strength properties for the material that best meet the overall materials requirements. While this code has been shown to be a powerful tool in guiding initial materials selection, it still must be used as an "aid" and not be a substitute for "human judgment."

4.5.3 Material Design

The design of a CCC material begins with selection of a fiber, matrix, and possibly a filler that appear to be most appropriate for the application. These constituents are combined to first form a unidirectional composite and then more complex materials such as a two- or multidirectionally-reinforced composite. The composite structures in this form represent various structural subelements such as plates, beams, shells, and attachments. Integration of the subelements produces the desired structure. Analytical modeling and experimental validation of the structural performance can then be undertaken to identify needed design changes. New and improved constituents are then selected for an iteration of the design process to achieve a more optimized structure. Simultaneous optimization of the materials and structural configurations generally takes place. Analytical and experimental techniques are used concurrently in the design of CCC articles. Analytical models are used to select the material configuration, identify a preliminary structural configuration, and identify the critical composite properties. Experimental techniques are then used to measure fundamental composite properties, evaluate subcomponents, and test the final article. Analytical predictions and experimental results are compared throughout the design process to (a) verify the suitability of the models and (b) understand and evaluate the test data. Once an appropriate model is developed, it can be repeatedly analyzed with different constituent materials and textile architectures to obtain an optimum design. Thus the material models can be useful in developing future material systems for advanced applications. The model can also serve the structural analysis community with an effective material property predictive tool to be used as a preprocessor to aerospace structural analysis codes.

Three-directionally reinforced CCC materials are analyzed by first specifying a unit cell or representative volume element. The basic material model is based on the concept that a material system is an assemblage of unit cells. The unit cell is the smallest portion of a weave which still retains all of the essential characteristics of the weave. Hence, if unit cells are stacked side-by-side in all directions, they will fully reproduce the whole weave. The unit cell is physically defined in terms of discrete unidirectional filament bundles, regions of interstitial matrix material, and the microcracked regions at the fiber bundle interfaces and those contained in the matrix. The matrix is assumed to be transversely isotropic with cylindrical or spherical voids and cracks. One correlative model that has been used extensively for component design is the Degraded Composites Analysis Program (DCAP). This mini-mechanics model was developed by the Materials Sciences Corporation and they describe it as follows.

> "The model is based upon a variational approach but uses more strictly defined displacement fields for the subregions of the unit cell."

The displacements within the fiber bundles are taken as those of the composite cylinders assemblage. The displacements within the interstitial regions are taken as those of the composite spheres assemblage. The composite spheres assemblage allows the model to assess the effects of spherical porosity or fillers within the matrix. The displacement fields between the subregions are assumed to be piecewise linear. The microcracked interfaces are modeled as effective extensional and shear springs which approximate the degraded load transfer across the interface due to microcracking. The nondimensionalized stiffnesses of the springs range from zero to one. They are set empirically by comparison with test data. A spring stiffness of zero represents a fully-cracked interface, whereas a spring stiffness of one represents a fully-bonded interface. The input to the DCAP model includes the dimensions of the unit cell, fiber volume fraction, fiber properties, matrix properties and information related to porosity, matrix shear volume fraction, and degree of subcell microcracking. The output of the model includes orthotropic Young's moduli, Poisson's ratios, shear moduli, thermal expansion coefficients, and strengths as a function of temperature. By summing and averaging the results on a particular cell face, the gross response of the cells is obtained. In the current state of the art, the model employs known constituents which are elastic, degraded regions between subcells, elastic response within subcells, and unknowns defined from a limited database. For 3-D composites the computed strengths are based upon the stresses carried by each subregion and the estimated strengths of those subregions. Composite tensile failure is based upon tensile failure of the unidirectional fiber bundle. Compressive strength is based upon compressive failure of the 1-D fiber bundles, which in turn is based on a microbuckling concept. For CCC materials the most probable microbuckling failure mode is shear mode failure of the unidirectional filament bundles. Shear failure has been limited to an estimate of the shear yield strength. The latter is based upon shear failure of the microcracked interface between yarn bundles and the interstitial matrix regions. DCAP contains two empirical parameters that are established by correlations with experimental data. They are termed the subcell efficiency and the sheath content. The latter value is the volume fraction of matrix that is highly oriented around the filaments.

The design of 2-D CCC materials is accomplished with existing analytical models which were originally developed for graphite fiber/epoxy structural materials. The composite microstructure is represented as many plies of oriented fabric or unidirectional lamina (parallel fibers embedded in a matrix material). Classical laminate plate theory is used to analyze 2-D composites, but it does not explicitly account for the microcracking in the CCC material. Thus, degraded matrix properties are used to account for the porosity and cracks within the matrix. The effective matrix properties are estimated by comparing measured data with computed properties and then adjusting the matrix moduli and coefficients of thermal expansion until the model is

brought into agreement with the experiments. To summarize, the DCAP is useful for calculating CCC stiffness and strength as functions of constituent properties. Composite stiffness and strength are functions of fiber volume, fiber orientation, fiber type and matrix type. Matrix constituent properties are generally not available, so the properties of an equal density polycrystalline graphite are substituted. DCAP includes rule-of-mixtures (ROM), Poisson's effect, matrix-fiber interface effects, and stress transfer efficiency. The code is capable of predicting directional properties of 2-D and 3-D constructions.

4.5.4 Mechanical Properties

Mechanical properties of CCC materials can be predicted by a ROM technique. This approach yields a fair approximation of the composite mechanical properties provided the matrix properties are assumed equal to zero. In general, the ROM equations tend to predict CCC mechanical properties higher than properties measured in the laboratory. This is due to degradation of the composite during processing.

4.5.5 Thermal Properties

Analytical equations for predicting the thermal properties of CCC materials are based on simplified models for the microstructure of the composite. For example, composite materials have been modeled as containing continuous, parallel filaments embedded in a matrix material or a particulate randomly-oriented fiber-reinforced matrix. Closed-form equations for predicting composite properties are based on the constituent material properties and their volume fraction. In-plane composite thermal conductivity and thermal expansion properties can generally be predicted with good accuracy. Less favorable predictions are obtained in the composite transverse direction because of difficulty in measuring the transverse thermal properties of fibers, weakly bonded interfaces, and possible anisotropic matrix properties.

Three-directional finite element models are used to analyze the heat conduction and thermoelastic response of a composite. In the finite element analysis, a repeating cell is used instead of a unit cell of the composite. It is preferable that the finite elemert model contain a certain degree of symmetry, so that the constitutive properties can he derived for the principal directions. For the unit cell no symmetry exists and the material appears to be anisotropic. The repeating cell in a 2-D laminate consists of two planes of symmetry which are perpendicular to each other and to the x-y plane. Hence the composite is orthotropic. With the repeating unit cell approach,the thermal transport and stress analyses are assumed to be uncoupled. That is to say, the nature of the heat flow is independent of the thermal stresses and vice versa. Hence these

analyses can be carried out independently. Coupling of the thermal and stress codes is complex and tedious.

4.5.6 Thermostructural Response

Two finite element codes that have been successfully used for thermostructural analysis of CCC parts are the PDA proprietary PATCHES II1 3D/axisymmetric analysis code and the ROSAAS 2-D/axisymmetric code. The latter code permits a fully nonlinear, temperature-dependent, anisotropic material description via bilinear curves to approximate nonlinear stress-strain behavior. Part stresses and strains are computed to calculate structural factors of safety based upon a fully-coupled Tsai-Wu failure criterion.

Some of the deficiencies of thermostructural analyses are that they are used sparingly in the initial design phase which leads to preliminary designs not based on quantitative data. The analyses are time consuming and labor intensive. Material property inputs are generally inadequate, and considerable time and money are required to generate the needed data. Nonlinear effects may be inadequately treated and results incompletely interpreted. Finally, it is relatively easy to make input errors which go undetected.

4.5.7 Ablative Response

Thermochemical ablation codes have been developed for accurately predicting the recession and shape change of CCC materials during exposure to high-temperature gaseous environments. These predictive techniques have been successfully used to: (a) correlate and extrapolate test data, (b) illuminate the mechanisms of mass loss and thermal protection, and (c) predict the performance of a given material in specified environments. Most of the codes in the public domain were developed by the Aerotherm Division of the Acurex Corporation (largely with U.S. defense funding). Some of the Aerotherm thermal codes used by the industry have included: (a) the Aerotherm Chemical Equilibrium (ACE) thermal code which calculates the thermodynamic and chemical state for a one-dimensional real gas isentropic expansion, (b) the Momentum/ Energy/Integral Technique (MEIT) which calculates heat transfer coefficients, (c) the Aerotherm Graphite Surface Kinetics Version B (Gasket 2B) code which generates surface thermochemistry tables, (d) the Charring Material Ablation (CMA) code which is a standard transient one-dimensional charring material code used to calculate transient recession rates, (e) the Aerotherm Axi-Symmetric Transient Heating of Material Ablation (ASTHMA) computer code which is a two-directional heat conduction code that can also accommodate in-depth material decomposition, and (f) the Nozzle Aero Thermochemistry (NAT) computer code for calculating

flowfields, heating conditions and surface thermochemistry. The ASTHMA code is widely used for reentry materials analysis. The code solves the transient heat conduction equation for axisymmetric bodies with temperature-dependent material properties. Surface thermochemical ablation can be modeled and the code can accommodate anisotropic materials. The NAT code is routinely used for rocket nozzle materials analysis. This code performs three separate analysis types including nozzle chemically-reacting boundary layer analysis and material surface thermochemical analysis. The NAT code has also been used as a major tool for guiding advanced materials development.

The general approach used with thermochemical ablation codes is to (a) first establish the boundary layer chemistry, (b) determine the flowfield parameters, (c) input the heating environment, (d) determine the recession (ablation) rates, and (e) determine the material temperature.

Predictive codes are typically difficult to learn and run, and they are time consuming. The codes can rarely be altered except by the individual or organization that created them.

Thermochemical ablation codes have also been coupled with hydrodynamic materials codes to predict the total thermal and erosive mass loss in a high-velocity particulate environment. This code development was in support of erosion-resistant missile nosetips which may experience particulate ice, dust, or rain during hypervelocity reentry flight.

4.5.8 Concluding Remarks

There are many computer codes available to the designer and materials developer. The degree of confidence in the predicted results varies greatly with individual organizations and with the type of application. To compensate for this general lack of confidence, CCC components are frequently overdesigned with an attendant weight penalty. Reliance on ground-test facilities and empirical tests have generally been high, particularly in the design of rocket motors. Some CCC components have never failed in service such as 3-D CCC nosetips and nozzle integral throat entrance caps (ITEs). Improving performance predictions thus invokes only modest interest. On the other hand, the numerous processing and in-flight failures of 2-D CCC exit cones suggest that major improvements are still required in performance predictions. It is apparent that direct evaluation of the relative performance capability of candidate materials is both time consuming and costly because of the large number of variables and the high unit cost for test

specimens or prototypes. The alternative or supporting approach is to utilize reliable material guidance models.

While much progress has been made in the development of material model systems, additional improvements are being sought to predict the basic response characteristics of CCC materials and their constituents. The role of the fiber-matrix interface region, debonding and slipping of composite constituents during loading, nonlinear response characteristics, proper definition of the composite failure mechanisms, and other areas are being researched.

In summary, the development of analytical, experimental, and computational tools are all necessary for the identification, classification and mathematical description of deformation, response and damage processes in emerging materials. These approaches do not compete with each other, but rather they are necessary and compatible approaches for understanding and predicting the behavior of materials in specified service environments. Current efforts are focused on constitutive modeling of multiphase materials, including the interactions associated with the material microstructure, and the onset and evolution of damage as a time-dependent process. Since CCC materials are used in extremely demanding environments, a fundamental understanding will be needed concerning their response to very high temperature and energy conditions, temperature gradients, mechanical loading, chemically-reactive and other service environmental parameters. Current research is focused on transient dynamic thermomechanical modeling, damage development and failure, life prediction, and associated diagnostic techniques. In the United States all three approaches to basic materials understanding have been highly developed because of the past multiple applications. In most other countries computational tools have been used to predict materials performance, but experimental confirmation of results has generally been lacking. A great deal of reliance has been placed on simulation of service environments and associated empirical testing. Such an approach generally results in a low level of confidence in the CCC material by component designers. In the long term this limited approach tends to greatly impede the introduction of CCC materials in new and upgraded applications.

4.5.9 Chronology

Pioneering developmcnts in computerized analytical modeling are given in Table 26.

4.5.9.1 The 1960s

CCC materials development in the United States was increasing rapidly during the late 1960s, but as noted earlier, the efforts were empirical. Several materials

TABLE 26
CHRONOLOGY OF CCC MATERIALS MODELING AND ANALYSES

YEAR	ANALYTICAL EVENTS	IMPORTANCE	ORGANIZATION
1973	3-D micromechanics model was developed to predict room temperature mechanical and thermal properties of CCCs	First application of micromechanics modeling to guide CCC heatshield development and design	Atomic Energy Commission/Sandia Laboratories/USA
1973	Shock wave characteristics of 3-D CCC materials were analytically modeled and experimentally verified	High shock wave attenuation by material fiber-matrix interfaces, porosity, and matrix cracks suggested future uses in nuclear x-ray environments	Kaman Sciences Corporation/USA
1973	Fracture mechanics formulas were developed for unidirectionally-reinforced CCCs	First attempt to understand and predict the unique fracture characteristics of simple CCC materials	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1973/76	Mini-mechanics modeling was used to identify promising 3-D orthogonal CCC constructions	First application of mini-mechanics to guide nosetip CCC materials development	Prototype Development Associates, Inc. (PDA)/USA
1974	Thermochemical ablation model was developed to predict CCC erosion rates in simulated solid propellant exhaust products	First accurate method for predicting linear erosion rate of CCCs in solid rocket motor environments	Acurex Corporation/Aerotherm Division/ USA
1974/75	Highly-instrumented 3-D CCC nosetip specimens were tested in a 50 MW air arc heater facility	Post-test analysis of the simulated reentry heated CCC materials revealed the importance of small-diameter yarns, small yarn-to-yarn spacing and high matrix density	Acurex Corporation/Aerotherm Division/ USA
1976	Micromechanics modeling was used to define the fibrous preform construction in a thick-walled cylindrical shape	Optimizing construction zones in a large ITE preform reduced process stresses and eliminated processing failures by providing strength where needed	Materials Sciences Corporation/USA
1976	Ablation-induced surface roughness of CCC materials was correlated with material characteristics	Material surface roughness influenced flow boundary layer transition, localized heating and ablation asymmetries of nosetip configurations	Science Applications International Corporation (SAIC)/Materials Sciences Division/USA

TABLE 26 (Continued)
CHRONOLOGY OF CCC MATERIALS MODELING AND ANALYSES

YEAR	ANALYTICAL EVENTS	IMPORTANCE	ORGANIZATION
1976	Analytical model was developed for predicting mass loss and cratering of 3-D CCCs during hypervelocity particle impact	Analytical capability aided in the development of missile reentry, erosion-resistant CCC nosetips	Systems, Science and Software (S^3)/USA
1978	2-D nonlinear stress-strain modeling was conducted on 3-D orthogonal and 2-D involute construction CCC materials	Upgraded thermostructural analyses aided in predicting CCC material performance	Prototype Development Associates, Inc. (PDA)/USA
1978	A mechanics of failure model was developed for a 3-D orthogonal carbon (PAN-based) tow/pitch coke-resin char matrices CCC	Provided new insights into the mechanism of failure of 3-D CCC having cartesian geometry	Southwest Research Institute/USA
1979	3-D finite element models were used to assess 2-D involute construction CCC configurations	First application of 3-D finite element modeling applied to solid rocket motor CCC exit cones	Prototype Development Associates, Inc. (PDA)/USA
1979	Analytical capabilities were developed for property predictions of n-D reinforced CCC materials	First architectural property predictions for n-D CCC materials	Prototype Development Associates, Inc. (PDA)/USA
1980	Analytical models were used to identify failure modes in 2-D involute CCCs during motor firings	Provided significant contributions to the understanding of in-service failures of 2-D involute construction CCC exit cones	Prototype Development Associates, Inc. (PDA)/USA
1980	Analytical process model was formulated and used to relate densification process parameters with CCC properties and performance	First comprehensive and scientific study to relate processing factors to end item properties	Science Applications, Inc./USA
1980	A thermophysical model was developed and verified for predicting composite thermal conductivity based on direct diffusivity, specific heat, and thermal expansion data	1-D and 3-D CCC thermal conductivity data were obtained with a large reduction in time and costs	University of Manchester/Manchester Materials Science Centre/ENGLAND
1981	Computer code was developed for optimizing ply pattern configurations in 2-D involute bodies of revolution	The amount and uniformity of carbon fabric was maximized for 2-D involute CCC exit cones	Air Force Wright Aeronautical Laboratories/Materials Laboratory/USA

TABLE 26 (Continued)
CHRONOLOGY OF CCC MATERIALS MODELING AND ANALYSES

YEAR	ANALYTICAL EVENTS	IMPORTANCE	ORGANIZATION
1982	A theoretical mechanics approach was developed and verified for 3-D CCCs having rectangular or cylindrical anisotropy	World-class approach for mathematically predicting certain properties of 3-D CCC materials	Institute of Polymer Mechanics/LATVIA
1982/92	Micromechanical models were created to predict 2-D CCC strength, nonlinear stress-strain and thermal expansion behavior including bimodularity	Models related deformational behavior and fracture to physical makeup of the CCC materials	Jortner Research & Engineering/USA
1982/87	Physico-chemical models were developed for predicting oxidation of CCC materials at high temperatures	Provided an improved theoretical and mechanistic understanding of the oxidation of bi-constituent CCC materials	The Ohio State University/Materials Science & Engineering Department/USA
1982	Initial damage to 3-D CCCs during processing cool-down was predicted with finite element thermal stress analysis	A model was demonstrated for predicting thermal stresses in a 3-D unit cell	Purdue University/School of Aeronautics and Astronautics/USA
1983	Strain response, shear stress, and ultimate strength of CCCs were predicted for the attachment regions of a CCC nozzle	Reliable behavior predictions of threaded region performance was obtained with finite element computer programs	Atlantic Research Corporation/USA Virginia Polytechnic Institute & State University/USA
1983	An inelastic finite element model was developed to predict thermostructural behavior of 4-D CCCs	Analytics were increasingly used to predict thermostructural response of n-D CCCs	Societe Europeenne de Propulsion (SEP)/ Division Propulsion a Poudre et Composites/FRANCE
1983	A new nonlinear material model was developed to define the loading and unloading of 2-D CCC materials	Enabled a better understanding of the structural response of 2-D CCCs	TRW, Inc./Ballistic Missile Division/USA
1985	Structural efficiencies were computed for 2-D, 3-D, 4-D, and 11-D CCC materials	4-D CCC materials had the highest reinforcement coefficient and reinforcement directions greater than four were unreasonable	Institute of Polymer Mechanics/LATVIA
1989	Upgraded failure criteria and margins of safety were formulated to predict in-plane failure of 2-D involute CCC materials	Enabled more reliable predictions of 2-D CCC exit cone failures during processing and motor firings	Aerojet Solid Propulsion Company/USA

TABLE 26 (Concluded)
CHRONOLOGY OF CCC MATERIALS MODELING AND ANALYSES

YEAR	ANALYTICAL EVENTS	IMPORTANCE	ORGANIZATION
1991	Integrated computer software was created to predict stresses and strengths of CCCs for different thermomechanical loading conditions	The composite material design code (ASCA) enabled CCC property predictions for highly-stressed applications	Adtech Systems Research, Inc./USA

properties:performance tradeoff studies were accomplished on nosetip and nozzle materials to identify the more promising composite type. There were no modeling activities performed to guide the CCC materials development.

4.5.9.2 The 1970s

The first modeling activities on CCC materials were undertaken in the early 1970s. Fracture mechanics formulas were developed in Germany for unidirectionally-reinforced CCC materials. In the U.S. the first micromechanics modeling efforts were devoted to the more complex 3-D needled felt and orthogonal-reinforced CCC materials. A 3-D micromechanics model was formulated to predict room temperature thermal and mechanical properties, and a mini-mechanics model was developed and used to identify an optimum 3-D CCC missile nosetip material. Existing hydrodynamic codes were also modified to predict the high strain-rate behavior of CCC materials during intense planar shocks.

Modeling activities intensified during the mid-1970s, although the collective efforts were still quite small. The primary focus of the efforts was to predict the ablation and thermostructural response of 3-D CCC nosetip and nozzle materials. Ablation codes were formulated or upgraded to incorporate the influence of material surface roughness on boundary layer transition, localized heating, and model asymmetries. Particle erosion of CCC materials also became important during this time period. Existing erosion models were also incorporated with ablation codes to predict combined ablation-erosion of nosetip and nozzle materials. Analytical studies were initiated to define the detailed materials requirements of CCC nosetip and nozzle materials. Composite properties were predicted as a function of the preform weave type. These efforts were the first formal use of analytics to identify the materials properties of importance needed in follow-on CCC optimization. Mechanics models were improved for 3-D CCC materials by incorporating subcell cracking. The concept of "zoned 3-D constructions" was formulated and successfully applied to the processing of thick-walled nozzle billets. Material strengths needed to accommodate processing stresses in the various ITE zones were predicted, and the textile preform weave having the needed structural properties was identified. Future billet cracking during processing was thus eliminated.

Material modeling, predictive code development, and analysis method developments spread in the late 1970s to domestic U.S. universities and overseas to the Former Soviet Union (FSU). In Russia a discrete matrix model was developed to mathematically predict the importance of certain defects on CCC mechanical properties. In the U.S. failure mechanics were defined, and 3-D finite element modeling was applied for the first time to involute CCC

constructions. These efforts significantly aided in the design and increased reliability of 2-D CCC exit cones. The 2-D nonlinear stress-strain behavior of CCC materials was also modeled for the first time for more accurate predictions of mechanical performance. Modeling was extended from 2-D and 3-D constructions to n-directionally-reinforced CCC materials. Architectural property predictions were made for the first time on these complex materials. By the late 1970s mechanics modeling of CCC materials had matured sufficiently that many organizations were interested in adapting modeling for processing control and guidance. A major U.S. government review was therefore conducted to (a) review the state-of-the-art analytical modeling techniques applicable to predicting the mechanical reponse of CCC materials, (b) determine the need and feasibility for future model developmental activities, and (c) establish priorities with respect to specific research efforts. It was concluded that analytical modeling efforts were severely limited because of variabilities present in realistic CCC materials and the general lack of needed materials properties and characteristics. Constituent material properties that changed during processing and fiber bundle-matrix interface considerations were not being properly addressed. Accurate constituent properties were needed as inputs to the code, but acceptable test methods were generally lacking to obtain these data. Static mechanical properties were usually measured for definition of the stress fields and failure characteristics, but the need for dynamic strength measurements and criteria were not well defined. Nonlinear stress-strain response of CCC materials was experimentally observed, but nonlinearity was just being incorporated into the models. Mechanical strength test methods were noted to be sensitive to the test method employed, and further improvements were needed to enhance the quality of the input data. The most important conclusion reached during the review was the great need for processing models and guidance. Some 2-D CCC exit cones were fracturing during processing or in flight. Other CCC articles were being manufactured without the desired material uniformity and properties. A process modeling program was thus initiated to (a) avoid future fabrication failures, (b) develop a systematic, cost-effective, and timely materials development approach, (c) provide simpler processing and fabrication conditions, (d) improve and obtain reproducible composite properties, and (e) produce composites with repeatable performance. This new processing model approach was later successfully demonstrated and greatly assisted in minimizing process-induced stresses and material fracture. The successful analysis and modeling efforts employed in the nosetip and nozzle areas suggested that CCC could possibly be applied to other major applications. One of these very important areas was the potential use of oxidation-protected CCC materials for limited-life gas turbine engines. An assessment was performed and it was noted that many systems benefits could be realized with the use of CCC materials in gas turbine engines.

4.5.9.3 The 1980s

The early 1980s witnessed a continuation of model upgrading and improved analytical capabilities. Various micromechanical models were generated for predicting composite strength, nonlinear stress-strain, and thermal expansion. The models related deformational behavior and fracture to the physical makeup of the composites, and more rational constitutive laws were developed for use in stress analyses. The first 3-D nonlinear stress-strain modeling of 2-D CCC mechanical response was accomplished. Complimentary work on material defects, damage, fracture, and failure contributed greatly to an understanding of CCC behavior and provided information for upgrading the models. These models assisted in identifying the failure modes of 2-D involute CCC exit cones which had failed during a space mission firing. Analytical models were also used to guide materials developmental efforts. Materials and architectural requirements for rotating turbine engine blades were analytically defined and successfully used. The ply pattern configurations of CCC involute exit cones were greatly improved with the use of a new computer code. In addition 3-D CCC exit cone constructions were modeled in anticipation of follow-on fabrication efforts. Analytical processing models were developed to relate process parameters with composite properties and performance. This activity was the first comprehensive and scientific study to relate CCC processing to end item properties. In support of oxidation-protected CCC materials development, various physicochemical models were formulated and used.

In the mid-1980s classical laminate theory was used to predict in-plane properties of non-warp-aligned thin section CCC materials from warp-aligned thick sections. This effort demonstrated that component properties could be predicted from a limited database. A unified theory was developed for predicting the stress-strain behavior and failure of 3-D orthogonal-reinforced CCCs in combined compression and shear, thus enhancing our knowledge in this area. In published Latvian research the structural efficiency was calculated tor 2-D, 3-D, 4-D and 11-D CCC materials. This predictive work demonstrated that 4-D reinforced composites had the highest reinforcement coefficient, and that fibrous reinforcement directions greater than four are not desirable. Analytical capabilities were also greatly improved to assist in selecting material constructions and tailoring them to specific solid-rocket motor part designs.

Modeling, analysis, and design procedures were upgraded in the late 1980s for prediction of 2-D CCC part failure during processing or motor firing. Failure criteria were formulated to establish margins of safety and in-plane material failure. Engineering mechanics were successfully applied to redesigning involute CCC exit cones for acceptable performance. Stress analysis codes were also improved to predict CCC delamination failures

using a new criterion. The high-temperature creep of CCC materials was predicted for a nonuniform temperature environment. These improved creep predictions more nearly represented actual service conditions. Lastly, the potential of CCCs for space structures was greatly enhanced by tradeoff studies and a definition of materials requirements to guide follow-on fabrication and development efforts.

4.5.9.4 The 1990s

Modeling and analytics became an integral part of CCC materials and prototype development by the early 1990s. Some of the recent improvements in this area are as follows. New computer structural 3-D finite element analysis techniques were extended for use with complex, contoured shaped nozzle configurations. These techniques were used to assist in materials selection and performance predictions of very large motor CCC parts. A new model was also formulated for predicting the effect of fiber crimp angle in fabric-reinforced CCC materials. Most of the modeling and analytical efforts, however, were devoted to assisting in the processing of new CCC materials. Artificial intelligence controllers and *in situ* sensors for real-time processing control were developed and employed to (a) obtain useful information for prediction models, (b) manufacture reproducible parts, and (c) significantly reduce processing time. The chemical vapor deposition (CVD) process was modeled for predicting initial carbon deposition rates and establish relevant CVD parameters needed to predict certain CCC materials properties as a function of time.

4.6 RESEARCH STUDIES

Research studies are generally of a fundamental or applied nature. Fundamental (basic) studies typically involve the generation of new scientific information with little or no regard to the practical utilization of this information. On the other hand applied research is generally oriented to elucidate new information, materials, methods, etc. for the advancement of a potentially useful or recognized area of technology. The distinction between the two types of research is not often evident. An examination of CCC materials science reveals that little fundamental information has been generated. Virtually all of the CCC research is of an applied nature, i.e., applied research.

A wide range of CCC research studies have been completed in the high-technology countries of the world. This research has been conducted in government laboratories, industrial facilities, universities, research centers, and small independent businesses. The objectives of the research varied greatly, depending upon the sponsor of the research and the country involved. For the most part, however, these in-depth studies sought to (a) create new CCC compositions,

constructions, and constitutents, and (b) generate knowledge required for the design, processing, behavior, and performance predictions of current and developmental material systems. Some of the specific research programs were: (a) synthetic carbon-forming matrices, (b) carbon and hybrid composition fibers from new organic precursors, (c) composite microstructural and microtextural features, (d) science-based processing methods, (e) materials behavior, (f) property measurements in extreme environmental conditions, (g) process:structure:property relationships, (h) mathematical modeling of processes and material performance, (i) mechanics and performance predictions, (j) process sensor upgrading and use, (k) life cycle predictive capabilities, and (l) others.

Government-funded CCC materials research in the United States presently involves the disciplines of mechanics, materials sciences, and chemistry. The mechanics of materials seeks to understand the thermomechanical behavior of CCCs. Mathematical models are developed and verified to predict CCC thermomechanical properties and to utilize these models in judging the merits of advanced material concepts. For example one research investigation sought to provide an understanding of the formation and growth of damage within CCC materials. This new knowledge will then be used to make judgments on the merits of both current and future material concepts. Additional details of CCC modeling have been given in Section 4.5 - Modeling. In the area of material sciences, emphasis is being given to an in-depth understanding of the fabrication, processing and microstructural characterization of CCC materials. Several specific projects involve (a) innovative processing methods to create novel structures of ultrahigh specific strength and specific stiffness (such as micro-tubes and foams), (b) graphitic structures having improved oxidation resistance, and (c) theoretical simulations of fiber-matrix interfaces and approaches for improving the same. The materials chemistry projects are focused on major limitations of CCC materials such as oxidation resistance. New boron-containing polymeric precursors are being synthesized and processed into oxidation-protected matrices. A second research project is studying the inhibition role of specific elements on oxidation of CCC surfaces. Yet another topic involves an investigation of fiber surface topography on CCC surface oxidation. Research results obtained in these and other studies throughout the world are intended to be used in follow-on exploratory development programs. Some of these major efforts include (a) new and improved constituent materials like ultrahigh thermal conductivity carbon fibers, (b) high shear strength composites using non-round carbonaceous fibrous reinforcements, (c) new low-cost processing methods like film boiling hydrocarbon matrix deposition into carbonaceous preforms, (d) new methods for investigating materials behavior, (e) measuring materials properties in extreme environmental conditions, (f) optimization of existing CCC processes using *in situ* measurements

and data output to alter processing conditions, (g) identification and quantification of material defects, fracture, and failure modes, and (h) life-cycle prediction models.

4.6.1 Centers of Excellence

There are at least two U.S. centers of excellence in CCC materials research. Southern Illinois University has conducted a wide variety of CCC research projects, and they have hosted annual workshops and conferences to promote the interaction of worldwide research personnel. Pennsylvania State University, although it is better known for its contributions to the science of bulk carbonaceous and graphitic materials, has also published a number of technical articles on the subject field. That university is presently leading a new, multidisciplinary research initiative on basic solutions for improving CCC oxidation resistance.

4.6.2 International Activities

Interest in the science of CCC materials has spread from the United States to many other parts of the world. In western Europe both Germany and France have had very visible and productive research efforts. One institution and individual stand out above all others in their contributions to the science of CCC materials. The University of Karlsruhe, under the leadership of Professor Doctor Eric Fitzer, has investigated many research issues and published extensively. One of his most significant accomplishments involved a study on fiber-matrix bonding effects on composite properties. Dr. Fitzer also trained many doctoral candidates, some of which were foreign-born and later returned to their respective countries to start new CCC research efforts. The author was privileged to know Dr. Fitzer for many years. In my opinion he is the foremost world authority on the science of CCC materials. France also has a very respectable CCC science program. Their program is mainly funded by government organizations, involves high caliber research institutes, and the efforts are well coordinated. Other countries of Western Europe that have published research results on CCC materials include England, Wales, The Netherlands, and Spain. In Eastern Europe six countries have published articles on CCC material sciences. They are Russia, Yugoslavia, Ukraine, Latvia, Czech Republic, and Poland. Very extensive efforts were conducted by the State Research Institute of Graphite in Russia, but very little of their research has been published. Much of the Russian research has been highly mathematical in nature, and little of it has been experimentally verified. In the Middle East only Israel has likely conducted CCC research. Several research projects have been reported in the literature. Quite a different situation exists in the Far Eastern portion of the world. Japan, People's Republic of China, Taiwan, Korea, and India have had numerous research activities because of the potential applications of this material for their defense and aerospace systems. In Japan over 25 different

organizations have performed CCC research and published their results in the open literature. The focus of their research appears to be on new processes, not new products.

Countries promoting the use of CCC materials in applications tend to sponsor the greatest number of research projects. Other countries having only a scientific interest in the subject have contributed little to the field.

4.6.3 Barriers and Impediments

During the past three decades of CCC materials development, the U.S. scientific community has been hampered by various factors. The fundamental science of CCC materials has not been the catalyst for composite creation, contrary to many other areas of technology. During the early years of CCC history, the scientific community continued to devote its attention to bulk carbonaceous and graphitic materials. Sponsors of carbonaceous materials were preoccupied with their many limitations and problems. They failed to recognize the impending advancements in composites including CCC materials. CCC research at that time was funded largely by defense organizations. Defense research was organized around classical areas of science, like chemistry, physics, etc. CCC materials didn't fit any of these categories and thus it was easy to ignore this new and promising area of technology. Meanwhile in the business sector of the CCC industry, namely brake disc components, resources were devoted to product upgrading. Essentially no resources were made available to the research community to study fundamental problems of friction, wear, and related scientific problems. The CCC brake disc industry, which has profited the most from this new business sector, contributed the least in available scientific direction and financial support. Another domestic impediment has been the restricted transfer of information and data from one source to another. Much of the technology was considered company proprietary and not published in the open literature, but many details could be found in issued patents. In 1977 CCC technology (except science) was restricted in the U.S. and COCOM countries by international agreements. The results of many science programs continued to be presented and published in the open literature. But without strong guidance from users and ties to the rest of the CCC community, the quality of research suffered.

The scarcity of graduate materials scientists and engineers throughout the history of CCC materials has and will continue to limit progress. CCC science and technology are presently treated as only a part of a materials sciences course, hardly the type of visibility it deserves in the academic community. Yet, the academic community must be careful not to train more professionals than it needs. The most notable example involved the University of Karlsruhe.

There were more graduates than positions to fill in Germany, and thus many of the graduates migrated to other fields of endeavor.

4.6.4 Chronology

The many research contributions of the establishment of CCC materials technology are given in Table 27. It is interesting to note that the basic research ideas in the field of CCC materials originated from many sources, including (a) university research organizations, (b) research institutes, (c) industrial and aerospace laboratories, and (d) other sources. Universities, which are traditionally chartered to carry out the fundamental research obligations in the U.S., were minor contributors because of (a) inability to acquire the necessary background information and (b) minimal financial support by the commercial world and the defense governmental organizations.

4.6.4.1 The 1960s

There were apparently no fundamental research studies on CCC materials during the 1960s. All of the research was of an applied nature in that it was oriented toward obtaining information, compositions, behavior, and properties useful for the development of this new family of advanced composites. There were actually very few applied research investigations. The efforts were more exploratory than the usual in-depth treatment of a scientific subject. The primary focus of the research was on constituent materials potentially useful in aerospace and CCC materials. Pyrolysis studies were carried out on various thermosetting resins, resin/pitch blends, and pitches including: (a) phenolics, (b) furfural/pitch, (c) furfural/ acenapthylene pitch, and (d) coal tar pitches. Some of these materials were originally developed for densification of graphite electrodes, but they had the potential for providing a higher carbon yield than the widely available epoxy and phenolic resins. Phenolic resins with higher aromatic contents were synthesized. Their char yields were increased versus state-of-the-art resins, and for that reason some of them were later commercialized. Synthetic polymeric research also produced polyphenylene resins, the ultimate in char-yielding resins. This polymer was available only as fine granular material. It was not processible by conventional means. Nevertheless, the author dissolved the gold "brick dust" in a liquid phenolic solution and obtained a usable, high char-yielding impregnant for porous CCC bodies. One should note that interest in polyphenylene-like polymers remained for at least two following decades, but in spite of continuing research, none of these matrix precursors were commercialized for the CCC industry. One of the brightest ideas advanced during the 1960s was the possibility of synthesizing a chemically-pure, high carbon-forming and processible matrix for densification of porous CCC preforms. Derivatives of indenes

TABLE 27
CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1963	Oxidation kinetics and rates of 2-D CCC materials were established in laboratory research	Unprotected CCC materials appeared to be useful for transient periods in high-temperature, oxidizing environments	Ling-Temco-Vought/Chance Vought Corporation/USA
1969	High-pressure graphitization of thermosetting resins produced unique char structures	Pioneering research approach for controlling resin char microstructure and properties	State Research Institute of Graphite/RUSSIA
1969	Microstructural features of 3-D discontinuous fiber-reinforced CVI PG CCCs were obtained with a newly-available scanning electron microscope	More detailed structural information was obtained on CCC constituents to guide future developments	Union Carbide Corporation/Oak Ridge Y-12 Plant/USA
1971	High-temperature heat treatment effects on 3-D graphite (rayon-based) felt/CVI PG CCC materials were investigated	First systematic study of CVD/CVI processing:structure:property relationships to guide material development	Atomic Energy Commission/Sandia Laboratory/USA
1971	1-D CCCs were produced from various resin chars and carbon or graphite fibers and their composite properties measured	Pioneering research that provided a more scientific understanding of the material constituents:processing parameters: composite property relationships	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1971	Particulate graphite fillers in resinous matrices were shown to greatly decrease dilametric changes during pyrolysis	Low-cost approach for minimizing resin char shrinkage and cracking, and dissipating newly-formed pyrolysis gases	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY

TABLE 27 (Continued)
CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1972	Pyrolysis of pitch under high gas pressure greatly increased the coke yield	Promising approach for obtaining higher density and greater coke yields from pitch infiltrants	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1974	Mechanical and thermophysical properties of phenolic resins were measured during carbonization	A detailed understanding of phenolic pyrolysis was obtained to guide CCC processing	McDonnell Douglas Astronautics Company-West/USA
1974	Oxidation behavior was investigated for 2-D CCC, pyrolytic graphite and glassy carbon	Porous CCC material oxidized faster than nonporous PG and glassy carbon	Tokyo Institute of Technology/Faculty of Engineering/JAPAN
1974	Strong bonding of phenolic resin to surface-treated carbon (rayon-based) fibers restricted resin shrinkage during composite pyrolysis and caused char matrix cracking	Nonsurface-treated carbon fibers were preferred for CCC fabrication	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1976	Properties and characteristics of commercially-available resins and pitches were measured in a laboratory	Provided detailed guidance for the selection of a precursory, liquid, carbon-forming densification matrix	Naval Surface Warfare Center/USA
1977	Transversely-oriented carbon matrix in composites was formed with CVD carbon and subsequent HIPIC pitch-based impregnation/carbonization	Coke matrix orientation in the vicinity of carbon fibers may greatly influence composite properties	General Electric Company/Re-Entry and Environmental Systems Division/USA

TABLE 27 (Continued)

CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1978	Rate-controlling steps were determined for the oxidation of 2-D frictional CCCs	Provided fundamental information for the improvement of aircraft brake disc materials	Bendix Research Laboratories/USA
1979	Curing stresses were predicted for precursory carbon fabric/phenolic resin composites	Basic materials information was needed to reduce process-induced stresses for the fabrication of 2-D CCC materials	Air Force Systems Command/Air Force Materials Laboratory/USA
1979	Microstructure of CCC materials was related to macro-properties	Bridged a major gap between research information and useful materials development guidance	The Aerospace Corporation/Materials Sciences Corporation/USA
1979	Ethynylated aromatic resinous compounds were synthesized in a laboratory	Precursory char matrix material with a very high carbon yield (95%) and good processibility	Hughes Aircraft Company/USA
1981	A method was developed for analyzing fibrous reinforcement wrinkles in CCC materials	Enabled computation of effective modulus, shear modulus, etc. of the disturbed CCC region	The Aerospace Corporation/Materials Sciences Laboratory/USA
1981	Hydrocarbon film boiling process was developed for carbon densification of fibrous carbon preforms	Very fast and economical densification process for CCCs	Commissariat a l'Energie Atomique/FRANCE
1981	Boron-containing inhibitors were used in 2-D carbon (PAN-based) fabric/phenolic char CCCs	Oxidation resistance of char substrates was greatly increased at high temperatures	Vought Corporation/USA

TABLE 27 (Continued)
CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1983	Influence of carbon powder additives on physical, thermal, and mechanical properties were measured for 2-D resin char matrix CCCs	Carbon powder additives to phenolic resins increased 2-D CCC matrix-dominated across-ply and shear strengths	Aerojet Strategic Propulsion Company/USA
1983	Composite modulus and yield strength of 3-D orthogonal CCC materials were measured and analyzed	Simple criterion was found to predict the onset of composite yielding	Purdue University/School of Aeronautics and Astronautics/USA
1983	Stressed region of a notched 2-D CCC was simultaneously observed with acoustic emission and scanning electron microscopy	A possible proof test for CCC, but further development was required	The Aerospace Corporation/Materials Sciences Laboratory/USA
1983	Pioneering research to understand the effects of oxidation on CCC materials	A decrease in flexural strength, Young's elastic modulus, work-of-fracture and fracture toughness due to oxidation was studied for short carbon (PAN-based) fiber/phenol furfuryl char-CVI PG CCCs	The Pennsylvania State University/Department of Materials Science and Engineering/USA
1984	Chemical vapor infiltration (CVI) studies were conducted with various porous carbonaceous preforms	Fundamental processing:property relationships were established for CVI carbon matrix deposition	Boris Kidric Institute of Nuclear Sciences/ YUGOSLAVIA

TABLE 27 (Continued)
CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1984	Carbon (PAN-based) fiber strength in fabricated CCCs was studied in terms of virgin fiber strength, surface treatment and other factors	Surface-treated carbon fibers lost 70% of their virgin strength, but nonsurface-treated carbon fibers retained 100% of their original strength	Universitat Karlsruhe/Institut fur Chemische Technik/GERMANY
1985	Porosity, pore size, and pore size distribution of 2-D CCCs were measured during and after processing steps	Porosity control during processing was important to relieve internally-generated gas pressure and avoid cracking or delamination	Aerojet Strategic Propulsion Company/ USA
1985	Single-filament pullout method was developed to quantify fiber-matrix bonding in CCC materials	Simple and inexpensive test for tracking degree of fiber-matrix bonding during CCC processing	University of Dayton Research Institute/ Edwards AFB/USA
1986	Electronic and structural characteristics of highly-graphitic 2-D CCCs were investigated	The degree of graphitization of CCC materials was quantified using experimental techniques	Massachusetts Institute of Technology/ Department of Physics/USA Nuclear and Aerospace Materials Corporation/USA
1986	Microstructure, pore size, and interlaminar strengths of 2-D carbon (PAN-based) fabric/phenolic char CCCs were measured at successive densification process steps	Process:property relationship information enabled optimized process conditions and higher shear strength composites	NASA Langley Research Center/USA
1986	Mechanism of graphitizable carbon formation in fiber bundles was defined for 3-D CCC materials	Matrix densification process details were provided for densifying 3-D CCC materials	The Aerospace Corporation/Materials Sciences Laboratory/USA

TABLE 27 (Continued)
CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1988	Theory generated to predict the effect of fabric weave crimp angle on the in-plane tensile and compressive strengths of 2-D CCCs	Provided a basis for identifying a major cause of strength variability in 2-D CCCs	Jortner Research & Engineering/USA
1989	Oxidation rates of silicon-carbide coated 2-D CCCs were investigated in laboratory-simulated active-to-passive transition conditions of hypersonic flight vehicles	Upper temperature limits were established for silicon-carbide coated CCC aerodynamic surfaces	NASA Langley Research Center/USA
1989	*In situ* electrical conductivity measurements were obtained on CCCs during their first pyrolysis cycle	A new method was demonstrated for monitoring the degree of carbonization during CCC processing	Rockwell International Corporation/Science Center/USA
1990	Crystallographic, microtexture and mechanical properties were measured for virgin and heat-treated carbon fibers	CCC processing temperatures may significantly change the properties of virgin carbon fibers	Centre National de la Recherche Scientifique (CNRS)/FRANCE University of Dayton Research Institute/ USA
1990/92	A digital image process technique was developed to obtain improved microstructural analysis of CCCs	Improved the prospects for correlating matrix and fiber microstructures with processing parameters	Clarkson University/USA
1990	Microstructure of carbon matrices from phenolic, pitch and CVI graphites was correlated with CCC tensile and short-beam shear properties	CVD matrix CCCs had the highest tensile and shear strength properties, and much additional information was obtained	Jet Propulsion Laboratory/California Institute of Technology/USA
1990	CCC specimen sectioning, mounting, microscopy, and nondestructive evaluation methods were developed	Improved laboratory procedures became available for investigation of CCC materials	University of Dayton Research Institute/ USA

TABLE 27 (Concluded)

CHRONOLOGY OF CCC MATERIALS RESEARCH STUDIES

YEAR	RESEARCH EVENTS	IMPORTANCE	ORGANIZATION
1991	Mechanical property test methods for 2-D CCC materials were evaluated for thin, space structural composites	Conventional ASTM test methods were not usable, especially for double-notch interlaminar coupon tests in the fill direction	University of Dayton Research Institute/ USA
1992	Preceramic silazane-based sealants were synthesized for oxidation-resistant CCC materials	Sealants exhibited improved chemical compatibility and bonding with 2-D CCC substrates	BFGoodrich/Aerospace Division & Super-Temp/USA
1992	Borate glass (boria-lithia-oxide) sealants were investigated and exhibited improved moisture resistance, substrate wettability and thermal cycling performance	Improved sealants for oxidation-resistant CCC materials	NASA Langley Research Center/USA
1992	High heat treatment temperature effects on 3-D needled (PAN-based) carbon tape/CVI PG CCCs produced noticeable property changes	The degree of graphitizability of CVI rough laminar carbon matrix significantly affected composite density, thermal conductivity and some mechanical properties	The Aerospace Corporation/Mechanics & Materials Technology Center/USA
1992	Efficient and reliable test method developed for measuring interlaminar tensile strength of 2-D CCCs	Accurate materials property data to guide design and materials development	University of Dayton Research Institute/ USA
1994	Microstructure and mechanical properties were investigated on rapidly carbonized 2-D carbon fabric/phenolic char CCCs	First carbonization cycle was shortened (in time) without influencing composite properties	Air Force Materiel Command/Wright Laboratory/Materials Directorate/USA University of Dayton Research Institute/ USA

were synthesized with the desired purity and coke yields, but limited processibility prevented their widespread use. Some progress was later made in this area, but lower-cost materials remained as a challenge for the future. Many years later the concept of synthetic pitches was successfully reduced to practice in Japan. They used this approach successfully to form precursors for high-strength, high-modulus carbon fibers. Hence, early research on precursor matrices did not contribute much to the overall CCC technology. On the other hand, research on carbonizable organic fibrous materials had an enormous impact on the developing field of advanced composites. Most of the research was focused on rayon and polyacrylonitrile fibers, but the potential of wool, nylon, cotton and others was also examined. In the area of processing research, basic CVD/CVI and liquid impregnating methods were already being used by the bulk graphite industries. Nevertheless, some of the densification techniques were further examined for use.

CVD methods were investigated for densifying fibrous carbon preforms. This research exhibited great promise in that high-density composites were obtained, but density gradients were commonplace. One interesting approach co-developed by the author was to rigidize a porous carbon fabric preform with pyrolyzed phenolic resin and then densify the structure with pyrolytically-deposited carbon material. This type of process was later upgraded and used for the production of solid rocket motor exit cones and other articles. Another interesting science project involved the influence of pressure on graphitization of organic polymers. This research indicated that a more ordered carbon structure from a resinous precursor could be produced by pyrolysis under high pressures. Matrix densities on the order of 1.7 g/cm^3 (0.061 lb/in^3) were obtained. This type of research was carried out in several different countries, but in spite of the knowledge gained, no known practical application has been made of this scientific knowledge. During the 1960s, sufficient CCC materials became available to conduct behavioral studies and to measure properties. It was clear that highly-directional properties were possible, and mechanical properties should be greatly improved over bulk graphitic materials. Some U.S. research was therefore initiated on CCC mechanical properties and fracture characteristics. Research results were reported on both resin-based and CVD PG-based CCC materials. Composite properties were not too attractive, because the quality of the materials was quite inferior; but as we shall later learn, the development of uniform and high-density CCC composites provided the approach for high mechanical properties, low ablation rates, and other sought-after attributes.

Research interest in CCC materials during the 1960s (or lack of it) can be inferred from an analysis of scientific and technical publications. During all of the 1960s, only

five articles appeared in the leading international journal on carbonaceous materials. One of the research publications dealt with the formation of resin-based CCC materials. The remaining articles discussed CCC properties and characteristics. In 1967 there were 186 presentations given at the Biennial Conference on Carbon; none of them dealt with CCC materials. At that meeting a discussion was held on the last 10 years of progress in carbons and graphites. The new field of CCC materials was not mentioned. At the Ninth Conference on Carbon in 1969, three presentations out of a total of 177 dealt with CCC materials. There was a general unawareness of CCC materials and a lack of research contributions. It was well over a decade later that the "science" of CCC materials began to emerge.

4.6.4.2 The 1970s

During the early 1970s, CCC developmental activities were on the increase. The research communities of the United States, Germany, USSR, and England began to take note. Microstructural research efforts were initiated on constituent materials and the fiber-matrix interface regions. Crystalline parameters of carbonized resins and pitch matrices were measured and compared to other types of carbonaceous materials. It was noted that carbon layers close to fibers (in composites) were preferentially oriented and parallel to the fiber axis. This observation sparked a number of investigations on the possible cause:effect relationship. It was hoped that such an explanation would ultimately lead to control of the carbon microlayers and provide some insight into controlling the directional properties of a composite. The orientation of the carbon microlayer apparently was associated with the reactivity of the fiber surface, but the phenomenon was never fully explained. This research area is perhaps typical of many encountered in the science of CCC materials. The general approach is to obtain as much basic information as possible on the subject using whatever analytical and instrumental approaches are available, and then apply this new knowledge to gain control over the material or the process for making the material. Synthesis efforts on higher char-forming and coke-forming matrices continued into the early 1970s but at a slow pace. It began to occur to the technologists that much of the CCC basic science was unknown. Classical material composition:process:structure: property relationships had not been developed, but such relationships were needed to help guide ongoing developmental efforts. The first systematic investigations of this type were carried out in the early 1970s. One study dealt with the pronounced effect of heat treatment on the properties of CVI PG graphitizable matrices and compounds. By control of the composite heat treatment process, composites could be obtained with a wide range of thermal, mechanical, and physical properties. The second investigation, and one of great and lasting value, dealt with the influence of inert gas pressure on the yield of coke (carbon) from pitch precursor. With increasing

pressure, the pitch coke yield increased up to some limiting pressure. The author was not familiar with this technology, which was domestically developed for atomic energy purposes. Upon the recommendation of a senior defense official, the author and his team evaluated the process being used to densify porous carbonaceous bodies. Eureka. There at last was a manufacturing approach needed to densify fibrous carbon preforms to very high density values. Composite materials could now be produced with densities as high as polycrystalline graphite and have equal ablation rates. Also of importance, the high density CCC materials potentially had better mechanical properties, erosion characteristics, and other properties of interest. Meanwhile in the laboratory, the research community began to fabricate their own versions of CCC composites. Most of the composite constructions were, of course, unidirectionally-reinforced CCC materials. This construction approach, while not resembling materials being developed, provided a simple approach for investigating key materials and process variables. It was during this time frame that one of the important problems of resin-based CCC materials became known. During pyrolysis, organic resins underwent large dimensional changes due to loss of matrix material. Materials and techniques were needed to reduce resin shrinkage and minimize any detrimental effect on composite properties. Graphite fillers were added to the resinous phase. It was found that such fillers (a) increased the local heat transfer, (b) acted as sites for the collection of pyrolysis gases, (c) promoted a more orderly dimensional change of the resin during carbonization, and (d) acted as an inexpensive filler in lieu of higher-cost fibrous carbon. Carbon powder-filled 2-D CCC materials were later developed for rocket nozzle exit cones and other high-temperature applications. Finally, the rapidly developing science of mini-mechanics modeling was applied to a very important and current topic. Mini-mechanics modeling was used to help identify a promising CCC material for missile nosetip uses. Many of the properties and characteristics of CCC materials needed for mechanics modeling were not available at that time, and thus the analyst synthesized whatever missing properties that were needed. For example, detailed properties of medium-density char matrices were not known, but the properties of a porous carbonaceous material of equal density were found to be useful in providing realistic composite performance predictions.

Applied research activities continued to expand during the mid-1970s, although there were still few open literature publications. During this time frame research activities were initiated in both France and Japan. Aerospatiale (a major French defense systems contractor) joined forces with LeCarbone-Lorraine (a dominant French carbon manufacturer) to conduct research and development on CCC materials. Funding for this research possibly came from the French government via the Commissariat A L'Energie Atomique (C.E.A). It was apparent that the French government had decided that CCC materials provided promising

solutions to important strategic materials applications. Japan, which is ever cognizant of research throughout the world, also initiated a pioneering investigation on the oxidation behavior of various composite matrices including (a) resin chars, (b) glassy or vitreous carbons, (c) synthetic pitch cokes, and (d) pyrolytic deposits. During this time frame, it also became apparent that the use of CCC materials involved more than ablation, thermal, thermostructural, and mechanical considerations. Research investigations were conducted on subsonic and hypervelocity particulate erosion of CCC materials to provide guidance for the development of (a) alumina particle erosion-resistant surfaces for solid propellant rocket nozzles and (b) ice crystal/ rain/dust erosion-resistant strategic missile nosetip materials. Pitch-based matrix materials began to attract more attention as a possible infiltrant for porous carbonaceous bodies. Most of the attributes, limitations, and key properties of pitch materials were assessed during this time frame. Both coal tar and petroleum pitches offered similar attributes, and these matrices were later used for CCC products. Investigators began to concentrate on intrinsic property limitations of CCC materials. For example, interlaminar shear strength of 2-D CCC materials was recognized as a limiting property. This property was a function of both materials and process variables and it could be varied within narrow ranges.

By the late 1970s, almost two decades of materials development had been accomplished. The carbon and graphite industries showed little interest in CCC materials because the prospects for large volume production and profit were not apparent. Systems organizations that used polycrystalline graphites were not convinced that CCC materials would eventually have superior properties to bulk graphites. One U.S. defense organization even went on record that aerospace graphites would be adequate for all future reentry vehicle nosetips. The lack of interest in CCC materials by the U.S. graphite industries precluded any meaningful research by those organizations. Those engaged in materials development essentially had no science base to use, and as a result the character of the work was highly empirical.

During the late 1970s more research was reported on the microstructure of CCC materials before and after exposure to selected service environmental conditions. More researchers became involved in predicting and measuring the thermostructural behavior of CCC materials. A 2-D nonlinear stress-strain modeling was performed on fabric-reinforced involute constructions and orthogonal 3-D composites. Nozzle and nosetip designers began to suspect that CCC materials were highly resistant to thermally-induced stresses and thermostructural failure. The author can recall a need to obtain the highest possible density material for the lowest possible ablation and greatest shape stability. But many practitioners argued that high-density CCC composites would fail thermostructurally like polycrystalline graphites. Later, intense

heating of CCC materials by various laboratory devices demonstrated their outstanding thermostructural performance. The key to this materials behavior was later shown to be the result of poorly bonded fiber and matrix in the CCC material. The author found it very interesting that this principle was not applied (for many years) to the development of ceramic-matrix composites.

4.6.4.3 The 1980s

A large number of CCC material concepts and composites were created during the 1970s. Some of these materials appeared to be useful for defense and aerospace purposes, and for that reason numerous composite scale-up and application projects were initiated. The U.S. and other nations undertook internal studies to determine the applications potential of such composites for defense, industrial, commercial, and other uses. Meanwhile, the CCC scientific community was growing slowly and continuing to expand the breadth and depth of the research projects. In the People's Republic of China (PRC), the microstructure was described for pretested and post-tested HIPIC 3-D CCC materials. This and other similar basic information was being used to guide ongoing 3-D CCC materials development. In France highly innovative research was underway to create new materials and processes. A novel CVI pyrolytic graphite densification process was originated based on enhancement with DC plasma. New oxidation-protected CCC materials were also created. Submicron particles of tantalum carbide, titanium carbide, and zirconium carbide were incorporated into pitch impregnants prior to infiltrating a porous preform. The resultant pitch-based coke contained dispersed carbide particles, thereby imparting some level of oxidation protection. The French researchers also created a novel family of oxidation-protective hybrid composites. Porous 2-D CCC substrates were CVI densified with silicon carbide, titanium carbide, or boron nitride. The CVI ceramic provided greatly improved oxidation resistance, but it also tended to embrittle the composite. The process was later scaled up in a new dedicated French CVD/CVI factory. Another great processing achievement was made by the French during the early 1980s. A film boiling process was conceived and reduced to practice in one of the French Atomic Energy Commission (C.E.A.) laboratories. The carbon-matrix densification process was very fast (150 or more minutes) and hence economical. The basic process is now being scaled up in the United States under a large government-funded research and development program aimed at low-cost CCC materials. In Japan the fracture behavior of CVI PG matrices was correlated with microstructure. In Germany many research efforts were underway at the renowned University of Karlsruhe. Scientists from many nations were engaged in high-quality and useful CCC research programs. In the U.S. acoustic emission and scanning electron microscopic observations were made of 2-D CCC materials while under stress. Analytical modeling efforts transitioned from a macro-scale to smaller material features;

namely, yarn or tow bundles which are the repeating elements of CCC materials. Properties of fiber bundles were experimentally measured and correlated with processing conditions. An analysis method was also developed for determining the effect of fabric wrinkles on composite moduli values. Pitch matrix research continued to be of great interest. Several organizations perfected methods for solvent extracting pitches to obtain a high-purity mesophase product. Important propertles of pitches were also measured, including viscosity at high temperatures and thermophysical properties.

Research investigations in the mid-1980s focused primarily on oxidation of CCC materials and a greater understanding of composite mechanical behavior at elevated temperatures. Compounds known to inhibit oxidation, such as boron oxide, were incorporated into CCC composites by way of particles, films, and coatings. Steady-state and transient oxidation rates were measured on protected CCC materials and their constituents. Oxidative studies were also carried out in the presence of other major influencing factors such as (a) partial pressure of oxygen, (b) various humidity levels, and (c) similar topics. In the area of materials behavior and property measurements, brittle-to-ductile failure transitions and modes were investigated with 2-D CCC materials. Fiber bundle properties at very high temperatures were measured and the data used for modeling. Quantitative data were also obtained on composite deformation at high temperatures. Fiber-matrix bonding in composites continued to be of great interest, and a single fiber pullout method was developed to help quantify the interface region. Fiber-matrix bonding experiments were repeated with surface-treated and non-surface-treated PAN-based (instead of rayon-based) carbon fibers. The deleterious effects of strong fiber-matrix bonding on certain mechanical properties were again noted.

In the late 1980s research on oxidation-protected CCC materials was still underway, better organized and beginning to yield results useful for new and improved materials. Oxidative research efforts were ongoing at a large number of organizations. In the U.S. the primary needs were to: (a) focus the research on the most critical problems, (b) obtain guidance from potential users, and (c) integrate the numerous research and development efforts to meet stated material performance goals. To answer these needs a major workshop on the subject was sponsored in 1987 by the Materials Directorate of the U.S. Air Force Wright Aeronautical Laboratory. About 100 representatives from the academia, industry, and government participated in the meeting. Some of the major conclusions were as follows. Major across-the-board advances would be needed to obtain long-life materials, but full utilization of existing research information and methodologies could enable further incremental gains. New research approaches will be necessary to create wide temperature ranges and higher-temperature coatings. The

prospects for achieving a crack-free coating system were judged to be very poor. There was a poor understanding of the property degradation phenomena and life characteristics in oxidizing environments. Laboratory test results could not be correlated with user-developed environmental tests. Available oxidative-prediction codes were only of limited value. Micromechanical modeling was not yet capable of combining all-important physical and mechanical characteristics of CCCs. To summarize, it was felt that a more fundamental understanding was needed on all of the constituents and the oxidation-protected material systems. This basic understanding included (a) deposition and microstructural control to achieve uniform thickness and stoichiometry, (b) details of the thermal, chemical, and physical interaction of sealants and inhibition constituents with the coating, (c) definition of failure mechanisms of the outer coating and the other constituents, and (d) a reliable predictive capability for estimating the maximum lifetimes and temperatures for high-quality materials.

Research efforts on CCC materials continued to increase during the late 1980s. Most of the accomplishments reported dealt with (a) constituent materials, (b) new processes for oxidation-protective materials, and (c) mechanical behavior and property generation. In the area of constituent materials, Indian researchers provided additional information on the relationship between glass (vitreous) char matrix properties and the preceding resin chemistry. Both PAN-based and pitch-based carbon fibers were prepared with improved oxidation resistance. Substantial amounts of PAN-based carbon fibers with metal-boron compounds were synthesized, processed into the corresponding carbon fiber, and investigated for oxidative resistance. PAN-based and pitch-based carbon fibers containing substitutional boron dopants were also prepared, and the oxidation characteristics of the carbonized fibers were studied. Oxidation-protective carbon matrices were synthesized by incorporating molecularly-dispersed inhibitors or oxygen scavengers in a high char-forming resin. The intent of the research was to provide oxidation protection at the molecular level. Ceramic coatings were prepared in the laboratory with novel preceramic polymeric coating processes. The resultant coatings were further investigated and found to have: (a) improved oxidation performance, (b) adherence to the substrate, (c) chemical consistency, (d) tailorability, and (e) ease of application. A colloidal ceramic particle coating process was also developed using electrophoretic deposition methods. Process science programs also yielded useful results. An apparatus and methodology were developed to conduct on-line quantitative analysis of multiple phenomena occurring during matrix carbonization. This research advancement provided a more intelligent approach for selecting time, temperature, and pressure cycles used in the preparation of CCC materials. With respect to material behavior and property measurements, a considerable amount of research was conducted and published. Theories were advanced to explain and predict the effect of fabric weave crimp

angle on composite in-plane tensile and compressive strengths. Critical failure modes of 2-D CCC materials were identified to assist in failure analysis and development of rocket nozzle exit cones. For cylindrical CCC materials restrained in the outer diameter, fabric fill direction compression was determined to be the critical failure mode. In addition cross-ply tension and interlaminar stresses generated during CCC processing could also play a role in material failure. Damage initiation and failure mechanisms of 2-D CCC materials were further investigated using flexural bending tests. The practical application of this research was reduced contact stresses in mechanically-fastened parts. Interlaminar shear strength of 2-D CCC materials, which is typically low and design limiting, was noted to be a difficult property to measure by available test methods. Analytical and experimental investigations resulted in a modified direct shear test method. Property measurements with this new test method produced more accurate results. Composite behavior and properties at very high temperatures continued to be of interest. Creep behavior at elevated temperatures was experimentally measured using 1-D CCC specimens. It was noted that the carbon matrix greatly reduced composite creep. Furthermore the initial transient creep of a CCC material should be used as a main design parameter.

4.6.4.4 The 1990s

Applied research on CCC materials likely reached its peak in the early 1990s. Hereafter the level of effort declined due to reduced defense budgets and a low level of support from the commercial sector. Nevertheless, important research programs are still evident in the United States, France, Russia, Japan, Taiwan, and Korea. Each of the individual projects are now more in-depth, scientific, and sometimes multidisciplinary in nature. Several countries have also initiated CCC projects for the first time. These countries were Spain, Poland, Ukraine, and possibly others. One of the characteristics of newly-initiated research in developing countries is a focus on previously-identified materials problems. Their effort may be duplicative in objective, but it generally turns out that the research adds substantial new knowledge to the field.

Applied CCC research in the early 1990s continued to focus on oxidation-protective materials, materials behavior, and materials properties. The new field of process science was gaining momentum. Its objective was to obtain desired materials with predetermined uniformity, composition, properties, and performance.

New and improved constituent materials continued to be synthesized and evaluated. Phenolic resins with char yields up to 71 weight percent were reported. Research was continued on polyarylacetylene resins because of their intrinsically-high char yields, but high cost and processibility remain as identified issues. Very high purity pitch matrices of

predetermined molecular weight fractions were obtained with the use of supercritical fluid extraction techniques. This method is not presently cost effective compared to solvent extraction or chemical synthesis approaches. Mesophase pitch was separated from isotropic pitch with the use of a high-speed centrifuge. Separation of the pitch types was difficult because of the small density differences between the two materials. Vinyl carboranes were incorporated into phenolic matrices to assess their potential for molecular inhibition of oxidation. Additional applied research was also conducted on mesophase pitch-based carbon fibers. Nonround fibers were synthesized, pyrolyzed, and properties determined. Their packing efficiency in a composite is not as good as round fibers, but other unique characteristics were uncovered. Because of the very high cost of mesophase pitch-based carbon fibers, research efforts were undertaken and promising approaches defined. One usable approach involved heat treatment of lower-cost, pitch-based carbon fibers to yield a much higher performance product. In heat treating the fibers above their original processing temperature, a marked increase was obtained in axial fiber modulus and thermal conductivity. Crystallographic and room-temperature mechanical properties were measured on the new heat-treated carbon fibers. Several new CVD ceramic coating compositions were also developed during the early 1990s, such as silicon carbide-silicon-zirconium silicide and hafnium-carbide-silicon carbide-hafnium silicide. The concept ot multilayered and multifunctional coatings began to take hold in an effort to improve the behavior and performance of materials. One functionally gradient coating, based on silicon-carbide-silicon-zirconium silicide, performed adequate oxidation protection to 1650°C (3002°F) and multiple thermal cycling. Because coated CCC materials were being used in service, the possibility existed for surface damage. To accommodate this problem, organometallic (polysilizane) polymers were prepared. This precursory silicon carbide coating powder was placed in the area of a damaged coating and pyrolyzed to a ceramic state. Hence, damaged coated parts were repaired with a ceramic coating and by a simple method.

Processing research centered on two different subjects. First, low-cost processes for obtaining CCC materials continued to be of high interest. Secondly, the development of suitable instrumentation and methodology for production of reproducible CCC materials also continued onward. A one-step, hot-pressing method was developed in an effort to produce low-cost materials. Japanese scientists were also successful in developing a hot-press molding process to yield very low-cost CCC materials. It was reported that the new materials were one-third to one-fifth the cost of conventional materials, thus making them competitive for various markets such as brakes, clutches, and furnace components. Empirically-derived cure processes for the manufacture of resinous composites were re-examined. Qualitative process automation was developed for controlling cure processes. Modern computer technology allowed

the integration of the latest in processing equipment with newly-developed artificial intelligence programming techniques. The resulting system was capable of autonomously producing high-quality precursory 2-D composites in greatly reduced times.

The entire field of CCC material behavior and property measurements also began to receive greater attention. Test materials were available with high quality and from numerous sources. This situation greatly helped the researcher in lessening the number of variables involved in an investigation. New specimen sectioning, mounting and microscopic approaches were documented. Nondestructive inspection techniques began to be used to assure specimen quality so that resources would not be wasted on testing inferior materials. Material property and performance prediction capabilities continued to be refined. Accurate engineering formulae were developed to calculate the strengths of 4-D CCCs in various reinforcement directions. Greater understanding was also acquired on fracture and failure modes. The mechanism of damage initiation and failure of 2-D CCC materials was investigated using three-point bending test methods. Tensile failure modes of 2-D CCC materials were identified and correlated with a variety of materials constituents and processing conditions. Tensile and shear properties of 2-D CCC materials were correlated with the microstructure of various carbon and graphitic matrices. It was found that the degree of matrix heat treatment increased composite tensile strength and lowered shear properties. CVD PG matrix composites had the highest tensile and shear strengths. Particle fillers, which are often present in matrices, inhibited resin graphitization and reduced the composite tensile and shear strength values. A more quantitative understanding of cracks and voids in CCC materials was also obtained. Voids were classified according to position, size, and orientation in 2-D composites. Cracks were classified as being straight, angled, or S-shaped. Cracks were reported to play an important role in the formation of tensile damage and delamination in 2-D CCC composites. Additional quantitative information was obtained on the damping behavior and resonance frequency of as-cured and CCC materials. The composites were shown to have high dampening characteristics, thus opening new avenues for uses in rotating and intense acoustic applications. Low-cycle fatigue mechanisms and damage were investigated using 2-D CCC materials. Tests conducted at less than 200,000 cycles revealed that a fine-scale microcrack damage was initiated and grew during material fatigue. More studies will be needed, however, to elucidate the mechanism(s) involved. Significant advances were also made in understanding oxidation of CCC materials. Oxidation tests were conducted on carbon fibers, pyrolytic carbon infiltrated carbon tows, and pyrolytic carbon-coated hybrid ceramic composites. The research revealed that composite oxidation is greatly reduced by using a silicon carbide matrix in lieu of a carbonaceous matrix. Pyrolytic carbon coatings on carbon fibers greatly reduced their oxidation rate except for the exposed fiber ends. Extensive

high-temperature oxidation investigations were performed on coated 2-D CCC materials. From the information obtained, the failure mechanisms were deduced. A material model for the oxidation of a CVI densified 2-D CCC material was also created. These and other programs have generated much new scientific information on oxidation-protected CCC materials. Additional studies are underway to understand the processing:structure:reactivity parameters involved as well their relationship with each other.

4.7 MANUFACTURING

The production of CCC materials involves preparation of a fibrous textile architecture and then its densification by (a) chemical vapor infiltration (CVI) process, (b) liquid matrix phase impregnation, or (c) combinations thereof. The specific manufacturing processes selected are guided by (a) desired composite properties, (b) available equipment, (c) economic factors, (d) time considerations, and (e) other lesser criteria. Additional manufacturing details are contained in section 4.2.4 - Composite Fabrication and Processing.

Manufacturing technology and follow-on production are integral and important steps in the development and application of a CCC material. These steps generally occur in the latter stages of materials development. See Figure 17. Manufacturing technology programs are usually initiated to resolve various issues, such as (a) scale-up of materials and processes, (b) reproducibility, (c) producibility, (d) cost reductions, (e) suitability of materials and process specifications, and (f) other considerations. It is desirable to evaluate and resolve all or most of these issues prior to any production run in order that manufacturing risks are lowered and the most suitable processes are used. In CCC manufacturing technology projects, it is customary to fabricate several full-size articles. These parts are checked for tolerances and conformance to specification values. They are then dissected for the generation of local composite properties. Several full-size components may also be retained for performance evaluation in ground-based test facilities or in actual service environments.

4.7.1 Critical Elements

The manufacture of CCC materials depends on the availability of certain precursor materials, manufacturing equipment, and detailed process know-how. Critical elements include (a) matrices, (b) fibrous reinforcements, (c) oxidation inhibitors, (d) various manufacturing methodologies (composite processing, carbonization, graphitization, oxidation protection), and (e) associated specialized process equipment.

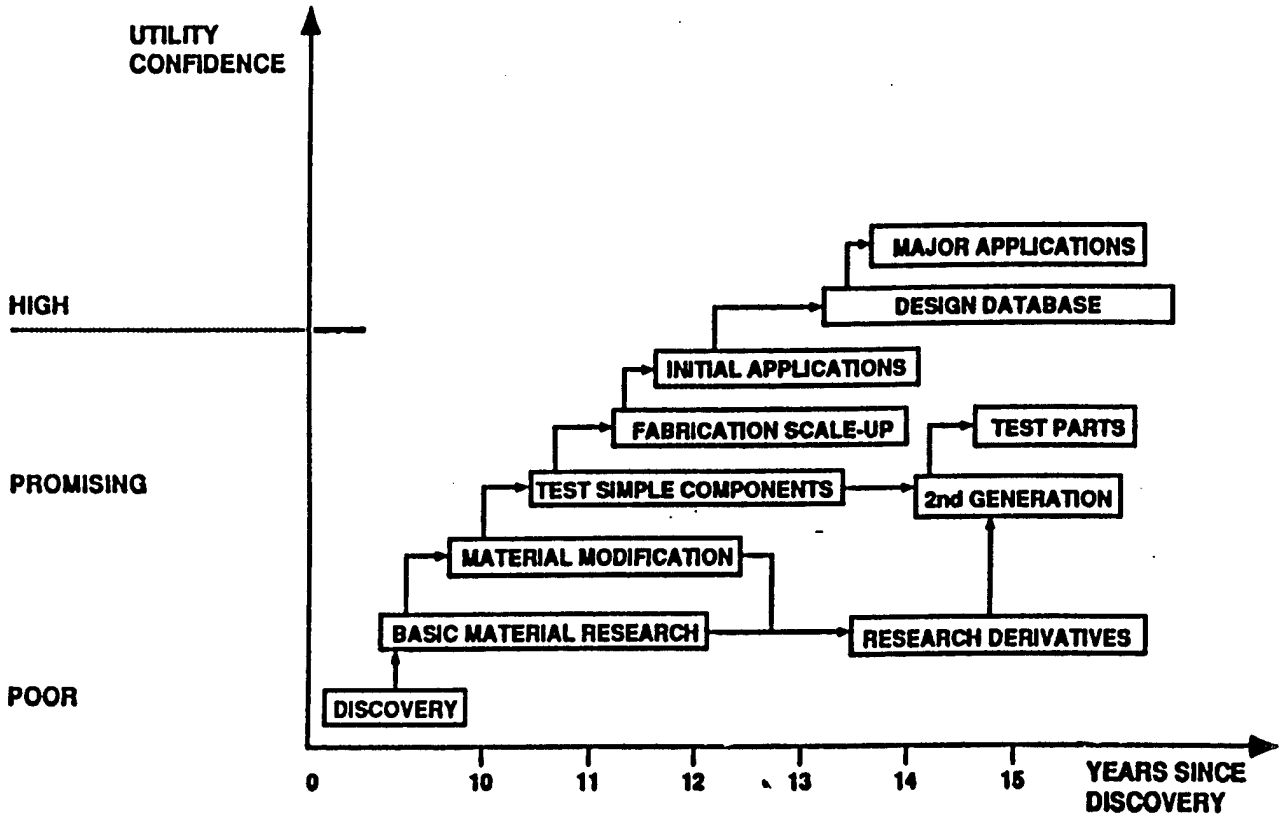


Figure 17. Typical Development Cycle for CCC Materials.

Carbon-forming matrices used in the manufacture of CCC materials are available in all of the high technology and most of the developing countries. Phenolic resins, for example, are produced in many countries or imported. Pitch impregnants are also available in countries that refine gasoline or make various coal products. Hence, matrices are usually not a critical limiting material.

Fibers used in the production of CCC materials are domestically manufactured in many high technology countries, including (a) England, (b) France, (c) Germany, (d) India, (e) Japan, (f) People's Republic of China, (g) Russia, (h) Taiwan, and (i) the United States. Low performance rayon-based and PAN-based carbon fibers are commercially available from many worldwide sources. The sale of higher-performance carbon fibers, however, is controlled in certain Western and Asian countries. Hence the production of high-performance CCC materials hinges on the availability of high-performance PAN-based or pitch-based carbon fibers.

The most critical elements of CCC materials technology are the detailed manufacturing process know-how and specifications required to make an acceptable part in a reasonable time and at a reasonable cost. Such know-how has been empirically developed in over 10 countries. The technology is generally not available in the published technical literature.

Manufacturing equipment used in the production of 2-D CCC materials is similar to that needed for organic-matrix composites and the high-temperature process equipment common to the graphite industry. Such equipment is available in all of the high technology countries. The equipment includes (a) prepreg machinery, (b) autoclaves, (c) matrix transfer equipment, (d) carbonization ovens, (e) graphitization furnaces, and (f) inert gases.

The production of 3-D and n-D composites requires highly specialized preform weaving equipment. Countries reported to have such equipment include: (a) France, (b) Japan, (c) People's Republic of China, (d) Russia, (e) Taiwan, and (f) the United States. This weaving equipment, particularly automated machinery and associated computer control technology are critical elements and thus usually have been controlled items. The fibrous textile architectures prepared on these machines have very few civilian uses. They are mainly used in key military applications. Low-cost 3-D fibrous preforms for commercial aircraft brake discs are one notable exception. High-pressure process equipment used in the densification of fibrous preforms is also a critical element of CCC manufacturing. HIPIC autoclaves and very high-temperature furnaces (gas, electric and induction) are keystone equipment items.

Enhancing the oxidation resistance of CCC materials is also a critical enabling technology. The approaches generally involve (a) precursor materials for matrix or fiber inhibition, (b) coating chemistries, (c) deposition processes, and (d) similar topics. Keystone equipment includes (a) computer-controlled vacuum furnaces, (b) CVD and CVI deposition/ infiltration furnaces, and (c) related equipment.

4.7.2 Manufacturing Equipment

CCC production in the United States has been carried out by organizations engaged in (a) materials development, (b) volume production of end items, or (c) both. In general materials research and development organizations have small laboratory-size equipment to perform all or most of the necessary fabrication steps. Production sources have much larger equipment and usually more than one piece of equipment for each process step. The maximum size of a part produced is generally limited to the working size of the equipment involved. Some of the largest CCC manufacturing equipment in the U.S. is about (a) 1.5 m (5 ft) by 1.8 m (6 ft) for liquid matrix infiltration vessels, (b) 3.0 m (10 ft) by 3.0 m (10 ft) by 3.0 m (10 ft) for graphitization furnaces, (c) 2.4 m (8 ft) diameter by 3.7 m (12 ft) high for CVD/CVI deposition furnaces, and (d) 0.9 m (3 ft) diameter by 2.4 m (8 ft) long for high-pressure impregnation vessels. The actual working dimensions in these facilities are slightly less than the sizes reported.

4.7.3 Product Forms

CCC materials are manufactured in a wide variety of configurations, sizes, and thickness. Parts have been produced in the form of (a) flat sheets, (b) rods, (c) cylinders, (d) hollow cylinders, (e) rectangular billets, (f) frusta, (g) contoured shapes, (h) intricate structural configurations, and (i) others. See Table 28. Other CCC shapes have been produced by machining billets into the desired part configuration (like a nosetip). Hollow frusta and cylinders have been manufactured in diameters up to 2.43 m (8 ft). Structural panels have been fabricated in 1.2 x 3.7 m (4 x 12-ft) sections. Cylindrical billets have been successfully manufactured in thicknesses up to about 0.3 m (12 in). Just about any fibrous preform architecture can be made with available equipment. The final shapes of CCC parts can be produced to close tolerance using standard graphite machining equipment and techniques. The composites can be sawed, drilled, ground, and polished. Care must be exercised during machining to avoid damaging the brittle matrix. The use of carbide or diamond tools has been recommended.

TABLE 28
CHRONOLOGY OF CCC PRODUCT FORMS

YEAR	PRODUCT FORMS	FIRST USE	ORGANIZATION
1960	PLATES - flat and thin	Specimens for property measurements	Chance Vought Corporation/USA
1960	FRUSTA - hollow and thin-walled	Specimens for property measurements	HITCO/USA
1961	HEMISPHERES - Thick-walled	Article for simulated earth reentry tests	Chance Vought Corporation/USA
1962	RODS - solid	Specimens for property measurements and simulated earth reentry tests	Chance Vought Corporation/USA
1963	CYLINDERS - hollow, contoured, and thick-walled	Articles for solid propellant motor tests	HITCO/USA
1963	FRUSTA - molded-to-shape, hollow, and thick-walled	Articles for solid propellant motor tests	Union Carbide Corporation/Carbon Products Division/USA
1963	CONES - molded-to-shape and thin-walled	Articles for graphite nosetip insulation tests	Union Carbide Corporation/Carbon Products Division/USA
1966	BILLETS - solid, rectangular, and thick	Machined specimens for simulated earth reentry tests	Avco Corporation/Research & Advanced Development Division/USA
1966	DISCS - solid and thin	Dynamometer specimens for simulated aircraft braking tests	Carborundum Company/USA
1981	DISC-BLADE ASSEMBLY - variable thickness	Rotating article for gas turbine engine tests	Vought Corporation/USA
1984	CONES - Contoured, thin-walled, large, and coated	Articles for cryogenic liquid propellant engine translating cone tests	HITCO/USA Chromalloy Research & Technology Division/USA
1985	PANELS - Rib-stiffened	Structural demonstration elements for high-temperature testing	Rohr Industries, Inc./Refractory Technology Aerospace Components/USA
1988	CYLINDERS - Hollow, very large, and very thick	Articles for solid propellant motor ITE tests	Societe Europeenne de Propulsion/Division Propulsion a Poudre et Composites/USA
1988	I-BEAMS AND CRUCIFORMS - Large and thick	Structural demonstration elements for hypersonic flight vehicle testing	LTV Aircraft Products & LTV Missiles and Electronic Groups/USA
1989	CYLINDERS - Hollow, thin-walled, very long, and very stiff	Articles for spacecraft truss structural tests	Kaiser Aerotech/USA

TABLE 28 (Concluded)
CHRONOLOGY OF CCC PRODUCT FORMS

YEAR	PRODUCT FORMS	FIRST USE	ORGANIZATION
1990	PANELS - Rib-stiffened, curved, very large, and coated	Demonstration articles for hypersonic flight vehicle structural testing	BFGoodrich Aerospace/Super-Temp/USA
1991	WING BOX - Coated, large, and structural	Structural demonstration article for hypersonic flight vehicle testing	LTV Aerospace & Defense Company/USA

4.7.4 Production Times

The manufacture of CCC materials takes from two to 12 months, but production times are being continually reduced. Simple shapes of 2-D CCC materials generally take about two months to produce, whereas very large 3-D ITE billets may take up to 12 months to manufacture.

All CCC materials are acquired by "batch" processing, although some of the fabrication and processing steps have been partially automated. Hence most production runs will require a large number of articles to be in various stages of processing at any one time.

Manufacturing times vary greatly depending upon the (a) type of reinforcement scheme selected, (b) specific processes required, and (c) final composite density and wall thickness. The longest processing times are generally associated with preform densification and preform assembly. Preform densification has typically involved many time-consuming steps such as (a) transfer of materials from one piece of equipment to another, (b) CVI deposition involving 100 or more hours, (c) very slow pyrolysis rates, (d) slow heat treatment (graphitization) rates, (e) slow equipment cool-down from high process temperatures, and (f) other factors.

Typical fabrication and processing times for a 2-D fabric-reinforced CCC panel are as follows: (a) several hours for the preparation of a resinous laminate, (b) five hours for curing the composite, (c) 125 hours for each carbonization step, (d) 75 hours for each graphitization step, (e) 100 to 150 hours for CVI/CVD densification, (f) 75 hours for final heat treatment, and (g) many additional hours for a surface coating if needed. Actual fabrication and processing times are on the order of about 17 to 30 days, but delivery times are more near two to four months from placement of an order.

4.7.5 Manufacturing Costs

CCC materials are high priced when compared to other competing engineering materials. The higher initial material costs are often offset by their longer service life, thus making the life cycle costs of the material reasonable, if not minimal. For comparative purposes, prices of low-cost CCC materials, high-performance graphites, and ablative thermal protection plastic materials will be cited. Medium-density CCC materials generally sell for about $440/kg ($200/lb). Aerospace-grade graphites have been furnished for about $7-$15/kg ($3-$7/lb), and ablative carbon fabric-reinforced phenolic composites have been priced at about $110/kg ($50/lb).

The price of CCC materials depends primarily upon the (a) specific manufacturing methods employed, (b) number of production units, and (c) size and shape of the article. Short fiber-reinforced and woven fabric-reinforced CCC materials, like those mass produced for aircraft brake discs, costs about $175-440/kg ($80-$200/lb). Higher-performance structural CCC materials which typically contain high-strength, intermediate-modulus carbon fabric sell for about $440-$2,900/kg ($200-$1,315/lb). 3-D and 4-D materials, like those employed in missile nosetips and nozzle throats, are priced at approximately $1,100-$3,300/kg ($500-$1,500/lb). Oxidation-protected CCC materials are five to 10 times more expensive because they contain particulate fillers, sealants, and surface coatings.

Production costs for CCC materials and their application components are company proprietary and rarely discussed in the open literature. However, a number of pre-production manufacturing technology programs have been completed, and relative cost figures have been obtained. Table 29 lists the apportionment of manufacturing costs for constituents, processes, and steps for each of four different types of CCC materials. These 2-D and 3-D CCC materials represent typical compositions, constructions, and applications intended for use in aircraft brake disc, turbine engine flap, strategic missile nosetip, and solid propellant rocket nozzle throat. From these data it is apparent that there are generally three high-cost aspects to the manufacture of CCC materials. 3-D woven fabrics and preforms may constitute up to one-half of the total material costs. This preform fabrication step is labor intensive and lengthy, but the introduction of semiautomation has helped reduce overall costs. The densification of fibrous performs is another costly and lengthy process. Expensive equipment may be needed. Many impregnation and heat treatment cycles are also required. The application of coatings for oxidation protection is yet another expensive process step. Coatings generally constitute between 35 and 50 percent of the total material costs. The importance of these cost apportionment estimates is that they suggest areas for future cost reductions in manufacturing and production.

During the last two decades of manufacturing CCC materials, a number of cost-reduction steps have been evaluated and successfully used. They include:

a. Low-cost, short carbon fibers in lieu of higher-priced, continuous-length tows and yarns,

b. Commercial-grade carbon fibers instead of higher-priced, specialty carbon fibers,

c. High filament tow, low-cost fibrous materials in lieu of higher-priced, smaller-diameter carbon tow,

TABLE 29
APPORTIONMENT OF MANUFACTURING COSTS FOR VARIOUS CCC MATERIAL COMPONENTS

Application Type	Brake Disc	Engine Flap	Missile Nosetip	Nozzle Throat
Fabricated Product	**3-D HS C-Fiber/CVI PC Matrix**	**2-D HT IM C-Fiber/ Phenolic Char**	**3-D HM C-Fiber/ HIPIC Pitch Coke**	**3-D HS C-Fiber/ LOPIC Pitch Coke**
Manufacturing Cost Apportionment, %				
Fibers, matrices & fillers	5	5	10	15
Woven fabrics & preforms	30	5	35	50
Densification & heat treatments	45	35	30	20
Coating	-	35	-	-
Machining	10	5	5	5
Nondestructive evaluation & quality control	10	10	10	5
Testing & analysis	-	5	10	5
Total	100	100	100	100

Costs are representative; not specific to an application.

d. *In situ* formation of high-modulus carbon fibers from lower-modulus carbon fibers during composite heat treatment, thus avoiding the initial use of expensive, high-modulus carbon fibers,

e. Heat treatment of woven, low-modulus, low-cost carbon fabrics to form high-modulus carbon fabrics,

f. High char-yielding resin/pitch-blended impregnation matrices in lieu of precursory phenolic or epoxy resins,

g. Very high coke-yielding pitch matrices instead of resinous impregnants to reduce the number of infiltration and heat treatment cycles,

h. Precured unidirectional fibrous rods for 3-D and n-D preform assembly instead of dry fibrous tow placement,

i. Woven carbon fabrics in lieu of X and Y dry yarns for assembly of 3-D orthogonal fibrous preforms,

j. Semiautomated weaving of 3-D orthogonal and pierced fabric preforms instead of hand weaving dry yarns or tows,

k. Contoured woven fibrous preforms for near net-shape constructions and less machining of the final composite part,

l. Hybrid fibrous preform constructions with at least one low-cost carbon reinforcement to provide adequate performance at the lowest cost,

m. High-pressure infiltration/carbonization (HIPIC) densification processing to obtain full-density parts with fewer process cycles,

n. Boiling hydrocarbon, fast carbon matrix densification of preforms in lieu of lengthy resin or pitch infiltration processes,

o. Co-pyrolysis of matched shrinkage constituents (matrix and oxidized fiber) to reduce or eliminate additional infiltration/pyrolysis cycles,

p. Vibratory filling of porous fibrous carbon preforms with carbon powders to reduce the amount of higher-priced carbon fiber,

q. Scientific process controls of the matrix densification steps to obtain vital processing information and real-time control for maximum composite performance, improved economics, and fewer rejects,

r. Large billet manufacturing followed by machining into smaller, but full-size articles, and

s. Reliable NDE/NDI methods to reject nonspecification parts earlier in the cycle and at their lowest value-added stage.

4.7.6 Manufacturers

Many high technology countries of the world produce CCC materials and components. These manufacturers are primarily located in the United States because (a) CCC materials were a U.S. invention and (b) aggressive development and application especially in the defense sector. Contrary to expectations, the U.S. carbon and graphite industry played only a limited role in the development of CCC materials. Two U.S. graphitic product manufacturers undertook developmental work, but only one of them aggressively pursued the subject for a long period of time. Most of the first-generation CCC materials were produced by plastic fabricating companies who had the skills to fabricate the precursory organic matrix composite. These companies empirically developed pyrolysis and densification processes for first-generation, moderate-density CCC materials. During that time CCC materials produced from plastic composites were known as "pyrolyzed plastics." Overseas, CCC materials were developed within the existing carbon and graphite industries or within the confines of restricted government facilities. These same organizations then produced whatever CCC materials were needed for applications.

The major and worldwide manufacturers of CCC materials are listed in Table 30. Major manufacturers of CCC materials are located in the United States, France, and possibly Russia. Lesser amounts of materials are produced in England, Germany, and Japan. Other advanced CCC countries involved in materials manufacture include (a) India, (b) Korea, (c) People's Republic of China, and (d) the Republic of China. The major CCC materials producers in the United States are:

(a) Allied-Signal Aircraft Landing Systems,
(b) BFGoodrich Carbon Products and Aerospace/Super-Temp,
(c) BP Chemicals (Hitco) Inc.,
(d) Fiber Materials, Inc. (FMI),
(e) Hercules Aerospace Co.,
(f) Kaiser Aerotech,
(g) LTV Aerospace and Defense Co.,

TABLE 30
MAJOR MANUFACTURERS OF CCC MATERIALS

- Allied-Signal Aerospace/USA
- BFGoodrich/USA
- BP Chemicals (HITCO) Inc./USA
- Carbon Industries/FRANCE
- Dunlop Ltd./ENGLAND
- Fiber Materials, Inc./USA
- Kaiser Aerotech/USA
- LeCarbone Lorraine/FRANCE
- LTV Aerospace & Defense Company/USA
- NiiGrafit/RUSSIA
- Societe Europeenne de Propulsion (SEP)/FRANCE
- Textron Specialty Materials/USA

(h) General Electric Company, and
(i) Textron Specialty Materials.

Some of these organizations have sold their CCC business during the mid-1990s as the industry underwent downsizing. The major CCC producers in France are:

(a) Aerolor (Aerospatiale and LeCarbone Lorraine),
(b) Carbon Industries (Alsthom and SEP), and
(c) Societe Europeene de Propulsion (SEP).

In England, Dunlop Ltd. is the major manuiacturer of CCC materials and products. Schunk Kohlenstofftechnik and Sigri Elektrographite are the major producers of CCC materials in Germany. Nissan Motor Company, Kawasaki Heavy Industries, Ltd., Kobe Steel, Ltd., and Showa Denko KK are reported to be the major manufacturers of CCC materials in Japan. In Russia, NIIGrafit produces a full range of CCC materials and products.

4.7.7 Manufacturing Sites

Production facilities for CCC materials cost many millions of dollars. A 91,000 kg (200,000 lb) per-year plant for 2-D CCC brake discs, for example, may cost in excess of $50 million. To protect this high investment, only personnel needed to run equipment are generally permitted access to the manufacturing floor and knowledge of the manufacturing details. In addition to protecting the proprietary rights of the manufacturer, additional safeguards are often necessary for military reasons. CCC defense components are normally manufactured in areas isolated from other operations or in a "dedicated and militarily restricted" plant.

4.7.8 Joint Manufacturing Ventures

There are few totally integrated CCC material manufacturers. New business opportunities often involve capabilities beyond a single organization, and thus two or more supporting organizations may be required to satisfy total requirements. This situation has given rise to (a) manufacturing license transers from one organization to another and (b) joint ventures to develop, manufacture, and market specific CCC products.

Many CCC joint ventures and manufacturing license agreements have taken place during the past two decades. Table 31 lists some of the important agreements that have been reached. Most of these agreements have been between United States and French organizations which are the largest CCC material producers in the world.

TABLE 31

CHRONOLOGY OF CCC JOINT VENTURES AND MANUFACTURING LICENSE TRANSFERS

YEAR	EVENT	IMPORTANCE	ORGANIZATION
1972/75	CVD/CVI manufacturing technology and equipment designs were transferred overseas	Greatly accelerated the establishment of CVD/CVI manufacturing densification faciities in France and England	Super-Temp Company/USA Societe Europeenne de Propulsion/FRANCE Dunlop Ltd./ENGLAND
1973	Joint commercial venture was formed to design and manufacture aircraft brake systems based on 2-D CCC discs	Integrating brake design with materials development and manufacturing capabilities led to rapid improvements in performance, life, and costs	Goodyear Aerospace Corporation/USA HITCO/USA
1975	Joint commercial venture was formed to conduct CCC research, development, and manufacturing in France	Leading French systems and materials manufacturing organizations joined forces to accelerate the use of CCC materials in defense and commercial markets	Aerospatiale/FRANCE LeCarbone-Lorraine/FRANCE
1983/86	Automated 3-D fibrous preform weaving technology and equipment was transferred from France to a U.S. defense company	A manufacturing capability for 3-D fibrous preform assemblies was obtained in the U.S. after several unsuccessful domestic developmental programs	J. Brochier & Fils/FRANCE Textron Specialty Materials/USA
1984/85	Automated 3-D fibrous preform weaving technology and equipment was transferred from France to a U.S. defense company	A manufacturing capability for 3-D fibrous preform assemblies was obtained to enable the first U.S. defense company to manufacture 3-D CCC nozzle ITEs and other shapes	Aerospatiale/FRANCE Hercules Aerospace Company/USA
1985	Joint commercial venture was formed to manufacture 2-D CCC discs for aircraft brake systems	Newly-formed Carbone Industries was needed to accommodate the rapidly-expanding aircraft brake CCC disc markets	Societe Europeenne de Propulsion/FRANCE Alsthom/FRANCE
1985	Automated 3-D short fiber tape manufacturing technology and equipment were transferred for aircraft brake production	A low-cost, 3-D fibrous carbon preform manufacturing capability was transferred to a leading U.S. CCC brake disc manufacturer	Carbone Industries/FRANCE BFGoodrich Aerospace/Super-Temp/USA

TABLE 31 (Concluded)

CHRONOLOGY OF CCC JOINT VENTURES AND MANUFACTURING LICENSE TRANSFERS

YEAR	EVENT	IMPORTANCE	ORGANIZATION
1987	Automated 3-D short-fiber tape manufacturing technology and equipment were transferred for propulsion part manufacturing	A low-cost, 3-D fibrous carbon preform manufacturing capability was transferred to a leading U.S. CCC rocket propulsion part manufacturer	Societe Europeenne de Propulsion/FRANCE Kaiser Aerotech/USA
1988	CVI ceramic densification process technology was licensed to a U.S. commercial organization	A manufacturing capability was established in the U.S. for hybrid carbon and ceramic matrix composites	Societe Europeenne de Propulsion/FRANCE DuPont Lanxide/USA
1989	Domestic joint venture formed to design, analyze, fabricate, and test CCC and oxidation-resistant CCC materials and components	An integrated facility was established to provide a complete CCC capability for domestic customers	Hercules Aerospace Company/USA Rohr Industries, Inc./USA
1991	Silicon-nitride coating technology was licensed to a domestic commercial coater	Increased aerospace interest in silicon-carbide coated CCC components	United Technologies Research Center (Coating Developer)/USA Chromalloy Gas Turbine Company (Licensee)/USA
1992	Russian CCC distribution rights were awarded to a U.S. defense company	High-performance and many forms of CCC materials became available without restrictive government licenses	NiiGRAFIT/RUSSIA Kaiser Aerotech/USA
1993	Joint commercial venture was formed to design and manufacture aircraft brake systems based on 2-D and 3-D CCCs	Integrated aircraft brake system design with CCC manufacturing capabilities led to increased worldwide market share	Societe Europeenne de Propulsion/FRANCE Messier-Bugatti/FRANCE
1994	Joint commercial venture was formed to share technology and sell frictional CCC materials	Unique Russian frictional CCC technology and manufacturing may become available to a U.S. source for aircraft brake discs	NiiGRAFIT/RUSSIA Allied-Signal Aerospace Company/USA

4.7.9 Chronology

Although hundreds of CCC materials compositions and constructions were originated, only a smaller number of these composites have reached production status. In Table 32 the types of materials that were produced in significant quantities, shapes, and sizes are listed. Also given are the organizations responsible for these manufacturing milestones.

4.7.9.1 The 1960s

Small lot manufacturing facilities were established for CCC materials within a decade after their discovery. This rapid development was due to the great defense need for a high-temperature material with better structural and thermal shock resistance than polycrystalline graphites.

In the early 1960s manufacturing facilities were made available for the production of CVD/CVI pyrolytic graphite CCC composites. These facilities were already in existence for the manufacture of pyrolytic graphite in bulk or coating forms. Coating processes were easily adapted for porous CCC preforms instead of porous refractories, but uniform densification of thick porous parts proved to be a great manufacturing challenge.

In the mid-1960s the first commercial CCC materials were manufactured in the United States. All of the materials were rayon-based carbon fiber in discontinuous, woven fabric or chopped reinforcement forms. Resin char composites with intermediate densities were commercially available in plate, billet, rod, cylinder, and other shapes. These configurations were intended for final machining into the desired part configuration.

In the late 1960s 17 different U.S. organizations had entered the CCC materials development area, and three of them were capable of manufacturing significant quantities of materials. Unfortunately the production of CCC materials had to wait on extensive development and testing activities that were underway at that time. Most of the pre-production efforts centered on flat plate configurations for possible aircraft brake discs, 3-D reinforced billets for potential missile nosetip uses, and 2-D frusta for missile heatshield applications. In 1969 the first full-scale 2-D filament wound CVD PG CCC missile heatshield was manufactured and later successfully survived a simulated reentry thermal test. Uniformity of material and reproducibility of manufacturing were noted to be key issues.

TABLE 32
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1964	Numerous 2-D graphite (rayon-based) fabric/resin char CCC shapes and sizes were manufactured	World's first CCC production plant for 2-D graphite fabric/resin char prototypes	Carborundum Company/USA
1964/65	Manufacturing capabilities were demonstrated for CVD/CVI PG densification of fibrous preforms and porous 2-D graphite (rayon-based) fabric/ resin char CCC materials	World's first 2-D CCC production plants for CVD/CVI PG coating or infiltration of porous substrate prototypes	Super-Temp Company/USA HITCO/USA
1967	2-D graphite (rayon-based) fiber or fabric/ resin char CCC materials were produced in rod, billet, plate, cylinder, and other shapes	Three grades of 2-D CCCs became commercially available for evaluation and uses	Carborundum Company/USA
1967	2-D graphite (rayon-based) fabric and mascerated graphite fabric/resin char CCC materials were manufactured in large (9 in. diameter by 6 in. long) billets	Large CCC billets became commercially available for machining into desired shapes	Union Carbide Corporation/Carbon Products Division/USA
1969	Full-scale, 2-D filament-wound graphite (rayon-based) yarn/CVI PG CCC was manufactured in frustum form	First flightweight missile reentry vehicle 2-D CCC heatshield for ground-based testing	Atomic Energy Commission/Sandia Laboratories/USA
1969/73	Semiautomated manufacturing process was demonstrated for producing 3-D fibrous graphite (rayon-based) preforms in 4 in. by 4 in. by 8 in. billet sizes	3-D fibrous graphite preform production time was significantly reduced in time and costs	Avco Corporation/Systems Division/USA
1970	Full-scale, 3-D needled graphite (rayon-based) felt/CVI PG CCC frusta	First flightweight missile reentry vehicle 3-D CCC heatshield for ground-based testing	Atomic Energy Commission/Sandia Laboratories/USA
1970/75	Semiautomated manufacturing process was demonstrated for producing larger (6 in. by 6 in. by 18 in.) 3-D fibrous graphite (rayon-based) preforms	Larger fibrous graphite preforms became available and weaving times were reduced from 15 weeks to 2 weeks, and labor costs were reduced by 40%	Avco Corporation/Systems Division/USA

TABLE 32 (Continued)
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1972	Industrial HIPIC (10,000 psi) manufacturing process was established for densifying fibrous graphite preforms	First commercial HIPIC densification facility became operational for obtaining high-density CCCs	Fiber Materials, Inc./USA
1973	Manufacturing HIPIC (15,000 psi) process became available for densifying fibrous graphite preforms	Manufacturing densification facility became available for producing high-density, 3-D CCC materials	Battelle Columbus Laboratories/USA
1974	Full-scale, 3-D graphite (rayon-based) yarn/ resin char CCC was manufactured in frusta configuration	Alternate flightweight missile reentry vehicle 3-D CCC heatshield for ground-based testing	Avco Corporation/Systems Division/USA
1975	Large, thick-walled 3-D graphite (rayon-based) yarn/resin char CCCs were produced in cylindrical forms	State-of-the-art resin impregnation facilities were adequate for preform densification, but many cycles were needed to reach the desired density	Avco Corporation/Systems Division/USA
1975	Dedicated manufacturing facility for 2-D CVD CCC brake discs became operational	World's first operational CCC manufacturing facility for the production of aircraft brake discs	Dunlop, Ltd./ENGLAND
1975	Full-scale, 2-D graphite (rayon-based) resin char CCC circular discs were manufactured	First large-scale production of 2-D CCC discs for aircraft braking systems	HITCO/USA
1975	CCC manufacturing facilities became operational in Europe	French manufacturing facility was established in anticipation of future rocket motor, nosetip, brake, engine, and other applications	Societe Europeenne de Propulsion (SEP)/ FRANCE
1976/77	High-density, 3-D CCC cylindrical billets were manufactured in various outer diameters up to 18 in., lengths up to 14 in., and wall thicknesses up to 5 in.	Large and thick-walled CCC billets were needed for the inertial upper stage (IUS) and Navy C4 nozzle ITEs of solid propellant motors	Fiber Materials Inc./USA General Electric Company/Re-Entry and Environmental Systems Division/USA

TABLE 32 (Continued)
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1976	Dedicated manufacturing facility was established for densifying 4-D preforms with either HIPIC or LOPIC methods and over 200 nozzle parts with throat diameters up to 300 mm (11.8 in.) were produced	Full-size rectangular billets and cylindrical shapes became available for ground testing	Societe Europeenne de Propulsion (SEP)/ FRANCE
1976	Industrial HIPIC (15,000 psi) manufacturing process was established for densifying large fibrous graphite preforms	First U.S. industrial facility for preform densification at higher pressures	General Electric Company/Re-Entry and Environmental Systems Division/USA
1977	Most CCC manufacturing, equipment, and technology added to the International Trade-in-Arms Regulations (ITAR)	Critical CCC materials technology limited to qualified buyers and requestees	Department of State/Office of Munitions Control/USA
1978	High volume production processes were developed for 3-D pierced fabric and 3-D orthogonal CCC billets	A production readiness was demonstrated to support future strategic missile reentry nosetip manufacturing	Avco Corporation/Systems Division/USA Battelle Memorial Institute/USA General Electric Company/Re-Entry and Environmental Systems Division/USA Pfizer, Inc./USA
1978	Integrated CCC manufacturing plant became operational in France	First dedicated CCC production plant on the European continent	Societe Europeenne de Propulsion/ Propulsion a Poudre et Composites Division/FRANCE
1978/84	Over 1100 high-density, 3-D fine-weave pierced fabric CCC billets were manufactured with very few rejects	3-D CCC nosetips became operational for the first time on a U.S. strategic missile reentry vehicle (Mark 12A)	Textron Specialty Materials/USA
1979	Domestic manufacturing facility was expanded to annually produce about 43,600 kg (96,000 lb) of CCC products	High demand for 2-D CCC brake discs resulted in the largest CCC production facility in the world	HITCO/USA
1980	Manufacturing times were reduced to four months for large and thick 2-D CCC brake discs	Fewer brake discs had to be in-process at any one time and delivery times were improved	Dunlop Ltd./Aviation Division/USA

TABLE 32 (Continued)
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1980	Twenty domestic companies were manufacturing and developing CCC products and materials for U.S. consumption	A wide variety of CCC materials became commercially available for testing and applications	Various Sources/USA
1981/86	Over 1400 high-density, 3-D fine-weave pierced fabric CCC billets were manufactured with very few rejects	3-D CCC nosetips were retrofitted on the operational U.S. Minuteman strategic missile reentry Mark 12 vehicle	Textron Specialty Materials/USA
1982	Over 1150 kg (25,300 lb) of CCC materials were manufactured including 2000 nosetip billets and 130 rocket nozzle billets	Routine manufacturing processes were demonstrated for various fibrous preforms and shapes	General Electric Company/Re-Entry Systems Operations/USA
1984	Manufacturing, fabrication, processing, production, and quality assurance procedures were standardized in the U.S. for 2-D involute graphite (rayon-based) fabric/resin char-CVI PG CCC exit cones	Manufacturing specifications were revised and verified to reduce exit cone rejection rate and increase reliability	Aerojet Strategic Propulsion Company/ USA HITCO/USA Kaiser Aerotech/USA Haveg-Reinhold/USA
1984	Large and thick-walled ITE fibrous graphite preforms were produced in 15-30 weeks and densified in 10-25 weeks	Full-size 3-D ITEs were produced in shorter times and at lower costs for use in solid propellant motor nozzles	Various Manufacturers/USA
1985	Annual production of CCC brake discs was increased to 25,000 units	French manufacturer became the world's leading source for commercial aircraft CCC brake discs	Societe Europeenne de Propulsion/FRANCE
1986/87	Very large and thick-walled 3-D fibrous graphite preforms were automatically woven and densified into CCC billets	French automated preform weaving equipment was successfully demonstrated, and full-size parts became available for nozzle ITEs	Textron Specialty Materials/USA Hercules Aerospace Company/USA J. Brochier & Fils/FRANCE Aerospatiale/FRANCE
1987	Production facility was established for weaving 3-D fibrous preforms and densifying with CVD PG or HIPIC pitch coke matrices	First U.S. rocket motor manufacturer to produce its own nozzle CCC components	Hercules Aerospace Company/USA

TABLE 32 (Continued)
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1988	$50 million production plant became operational with an annual CCC capacity of 90,900 kg (200,000 lb)	Major domestic expansion of CCC production capacity to support the rapidly growing aircraft brake disc market	BFGoodrich Aerospace/Carbon Products-Pueblo/USA
1989	Over 770 silicon-carbide coated 2-D CCC wing panels, T-seals, nosecaps, nosecap seals, arrowheads, chin panels, chin panel seals, and shoe boxes were manufactured to date for U.S. shuttle orbiters	Each shuttle orbiter contained about 7,270 kg (16,000 lb) of coated CCC parts	LTV Aerospace and Defense Company/ USA
1989	Very heavy, large, and thick-walled CCC billet was manufactured	World's heaviest CCC part was machined into an ITE for the heavy lift, Ariane V solid propellant motor nozzle	Societe Europeenne de Propulsion/FRANCE
1990	Foreign CCC manufacturer increased annual production to 90,000-100,000 kg (198,000-220,000 lb)	A 30,000 CCC brake disc production capacity was needed to support anticipated commercial and military needs	Carbon Industries (SEP and Alstom)/ FRANCE
1990	Domestic leading manufacturer of 3-D CCC materials produced over 31,800 kg (70,000 lb) in a single year	The second largest domestic use for CCC materials was solid rocket motor components	Textron Specialty Materials/USA
1991	A very large (12 ft by 8 ft) silicon-carbide coated 2-D CCC structural panel was manufactured	Large structural parts were manufactured to support hypersonic flight vehicle needs; world's largest oxidation-protected structural panel was manufactured to support potential needs of hypersonic flight vehicles	BFGoodrich Aerospace/Super-Temp/USA
1991	Over 15,000 worn CCC discs were refurbished for continued use on aircraft brake systems	Cost-effective refurbishment method greatly reduced the cost-per-landing for CCC brake materials	Messier-Bugatti/ FRANCE

TABLE 32 (Concluded)
CHRONOLOGY OF CCC MATERIALS MANUFACTURING

YEAR	MANUFACTURING EVENTS	IMPORTANCE	ORGANIZATION
1991	1,000 scientists and 20,000 manufacturing engineers were made available for CCC contracted research, advanced technology and production of CCC and oxidation-resistant CCC materials	Wide variety of CCC materials were made available to world customers	NIIGrafit/RUSSIA NIIGrafit/Europa GmbH/GERMANY NIIGrafit USA Corporation/USA
1992	Three metric tons of 3-D carbon fiber tape/pitch coke CCC parts were manufactured in a single year	Large increase in the use of lower-cost, 3-D CCC materials in French solid rocket motor nozzles	Societe Europeenne de Propulsion/Propulsion a Poudre et Composites/FRANCE
1992	A very heavy (1820 kg, 4000 lb), large-diameter (2.4 m, 8.0 ft) and thick (0.18 m, 0.58 ft) 3-D CCC ITE was manufactured	World's largest 3-D CCC ITE for testing on the advanced solid propellant motor of the U.S. shuttle system	Textron Specialty Materials/USA
1994	Large-diameter (33 cm, 13 in) CCC brake disc was densified in about 8 hr	Fast and possible alternate densification method for producing aircraft brake discs	Textron Specialty Materials/USA
1994	Annual world production of CCC materials was estimated at about 230,000-450,000 kg (506,000-990,000 lb)	CCC materials are still specialty composites with a major outlet in aircraft brake systems	Various Sources/USA
1996	CCC annual consumption estimated at 1.14 Mkg (2.50 Mlb) CCC products estimated to be worth about U.S. $200M CCC annual growth rate was about 12%	Markets for CCC materials continued to expand Frictional applications continued to dominate CCC markets	The Huntex Report, Charleston, SC/USA

4.7.9.2 The 1970s

Extensive manufacturing technology and production efforts were undertaken in the 1970s, particularly in support of the aircraft brake disc, missile nosetip, and rocket nozzle applications.

Activities in the early 1970s centered on refinements of the CVI PG process for manufacturing CCC brake disc materials and scaling up 3-D CCC billets. Full-size aircraft brake discs were manufactured for the commercial Anglo-French aircraft Concorde and for the U.S. F-15 and B-1 military aircraft. CVD production equipment designs and technology, which were developed in the U.S., were transferred to England and France for subsequent CCC development work. With respect to 3-D CCC billet manufacturing, part sizes were scaled up to 15.2 x 15.2 x 45.7 cm (6 x 6 x 18 in). These sizes were adequate for full-size nosetips and some nozzle throats. Great progress was demonstrated in reducing manufacturing time (15 weeks to two weeks) and production costs (40 percent less) for 3-D pierced fabric preforms. Perhaps of greatest importance, however, was the first manufacturing demonstration of the High Pressure Infiltration/Carbonization (HIPIC) process for densification of fibrous carbon preforms. High-density 3-D CCC nosetip billets were produced by two different manufacturing organizations, including a commercial production house.

Additional manufacturing scale-up and productivity demonstrations were accomplished in the mid-1970s. 3-D CCC frusta configurations were scaled up to full-size missile heatshields. 2-D, 3-D, and 4-D CCC rocket nozzle throat sections were manufactured for full-scale motor nozzles. These large and thick cylindrical parts were manufactured with newly-developed low-pressure matrix infiltration/carbonization processes. Many densification cycles (nine or more) were needed to obtain high-density (1.95 g/cm^3, 0.070 lb/in^3) parts. HIPIC manufacturing processes were upgraded to higher pressure capabilities (103 MPa, 15,000 psi) and larger size fibrous carbon preforms. Alternate HIPIC manufacturing sources were also estahlished. Manufacturing methods were established for assembling 4-D preforms using precured rods. The process was labor intensive in that each reinforcement rod had to be handled and positioned in the assembly frame. Nevertheless, over 200 fibrous carbon preforms were manufactured and densified into CCC rocket nozzle parts, some with throat diameters up to 300 mm (11.8 in).

The key applications manufacturing programs during the late 1970s concerned 2-D CCC brake discs and 3-D CCC missile nosetips. A major CCC brake disc manufacturer expanded production capacity to about 44,000 kg (96,000 lb) per year to meet

anticipated demand. Production readiness of 3-D orthogonal-reinforced CCC billets was also accomplished with the aid of an integrated contractor team. Two manufacturing sources for each of the main production steps were qualified in anticipation of high volume manufacturing of Air Force Minuteman Mark 12A reentry vehicle nosetips. In follow-on orders, over 1,100 3-D pierced-fabric CCC billets were produced with only a few rejects. The production billet costs were only one-half of previous developmental billet costs. Similar high-density 3-D CCC billets reportedly were produced in France for their military programs. Meanwhile in the U.S. pyrolytic graphite and pyrolytic graphite/silicon carbide-coated graphite were being developed and evaluated for rocket nozzle throat applications. Test results were not promising, and for that reason the production of high-density, thick-walled 3-D cylindrically-reinforced CCC became of prime interest. Manufacturing methods were developed for this class of materials, and full-size articles became available for motor firing tests.

4.7.9.3 The 1980s

Manufacturing technology and production continued to grow in the 1980s. Additional companies established CCC manufacturing lines, and a few dedicated CCC manufacturing plants were established. CCC brake discs production expanded greatly, although manufacturing remained batch processing. Certain foreign manufacturing technology was licensed by various U.S. companies and used for lower cost and faster production of aircraft brake discs and rocket nozzle parts.

During the early 1980s 20 different U.S. organizations were involved in the development and manufacturing of CCC materials and parts. These companies included: (a) Acurex/Aerotherm Corporation, (b) Avco Corporation, (c) Atlantic Research Corporation, (d) Bendix Corporation, (e) BFGoodrich Aerospace/Super-Temp, (f) Carborundum Company, (g) Fiber Materials, Inc., (h) General Electric Company, (i) Great Lakes Carbon Company, (j) Haveg Industries, (k) Hercules Aerospace Company, (l) Hitco, (m) Kaiser Aerotech, (n) Lockheed Missile & Space Company, (o) McDonnell Douglas Astronautics Company, (p) Polycarbon, (q) Refractory Composites, (r) Science Applications, Inc., (s) TRW, Inc., and (t) Union Carbide Corporation. About half of these companies were engaged primarily in developing new and improved CCC materials, while the remainder of the companies were major manufacturers of materials and parts. The manufacturing processes being used were actually scaled-up laboratory processes, and up to this point only minor consideration was given to reducing the production time as well as the materials and part costs. One manufacturing assessment study on 3-D CCC rocket nozzle ITEs indicated that the major cost was preform weaving (53 percent) followed by fiber (20 percent), densification (18 percent), quality assurance

(six percent) and tooling (three percent). Automated processes were obviously needed to reduce both costs and time, but previous U.S. efforts on automated weaving of 3-D quartz cylindrical shapes were not successful. Quality parts could be woven at very slow speeds which made the process uneconomical. Higher rates of weaving were possible, but the fibrous preforms produced had wavy constructions. Meanwhile in France automated weaving machinery was being designed, patented, built, and demonstrated in a factory environment. These efforts were primarily at Brochier, SA and Aerospatiale. In the U.S. the highly successful 3-D fine-weave pierced-fabric CCC billet manufacturing program led to a second nosetip production program in support of retrofitting the operational Minuteman Mark 12 reentry vehicles with similar materials. During the following five years, over 1,400 3-D fine weave, orthogonal-reinforced CCC billets were manufactured. This program was uneventful in that only several rectangular billets were rejected as being outside the specification limits. At this point in time, it is interesting to note that one U.S. company had already manufactured over 25,000 pounds of high-performance CCC materials, including over 2,000 rectangular billets and 130 cylindrical configurations.

In the mid-1980s CCC materials for aircraft brake discs continued to be the major product form. Most of the disc manufacturing was being performed in France and the United States. The Societe Europeenne de Propulsion annual production of aircraft brake discs was about 25,000 units which made them the leading world producer for this type of product. SEP was also cited as being the world's second largest manufacturer of CCC materials. Automated weaving technology, which had been previously developed in France, was licensed to three different U.S. firms. Automated weaving equipment, which was designed and built by Brochier SA in France, was installed at Textron Specialty Materials. This equipment was intended to produce thin-to-thick wall fibrous graphite preforms for nozzle throats and exit cones. A technology transfer agreement dealing with automated weaving equipment was also finalized between Aerospatiale in France and Hercules Aerospace Company in the U. S. Later, Hercules Aerospace Company used the French-designed equipment to manufacture 3-D cylindrical preforms. The preforms were then densified by Hercules Aerospace Company, making them the first U.S. propulsion company to manufacture their own 3-D CCC materials. Thirdly, the SEP developed short-fiber 3-D preform weaving technology, which was originally created for nozzle exit cone composites, was licensed to BFGoodrich Aerospace for use in the manufacture of CCC brake discs intended for the North American market. Lastly, manufacturing capabilities were established in Asia for HIPIC densification of 3-D fibrous carbon preforms. Facilities were established in both the People's Republic of China and Taiwan.

Worldwide manufacturing of CCC materials and parts reached a peak in the late 1980s. In the U.S. there were at least seven major producers of CCC materials. All of the CCC brake manufacturers had completed a major expansion of their production facilities. In at least one case, a new CCC production plant was commissioned to fill the increased demand for aircraft brake discs. BFGoodrich Aerospace Carbon Products, for example, built a new facility having an annual capacity of about 90,900 kg (200,000 lb). CCC materials for solid propellant rocket nozzles also were in high demand for medium-to-large launch boosters. The world's heaviest CCC ITE was also built during this time period. SEP in France successfully manufactured a thick-walled and very large CCC ITE for the throat section of the new Ariane V solid propellant motor. Extensive manufacturing experience was also being gained in the area of oxidation-protected CCC materials. LTV Aerospace and Defense Company in the U.S. had accumulated over 20 years of production experience and fabricated over 700 large complex-shaped components for the space shuttle orbiter. This hardware collectively weighed over 7,300 kg (16,060 lb) and included: (a) 310 wing panels, (b) 310 wing T-seals, (c) 11 nosecaps, (d) 63 nosecap seals, (e) 33 arrowheads, (f) seven chin panels, and (g) seven chin panel seals. One-hundred seventy-five LTV people were working on CCC materials programs. Elsewhere, additional technology and marketing agreements were being promoted between various countries. A French and a U.S. company agreed to jointly develop and market CCC brake systems for the French Airbus A330/A340/A321 commercial transports. The French manufacturing firm for "Novoltex-TM" fibrous carbon preforms granted a license to a U.S. aerospace company for the production of similar materials which were to be used in CCC nozzle parts. The French company also issued an exclusive license to a U.S. firm for the manufacture of hybrid (carbon-ceramic) composite materials. These oxidation-protection composites were intended for both commercial and defense markets.

4.7.9.4 The 1990s

Volume production of CCC materials remained high during the early 1990s. Annual production was estimated at between 0.23 Mkg (0.51 Mlb) and 0.45 Mkg (0.99 Mlb). Closer estimates were not possible due to the proprietary and competitive nature of the business. The projected annual growth rate in this business sector was about 10X. CCC brake discs production for commercial aircraft remained strong, but there was a significant decline in brake disc production for military aircraft. Production of CCC materials for all other defense applications, including nosetips and nozzles, fell rapidly as current system contracts were completed. Facilities dedicated to the production of CCC materials for military uses have either been "mothballed" or are greatly under-utilized. Industrial and commercial uses for CCC

materials have slowly increased, but not a single new use was established for high-volume production. It appears that these high-volume commercial outlets will await the successful development of next generation "lower-cost" CCC materials.

By the mid-1990s the world (not including the FSU) production of CCC materials increased substantially. The annual growth rate was estimated to be about 12-14 percent. The major product form continued to be flat disc rotors and stators for aircraft brake systems. About 90-95 percent of the total CCC market was dedicated to commercial and military aircraft brake systems. In France alone, over 28,000 aircraft brake discs were being produced on an annual basis. The major fabricators of aircraft CCC brake systems were: (a) BFGoodrich Aerospace-Pueblo, CO, (b) Messier-Bugatti-Paris, France, (c) Allied Signal Aerospace-South Bend, IN, (d) Dunlop Aerospace-Coventry, England, and (e) Aircraft Braking Systems-Akron, OH. Some of these brake manufacturers purchased their CCC rotors and stators from outside sources, like the BP Chemicals (Hitco) Inc., Carbone Industries, and Societe Europeenne de Propulsion.

One of the significant manufacturing demonstration programs during the early 1990s involved the production of a very large CCC ITE prototype for the U.S. NASA Advanced Solid Propellant Rocket (ASRM) program. Previous throat sections for the U.S. Space Shuttle solid propellant motor boosters were composed of ablative plastic thermal protection materials. The new CCC ITE was a high-density, autowoven 3-D reinforced composite with a 2.44 m (8-ft) outer diameter and a weight of about 1,820 kg (4,004 lb). This was the largest CCC prototype manufactured in the world. Unfortunately NASA later chose to use an ablative plastic throat section. Subsequently, the ASRM program was cancelled.

The manufacture of 2-D, 3-D, and 4-D CCC materials has matured greatly during the past two decades. One U.S. company, for example, has manufactured tens of thousands of CCC components during the past two decades. With this type of experience, one would be tempted to assume that all or most of the manufacturing parameters are well understood and the processes are highly controlled. This situation does not seem to be the case. For nonprotected CCC materials used in a thermal protection mode, the property variability does not have much importance because the intrinsic materials properties are usually greatly in excess of what is needed. For structural applications the limiting mechanical properties (usually matrix dominated) play a dominant role in part design. Hence, property variability may greatly influence material acceptance and performance. This is particularly true for both noncoated and oxidation-protected CCC materials. To alleviate this situation a scientific CCC manufacturing approach is being developed in the United States. Great progress has been made in understanding the critical

parameters that control properties of the composite precursor. Advanced sensor technology has been applied to the individual process steps, and vital information on temperature, time, pressure, chemistry, etc. have been obtained and are being used in a timely manner to alter the ongoing materials processing. The end objective of this work is to make composite fabrication faster, smarter, more automatic, less labor-intensive, and above all cheaper. Yet all this new technology will be for naught unless it is fully utilized in manufacturing plants to achieve highly-reproducible materials having predetermined composite properties.

4.8 PROTOTYPES

Over 125 different types of prototypes have been fabricated with CCC materials and successfully evaluated for (a) defense, (b) aerospace, (c) industrial, (d) nuclear, (e) scientific, (f) nuclear, and (g) other potential applications.

A chronology of the major CCC components for various systems is presented in Table 33. Each prototype is described in terms of its (a) year of accomplishment, (b) ultimate application, (c) general material description, and (d) organization responsible for fabricating the item.

4.8.1 Approach

CCC components are generally prototyped when there are favorable performance (material properties and characteristics), economic, production, and life-cycle factors. Performance aspects are typically the most important consideration for military systems, but other factors mentioned are becoming more significant. Economic and life-cycle considerations are usually the most important parameters for nondefense uses.

The first step in a prototype design is to define the fiber and reinforcement complexity which is best suited for the intended component. The designer then defines the service environmental parameters and the complexity of the stress states which are to be carried by the material. The next and very important step is to work with materials producers to develop a suitable processing approach for manufacturing the material of choice.

The composition and construction of a material to be used must be defined, as noted. In general 2-D CCC materials are suitable when the loading is primarily in one plane, and the attachment loads are not significant. Naturally the loads are to be carried primarily in-plane or parallel to the structural fiber direction. 3-D CCC materials are a more appropriate choice when the loading is complicated or the part is relatively thick (like a nozzle ITE). Composites containing fibrous reinforcements in three or more directions are better able to carry complex

TABLE 33
PIONEERING AND OPERATIONAL CCC PROTOTYPES

YEAR	PROTOTYPE	APPLICATION	MATERIAL	ORGANIZATION
1962	Exit cone	Solid rocket motor nozzle	2-D involute graphite fabric/resin char CCC	HITCO/USA
1963	Throat	Solid rocket motor nozzle	2-D tapewrapped graphite fabric/ resin char CCC	HITCO/USA
1964	Thrust chamber	Liquid propellant space engine	2-D tapewrapped graphite fabric/ resin char CCC	San Rafael Plastics/USA
1966	Heatshield	Strategic missile reentry vehicle	2-D filament-wound graphite yarn/CVI pyrolytic graphite CCC	Super-Temp Company/USA
1966	Protective thermal shield	Apollo spacecraft optical telescope	2-D graphite fabric/resin char CCC	LTV Aerospace Company/USA
1967	Hot pressing dies	Ceramic parts	2-D graphite fabric/resin char CCC	Carborundum Company/USA
1968	Frictional discs	Aircraft brake system	2-D graphite fabric/resin char CCC	Carborundum Company/USA
1968	Nosetip	Strategic missile reentry vehicle	3-D short-fiber needled graphite felt/CVI pyrolytic graphite CCC	Super-Temp Company/USA
1968	Canister	Space radioisotope thermoelectric power	2-D graphite fabric/resin char CCC	HITCO/USA
1968	Furnace elements	Heater rods, shelves, heatshields, and trays	2-D graphite tow/resin char CCC	Carborundum Company/USA
1971	High-temperature insulation	Vacuum/inert gas furnaces	2-D chopped graphite fiber/resin char CCC	Union Carbide Corporation/Oak Ridge Y-12 Plant/USA
1971	Nosecap, leading edges, and seals	Space shuttle earth orbiter flight vehicle	Silicon-carbide coated 2-D carbon fabric/oxidation-inhibited resin char CCC	LTV Aerospace Corporation/USA
1974	Nosetip	Strategic missile reentry vehicle	3-D continuous filament graphite tow and fabric/HIPIC pitch coke CCC	Avco Corporation/Systems Division/USA

TABLE 33 (Continued)
PIONEERING AND OPERATIONAL CCC PROTOTYPES

YEAR	PROTOTYPE	APPLICATION	MATERIAL	ORGANIZATION
1974	Integral throat-entrance section	Solid rocket motor nozzle	3-D orthogonal graphite yarn/HIPIC pitch coke CCC	Avco Corporation/Systems Division/USA
1978	Flaps, seals, and liners	Turbine engine	Silicon-carbide coated 2-D carbon fabric/oxidation-inhibited resin char CCC	Vought Corporation/USA
1980	Molten glass transfer parts	Glass manufacturing	2-D carbon fabric/CVI pyrolytic graphite CCC	Kaiser Aerotech/USA
1980	Frictional discs	Racing car brakes	2-D carbon fabric/CVI pyrolytic graphite CCC	HITCO/USA
1984	Nozzle extension skirt	Liquid propellant engine	Silicon-carbide coated 2-D carbon fabric/oxidation-inhibited resin char CCC	HITCO/USA
1985	Superplastic metal-forming parts	Aircraft titanium components	2-D carbon fabric/resin char CCC	Sigri GmbH/GERMANY
1986	Frictional clutches	Racing cars	2-D graphite fabric/CVI pyrolytic graphite CCC	BP Chemicals (HITCO) Inc./USA
1988	Boats, crucibles, trays, and tubes	Semiconductor manufacturing components	2-D graphite fabric/CVI pyrolytic graphite CCC	BFGoodrich Aerospace/Super-Temp/USA
1988	Antenna parabolic reflector	Satellite component	2-D carbon fabric/CVI pyrolytic graphite CCC	BP Chemicals (HITCO) Inc./USA
1988	High-temperature structural panels	Aircraft structures	Silicon-carbide coated 2-D carbon (PAN-based) fabric/CVI pyrolytic graphite CCC	BFGoodrich Aerospace/Super-Temp/USA
1988	Piston	Small gas engine	Silicon-nitride coated 4-D carbon tow/HIPIC pitch coke CCC	Fiber Materials, Inc./USA United Technologies Research Center/USA
1989	Limiter, diverter, and container walls	Fusion power reactor	3-D and 4-D graphite (pitch-based) tow/pitch coke CCC	BFGoodrich Aerospace/Super-Temp/USA Fiber Materials, Inc./USA

TABLE 33 (Concluded)

PIONEERING AND OPERATIONAL CCC PROTOTYPES

YEAR	PROTOTYPE	APPLICATION	MATERIAL	ORGANIZATION
1989	Wingbox structure	Hypersonic boost glide flight vehicle component	Silicon-carbide coated 2-D carbon fabric/oxidation-inhibited resin char CCC	Kaiser Aerotech/USA Chromalloy American Company/ USA
1990	Integral fin-heat pipe	Satellite radiator	2-D graphite (pitch-based) fabric/ CVI pyrolytic graphite CCC	Rockwell International Corporation/Rocketdyne Division/ USA
1990	High-temperature rib-stiffened structural panels	Hypersonic flight vehicle components	Silicon-carbide coated unidirectionally-reinforced graphite fabric/CVI pyrolytic graphite CCC	BFGoodrich Aerospace/Super-Temp/USA

loads. The disadvantages of these multiaxial woven materials are high material costs and a reduction of in-plane properties in order to add fibers in other directions. Thus material selection is a very important part of designing and applying CCC materials to new applications.

4.8.2 Service Conditions

A variety of CCC materials are needed to accommodate the great diversity of environmental conditions which are noted in Table 34. Some of the applications involve a single mission, like a rocket nozzle. Other applications involve reuse capability, like aircraft brake discs. Operating temperatures range from the cold regimes of space to many thousands of degrees characteristic of missile reentry nosetips. Peak operating temperatures are often twice as high as routine service temperatures, but in general CCC materials easily accommodate these thermal excursions. The total hot lifetime of CCC components also varies over great ranges. Strategic ballistic reentry vehicle nosetips are intensely heated for less than a minute, but the surface temperature changes constantly as the vehicle velocity, altitude, and pressure also change. Component stresses induced by thermal and mechanical considerations also vary greatly. Nevertheless the high-temperature structural properties of CCC materials will generally withstand these forces. For the most part CCC materials operate in a vacuum, high-temperature air, or hot combustion gaseous environments. Short times in hot air can be tolerated without significant ablation or loss of structural properties, like in a missile nosetip. Longer air exposures at high temperatures require the use of an oxidation protective scheme.

4.8.3 Properties Dictate Uses

Unique CCC properties or combination of properties will dictate their application outlets. Table 35 gives a variety of CCC uses that advantageously use intrinsic properties. Most of the applications cited utilize the high-temperature structural properties of the materials, together with one or more other key composite characteristics. For example, aircraft brake discs are highly dependent upon the thermal dissipation properties of CCC materials along with their relatively unique frictional characteristics.

4.8.4 Structural and Nonstructural Uses

The applications of CCC materials generally falls into two categories, i.e. (a) nonstructural or low-stressed components and (b) structural or load-bearing components. Nonstructural CCC materials have been developed for over 30 years, and they are relatively mature. Such materials have been used in a variety of current applications, including (a) aircraft brakes, (b) thermal protection parts, (c) rocket nozzle throats, and (d) other commercial uses.

TABLE 34
TYPICAL SERVICE ENVIRONMENTS OF CCC APPLICATIONS

Application	Number of Heating Cycles	Typical Operating Surface Temperature, °C (°F)	Peak Operating Surface Temperature, °C (°F)	Total Hot Lifetime, h	Service Pressure, MPa (atm)	Environment
Commercial aircraft brake disc	3,000	1,650 (3,002)	3,000 (5,432)	30	0.1 (1.0)	air
Large solid propellant rocket nozzle throat	1	3,200 (5,792)	3,480 (6,296)	0.02	10.1 (100)	combustion gases
Strategic missile reentry vehicle nosetip	1	variable	6,600 (11,912)	0.01	12.2 (120)	air
Orbital entry flight vehicle nosecap	100	1,500 (2,732)	1,650 (3,002)	50-100	<0.1 (<1.0)	air
Spacecraft liquid propellant thrust chamber	1,000	1,650 (3,002)	1,925 (3,497)	15	7.1 (70)	combustion gases
Hypersonic flight vehicle control surface	50	1,650 (3,002)	1,650 (3,002)	200	<0.1 (<1.0)	air
Turbine engine flap	500	1,035 (1,895)	1,375 (2,507)	2,000-4,000	1.0 (10)	combustion gases
Spacecraft radiator	10,000	80 (176)	232 (450)	87,000-131,000	0.0	vacuum

TABLE 35
CCC MATERIAL ATTRIBUTES ENABLED UNIQUE APPLICATIONS

ATTRIBUTES	*APPLICATIONS*
• COEFFICIENT OF FRICTION	• Aircraft Brake Discs • High-Speed Motorcycle Brakes • Racing Car Rotors and Clutch Plates • High-Temperature Bearings
• ABLATION/EROSION RESISTANCE	• Rocket Nozzle Throats and Exit Cones • Reentry Missile Nosetips • Shuttle Orbiter Nosecap and Wing Leading Edges • Planetary Entry Vehicle Shields
• THERMAL CONDUCTIVITY	• Thermal Radiators and Heat Pipes • High-Temperature Insulation • Furnace Heating Elements and Trays
• DIMENSIONAL STABILITY	• Spacecraft Structures • Hot Pressing Dies • High-Temperature Tooling • Radio Frequency and Optical Mirrors
• CHEMICAL INERTNESS	• Turbine Engine Parts • Liquid Propellant Thrust Chambers • Medical Prostheses and Bone Implants • Foundry Molds • Molten Glass Troughs • Battery Containers

TABLE 35 (Concluded)

CCC MATERIAL ATTRIBUTES ENABLED UNIQUE APPLICATIONS

ATTRIBUTES	*APPLICATIONS*
• FRACTURE TOUGHNESS	• Space Thermoelectric Generator Containers
• THERMAL STABILITY	• Heat Barriers
• NUCLEAR RADIATION RESISTANCE	• Plasma Shields • X-ray Absorber Shields
• FATIGUE RESISTANCE	• Springs
• ELECTRICAL CONDUCTIVITY	• Specialty Electrodes • Heater Elements • Space Antennas

Structural applications, for the most part, are less developed and used. They are generally unsupported and must carry the primary structural or thermostructural loads. Several examples of structural CCC applications include (a) rocket nozzle exit cone, (b) turbine engine parts, (c) liquid propellant engine thrust chambers, (d) aerospace vehicle structures, (e) satellite structures, (f) hip replacement parts, and (g) others. Most of the current CCC prototype design, evaluation, and test activities are centered on structural applications. Successful demonstrations with these prototype parts will greatly enhance future application prospects and a larger CCC materials market.

4.8.5 Frictional Components

Brake linings and clutch facings are common frictional materials used in the transportation industry. Brakes convert the kinetic energy of a moving vehicle or machine part into heat, absorb the heat, and then slowly dissipate it into the surrounding atmosphere. A brake is a sliding friction couple which consists of a rotor (disc or drum) connected to the wheel or machine and a stator on which is mounted the friction material. The friction material is the expendable portion of the brake couple, and over a period of time it is reduced to wear debris and pyrolytic gases. Clutches transfer the kinetic energy of a rotating crankshaft (coupled to a power source) to the transmission and wheels during the engagement process. Hence, the clutch is essentially a static friction couple that momentarily slides during gear shifts or other engagements. Like in brake designs, the clutch friction material facing is expendable during use. Brakes and clutches operate in both dry and wet environments depending upon system design. In dry friction applications like an aircraft brake, heat is removed by surrounding air and by the heat sink capability of the adjacent structural members.

CCC materials have many features that lend themselves to uses in brake and clutch systems of high-performance or heavy mass vehicles. Some of these composite characteristics include (a) near-constant coefficient of friction (COF), (b) high specific heat, (c) nonmelting, (d) high thermal conductivity, (e) high thermal stability, (f) low thermal expansion coefficient, (g) thermal shock resistance, (h) ease of machining, and (i) nontoxic. Static and dynamic friction coefficients are attractive at ambient temperatures, and they remain relatively constant at elevated temperatures. The COF of a state-of-the-art CCC material is about 0.15-0.20 at 50°C (122°F), rises to about 0.45-0.50 at about 60°C (140°F), decreases to about 0.35 at 250°C (482°F), and then remains relatively constant at higher temperatures. This material feature is very important because it eliminates braking fade with constant foot pedal pressure. CCC materials maintain their frictional characteristics to much higher temperatures than competitive cermet materials, thus providing added safety and reduced brake overhaul. Thermal properties of the CCC materials are

also of equal importance because a very large amount of energy must be absorbed and dissipated over a short period of time. Thermophysical properties of importance include (a) specific heat, (b) thermal conductivity, and (c) density. The specific heat values of CCC materials are several times that of competitive materials at room temperature, and when coupled with their thermal stability at very high temperatures, enormous amounts of thermal energy can be contained in the material without melting or appreciable degradation. The thermal conductivity of CCC materials varies with material composition and direction. Directional control of the reinforcing fibers generally provides high heat transfer parallel to the fibers and a lower mass temperature. Controlled CCC brake disc temperature is very important because oxidative losses may be excessive at high temperatures. Other material thermal properties like melting point and thermal shock resistance are also important. CCC materials also have anisotropic thermal expansion coefficients, but in general the values are low which lend themselves to high dimensional stability during heating. Another thermophysical property of great importance is the low material mass density. This particular material property has enabled large weight savings in aircraft brake systems. Up to 450-680 kg (990-1500 lb) of aircraft weight savings has been realized in large military and commercial liners. Somewhat lower but important weight savings have been demonstrated in medium-size and high-performance military aircraft. For a commercial aircraft, weight savings provided by CCC brake discs have enabled millions of dollars in fuel savings over the lifetime of the transport. CCC materials do not melt like competitive metallic or cermet materials. Material structural properties are also important to preserve the functional use of brake systems. CCC materials have high and directional strength and stiffness properties. They exhibit these structural properties at high temperatures but, except for rejected aircraft braking conditions, the temperature of CCC frictional materials is maintained below their oxidative temperature limitation. For repeated excursions to high temperatures during braking, oxidation protection is provided to the materials. This is accomplished by applying a penetrant that blocks active oxidation sites or by the use of an oxygen barrier coating that prevents diffusion of oxygen to the carbonaceous surface. Hence, thermal control of the CCC frictional material greatly increases the wear resistance.

The major limitations of CCC materials for frictional applications has been high initial costs and long delivery times. While initial material delivery costs are several times that of competitive materials, their long life (low wear rate) makes them cost effective when viewing life-cycle costs. In Table 36 the properties of heavy-duty braking materials are listed. Note the many property advantages of CCC materials for frictional applications.

TABLE 36
PROPERTIES OF AIRCRAFT BRAKE MATERIALS

Properties/Characteristics	CCC Materials	Steel	Beryllium
Friction Coefficient	0.17-0.50	0.60	-
Density, g/cm^3 (lb/in^3)	1.70-1.85 (0.061-0.067)	8.0 (0.29)	1.85 (0.067)
Specific Heat, 25°C (77°F) J/g·K (Btu/lb·°F)	0.62-0.75 (0.15-0.18)	0.59 (0.14)	1.93 (0.46)
Thermal Conductivity, W/m·K (Btu/ft·h·°F)	30-100 (17-58)	59 (34)	151 (87)
Linear Expansion Coefficient, ppm/°C (ppm/°F)	0.3-10.0 (0.17-5.6)	14.0 (7.8)	11.5 (6.4)
Thermal Shock Resistance	Excellent	Acceptable	Good
Tensile Strength, MPa (ksi)	48-234 (7-34)	414 (60)	483 (70)
Tensile Modulus, GPa (Msi)	20-110 (2.9-16)	193 (28)	303 (44)
Elongation, %	0.3-0.6	30	3-6
Costs, $/kg ($/lb)	110-220 (50-100)	22 (10)	880-1320 (400-600)
Maximum Use Temperature, °C (°F)	2200 (3992)	1200 (2192)	980 (1796)

CCC materials have been prototyped for a variety of frictional components as noted in Table 37. These applications have included (a) commercial, military, and aerospace vehicle applications, (b) helicopter braking systems, (c) high-performance racing car brake and clutch systems, (d) luxury car and truck braking systems, and (e) very high-speed train emergency braking units. New frictional uses are anticipated, with most of the outlets in the wet lubrication fields.

The aircraft brake acts like a multiplate clutch system. The actual brake unit consists of multiple discs of rotors sandwiched between stators. The entire rotor and stator assembly function as a frictional unit, whereas previous designs used only a portion of the available frictional surface in the form of pads. The rotor discs are driven by the wheel, and the stators are held stationary by the brake structure. Stopping the aircraft at high speeds is accomplished by pressing the discs together with hydraulic pressure. In the process the kinetic energy of the braking components is converted to thermal energy through friction. Heat is initially concentrated on the brake disc surface, and the temperature may reach several thousands of degrees. Over time, the thermal energy is conducted into the CCC mass and radiated from the brake surfaces. For illustrative purposes consider the case of a U.S. Boeing 767 commercial aircraft weighing about 170,000 kg (374,000 lb) and moving at 320 km/h (199 mph) is about 670 MJ (494 Mft-lb). The kinetic energy of this aircraft takeoff speed is equivalent to about 2000 automobiles moving at highway speeds. Yet in spite of these severe wear conditions, the average erosion rate for a single aircraft landing (one high-speed landing and several low-speed taxing stops) is only on the order of 10-15 nm per meter of interfacial sliding. Most of the wear occurs during the low-temperature taxi stoppings. In rare instances the aircraft has to be stopped in a refused (rejected) takeoff mode. State-of-the-art metallic and cermet frictional materials may warp or melt under these thermal conditions, thus requiring a long delay and brake system overhaul. CCC brake discs have been known to experience similar and even more severe emergency braking conditions with minor wear and no significant damage. CCC brake discs have provided absolute safe braking under all conditions.

Virtually all high-performance military aircraft, and most of the medium-to-large commercial aircraft, use CCC structural brake systems. Military and commercial aircraft that have used CCC brake systems are listed in Tables 38 and 39. The year in which the CCC brake discs were prototyped and manufactured is also given. In most cases the full-size brake discs were ground and flight tested within several years for the respective aircraft. In virtually every case the CCC structural/frictional materials have proven to be superior to state-of-the-art brake designs employing cermet frictional materials and either steel or beryllium structural materials.

TABLE 37
PROTOTYPES OF FRICTIONAL CCC MATERIALS

YEAR	PROTOTYPE	ORGANIZATION
1968	Commercial aircraft brake discs	Goodyear Aerospace Corporation/USA
1968	High-temperature, nonlubricated frictional bearings	Carborundum Company/USA
1970	Military aircraft brake discs	Goodyear Aerospace Corporation/USA Carborundum Company/USA
1972	Shuttle orbiter vehicle brake discs	Super-Temp Corporation/USA
1979	Helicopter brake discs	BFGoodrich Aerospace/USA
1980	Racing car brake discs	HITCO/USA
1986	Racing car clutches	HITCO/USA
1988	Luxury car brake pads	Daimler-Benz AG/GERMANY Schunk & Ebe/GERMANY
1990	High-speed train emergency brake	Kobe Steel, Ltd./JAPAN Japan Railway Technical Research Institute/JAPAN
1990	Wet (lubricated) frictional parts	BFGoodrich Aerospace/Super-Temp/USA

TABLE 38

MILITARY AIRCRAFT BRAKE SYSTEMS USING FRICTIONAL CCC MATERIALS

YEAR	AIRCRAFT	COUNTRY
1970	F-15	U.S.
1971	B-1	U.S.
1974	AV-8A	U.K.
1974	AV-16A	U.K.
1975	F-16	U.S.
1978	F-18	U.S.
1978	Mirage 2000	FRANCE
1979	F-4 Retrofit	U.S.
1982	B-1B	U.S.
1984	C-5B	U.S.
1984	JAS 39	SWEDEN
1985	Mirage F1	FRANCE
1986	AMX	BRAZIL/ITALY
1987	C-5A Retrofit	U.S.
1989	V-22	U.S.
1989	C-17	U.S.
1990	J-7M	PEOPLE'S REPUBLIC OF CHINA (PRC)
1990	Grumman X-29A	U.S.
1991	F-117A	U.S.
-	Tupolev TU-160	RUSSIA
-	Sukhoi SU-25	RUSSIA

TABLE 39

COMMERCIAL AIRCRAFT BRAKE SYSTEMS USING FRICTIONAL CCC MATERIALS

YEAR	AIRCRAFT	COUNTRY
1970	Concorde	U.K. & FRANCE
1973	Super VC-10	U.K.
1978	Canadair Challenger CL 600	CANADA
1978	Gulfstream III	U.S.
1980	Gulfstream American G-11B	U.S.
1980	BAe 146	U.K.
1982	Boeing 757	U.S.
1982	Airbus 300	FRANCE
1983	Saab Fairchild 340	SWEDEN
1984	Boeing 767-300	U.S.
1984	Lear Fan 2100	U.S.
1984	A310-200 Retrofit	FRANCE
1984	Airbus A-310-300	FRANCE
1984	Dassault-Brequet Falcon 900	FRANCE
1984	Fokker 100	THE NETHERLANDS
1985	Gulfstream IV	U.S.
1986	Boeing 747-400	U.S.
1987	Airbus A-320	FRANCE
1987	Dornier 228	GERMANY
1988	McDAC MD-11	U.S.
1989	Boeing 737-500	U.S.
1989	Space Shuttle Orbiter	U.S.
1989	Airbus A-330	FRANCE
1989	Airbus A-340	FRANCE
1990	Airbus A-300-600	FRANCE

TABLE 39 (Concluded)

COMMERCIAL AIRCRAFT BRAKE SYSTEMS USING FRICTIONAL CCC MATERIALS

YEAR	AIRCRAFT	COUNTRY
1990	Airbus A-321	FRANCE
1991	Boeing 777	U.S.
1992	McDAC MD-90	U.S.
1995	Airbus A-319	FRANCE
-	Beechcraft 2000	U.S.
-	BAe 146	U.K.
-	Aeritalia/Aerospatiale ATR 72	ITALY & U.K.
-	Dassault Aviation Falcon 2000	FRANCE
-	Saab 340B	SWEDEN
-	Antonov AN-225	UKRAINE
-	Antonov AN-124	UKRAINE
-	Antonov AN-70	UKRAINE
-	Antonov AN-325	UKRAINE
-	Ilyushin IL-96	RUSSIA
-	Tupolev TU-204	RUSSIA

High-performance, safety and life-cycle costs have been the major systems improvements. To summarize, aircraft brake materials have evolved over the past 50 years of flight. Brakes of 1940 vintage aircraft used organic frictional lining materials. In 1949 metal-ceramic composite (cermet) brake lining materials of high thermal stability and high density became the mainstay of the aircraft brake industry. About 1500 aircraft landings between overhauling the brake system was about the performance expected. CCC materials have emerged as the third-generation material for aircraft brake systems. Unlike previous frictional materials and attached structural elements, the CCC materials have been able to serve the dual function of frictional and structural elements. The CCC brake materials have a heat storage capacity about 2.5-3.0 times that of steel and strength properties about twice those of steel at elevated temperatures. The low intrinsic density of CCC materials has provided large (up to 40 percent) weight savings, and the materials have been used with absolute safety.

In another high-performance frictional application, CCC materials have been a viable product for usage as pads on automotive vehicles. The materials have the desired thermal, structural, density, and frictional properties preferred for high-performance racing cars. Virtually every Formula One race car uses CCC brake material, and some of them use CCC materials for clutches. With proper design and material selection, CCC clutches have outlasted competitive materials by several times. Past clutch applications have been for high-performance vehicle uses, but continued material improvements and evaluations will enable new uses in heavy-to-medium duty trucks, off-road vehicles, sports and luxury cars, ultrahigh speed trains, possibly tanks, and other critical applications. The key to future frictional uses appears to center on a better understanding of the material composition:construction:property:performance relationships coupled with the development of lower-cost materials.

The future market for CCC clutches will not be as large as for CCC brakes. The clutch market in Formula One racing cars was created solely on a weight-reduction basis, and because there are few racing cars, the volume production to satisfy this market will be limited. Only the Indianapolis or "cart" and the Formula One racing cars have enough weight-related considerations and cash flow to use CCC clutches. CCC clutch installations cost about $3,000-$6,000 per racing car installation.

4.8.5.1 Chronology

Graphite is a self-lubricating material of high thermal stability. It was only natural then that consideration was given in 1966 to using newly-available CCC materials for aircraft braking systems. Materials available at that time were 2-D composites based on either

pyrolyzed resin or pyrolytic carbon matrices. Resin-based CCC composites had low densities and low strength. Pyrolytic carbon-based CCC composites had higher densities, but they were difficult to manufacture in thick sections and contained density gradients. Since that time, however, much progress has been made in material improvements including (a) higher density composites, (b) near-constant coefficient of friction materials for both dry and wet service environments, (c) lower wear rates, (d) stronger and stiffer materials, (e) more uniform densities through thick composites, (f) greatly reduced costs, and (g) faster production runs.

The chronology of frictional CCC components from their conception in the 1960s to the present time is given in Table 40.

4.8.5.1.1 *The 1960s*

Frictional uses for CCC materials originated in the mid-1960s. Perhaps the first concept involved aircraft braking systems, but in any event this application outlet appeared highly promising because of the balance of material properties. Within two years of concept definition, a U.S. manufacturer of aircraft brake systems prototyped 2-D CCC brake discs and successfully flew them on a commercial aircraft. This event, needless to say, was of exceptional importance and provided the rationale for (a) exploring new brake designs, (b) material upgrading, and (c) prototype fabrication and evaluation. Candidate frictional materials were supplied by various domestic vendors and then evaluated by aircraft brake system companies. All of the work was highly proprietary and controlled by the aircraft brake companies. U.S. Government-funded research and development in this area was essentially nonexistent and has remained so throughout the history of aircraft brake systems.

4.8.5.1.2 *The 1970s*

Exciting developments took place in aircraft brake materials during the early 1970s. Four or more domestic aircraft brake manufacturers were evaluating materials and attempting to identify what constituted a "good" structural brake disc. Full-size aircraft brake discs were fabricated with state-of-the-art CCC materials and successfully tested on the Anglo-French Concorde supersonic commercial aircraft, the U.S. shuttle orbiter vehicle, military B-1 and F-111 bombers, and the high-performance military F-15 aircraft. Material performance was very impressive, despite the quality of the composites. Up to about one million foot-pounds of energy were dissipated by the CCC brake discs during aircraft deceleration. The low-density materials permitted large aircraft weight savings. Weight reductions ranged from about 1000 to 1400 pounds for a large aircraft to about 150 pounds for smaller military fighters.

TABLE 40
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1962	Developmental work initiated on pyrolytic graphite matrix CCC materials for frictional uses	Potential military and commercial markets for CCC materials	Super-Temp Company/USA
1966	Concept originated for using CCC materials for aircraft braking systems	Potential, high-volume military and civilian markets for CCC materials	Goodyear Aerospace Corporation/USA
1968	2-D CCC brake discs tested on a commercial Beech Debonaire aircraft	First flight demonstration of CCC brake discs for a commercial aircraft	Goodyear Aerospace Corporation/USA
1970	High-density CVD PG/resin char CCC fabricated for large commercial airplane transport brake system	First full-size CCC brake discs for the Anglo-French Concorde supersonic aircraft CCC brake discs provided about 1200 lb savings compared to state-of-the-art materials	Super-Temp Company/USA
1970	2-D resin char CCC brake discs were baselined for the U.S. military F-15 fighter	Contract awarded to develop CCC brake disc prototypes First production military aircraft to use CCC brake discs CCC frictional materials were expected to cost about $150-200/lb Cost of CCC brake landing was estimated to cost about $100 per landing	Goodyear Aerospace Corporation/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1971	2-D fibrous carbon (rayon-based) felt/CVI matrix CCC brake discs survived simulated rejected takeoff of 182-ton Concorde with 47.17M ft-lb energy dissipation	High safety and reliability of CCC brake discs demonstrated Only 0.5 lb of CCC brake disc consumed	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd./Aviation Division (Aircraft Brake System)/ENGLAND
1971	2-D resin char CCC brake discs baselined for large USAF B-1 strategic bomber aircraft	Five rotors and six stators for the largest diameter CCC aircraft brake system Eight 64-lb CCC disc stacks saved about 1100 lb compared to steel brakes Normal B-1 stopping involved 213M ft-lb energy dissipation and about twice that level for maximum energy stops 1M ft-lb of energy were dissipated for each pound of available CCC brake disc during maximum energy stops Landing costs were estimated at $50 per landing CCC brakes were expected to provide only 100 brake landings; great need was obvious for lower wear rates	Super-Temp Company (Brake Discs)/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1972	2-D CCC brake discs successfully flight tested on USAF F-15 aircraft	First flight test demonstration of CCC brake discs on an advanced military fighter Three CCC rotating discs and four CCC stationary discs (eight total working surfaces) weighed only 29.5 lb for each of the two brakes; weight savings with the CCC brake discs were 150 lb per aircraft compared to equivalent forged steel alloy brakes Each pound of CCC brake disc was required to absorb 425,000 ft-lb of kinetic energy during normal landing stops and 900,000 ft-lb of energy during rejected takeoff situations CCC brake discs projected to survive rejected takeoff temperatures of 2600°F; equivalent steel brake surfaces typically melt and then require overhaul $350/landing costs estimated from first-generation CCC wear rate data	Goodyear Aerospace Corporation/USA
1972	2-D CCC brake discs successfully flight tested on USAF F-111 bomber	First flight test demonstration of CCC brake discs on an advanced bomber aircraft	Goodyear Aerospace Corporation/USA
1972	CCC frictional brake development contract awarded	Lightweight braking system needed by the U.S. space shuttle orbiter	Super-Temp Company/USA
1972	2-D fibrous (rayon-based) graphite felt/CVI PG matrix CCC brake discs successfully tested on large Anglo-French Concorde transport aircraft	First full-scale demonstration of CCC for a commercial aircraft brake system	Super-Temp Company (Brake Discs)/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1972	2-D fibrous (rayon-based) graphite felt/CVI PG matrix CCC structural (five) rotor brake assembly successfully used for 320 brake stops; wet and dry stops	High-density CVI PG CCC brake rotors and stators demonstrated to have properties useful for the Anglo-French supersonic Concorde aircraft First ground-based tests indicated acceptable frictional characteristics, light weight and durability for later use on the Anglo-French supersonic commercial aircraft	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd. (Brake Design & Tests)/ ENGLAND
1972	CCC brake discs assembly for the Concorde aircraft successfully completed a rejected takeoff test from a 174-knot speed and an energy of 47.2M ft-lb	High safety feature of CCC brake system demonstrated Only 0.43 kg of material lost during RTO test	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd. (Brake Design & Tests)/ ENGLAND
1973	Joint development program initiated on aircraft CCC brake disc materials	Major aircraft brake systems company and major CCC producer joined forces to design and produce high-performance carbon brakes	HITCO (CCC Brake Discs)/USA Goodyear Aerospace Corporation (Brake Systems)/USA
1973	CCC brake system qualified and production initiated for U.S. shuttle orbiter	Another aerospace outlet for CCC brake discs on heavy flight vehicles The lightest braking system designed was a CVD CCC lined beryllium assembly	Super-Temp Company (Brake Discs)/USA
1973	Extensive dynamometer and full-scale testing completed on large CCC brake discs	CCCs demonstrated full range of energy absorption in 95 normal energy stops (25 million ft-lb), four overload stops (31.3 million ft-lb), and one RTO (aborted takeoff) of 51.6 million ft-lb	Super-Temp Company/USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1973/74	Structural 2-D CVD CCC brake discs completed over 500 landings on the British Airways Super VC-10	First commercial airline use of CCC brake discs One of eight wheels fitted with 2-D CCC brake discs which replaced a steel brake Frictional performance of 2-D CCC brake discs demonstrated in regular aircraft service	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd. (Brake Design)/ENGLAND
1974	Molded random fiber resin char CCC friction material developed & laboratory tested	First use of random fiber CCC material for an aircraft frictional brake disc applications	Bendix Energy Controls Division/USA
1974	Structural 2-D CCC brake discs fabricated and four sets delivered for Boeing 747 service tests	High interest expressed in the potential use of CCC in very large commercial aircraft brake systems	Bendix Energy Controls Division/USA
1974	Full-scale (22 in. diameter) 2-D CVD CCC brake discs manufactured for the Anglo-French Concorde supersonic aircraft brake system	Largest CCC brake disc manufactured in a production facility Proven beryllium brake system was abandoned with production and demonstration of CCC brake discs CCC brake system expected to save 1200 lb per aircraft CCC brake system expected to have 3000 landings compared to 600 for the qualified steel brake material	Dunlop, Ltd./ENGLAND
1974	2-D CCC brake discs successfully flight tested on USAF B-1 strategic bomber aircraft	First operational use of CCC brake discs on a large military aircraft Initial wear life indicated about 100 landings per CCC brake set	Goodyear Aerospace Corporation (Brake Discs)/USA U.S. Air Force Flight Test Center (Flight Test)/USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1974	Operational USAF F-15s CCC brakes accumulated more than 3000 brake landings	Reliability of CCC structural brake discs demonstrated brake disc wear rate significantly higher (x2-3) than predicted	U.S. Air Force (Flight Tests)/USA
1974	CVD 2-D CCC brake liner production contract awarded for U.S. space shuttle CCC lined beryllium brake system	Earth braking of U.S. manned aerospacecraft entrusted to CCC frictional materials	Super-Temp Company/USA
1974	2-D fibrous (rayon-based) graphite felt/CVI PG CCC brake discs passed qualification tests for British Hawker Siddeley AV-8A and AV-16A Harrier vertical takeoff and landing (V/STOL) attack aircraft	CCC brake disc systems qualified for an advanced military aircraft	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd. (Brake Design)/ENGLAND
1974	Large-diameter, single-disc transmission mounted CVD CCC brake stopped both rotor blade systems of a heavy lift helicopter	First qualification testing of CCC frictional material for helicopter use Disc weight reduction was 82% Brake life extended four times at high energy levels	Super-Temp Company/USA
1974	Three types of 2-D CCC materials developed for aircraft brake systems	Promising CCC concepts employed either woven carbon fabrics, semi-random chopped carbon fibers, or carbon fiber mats with cross-ply reinforcement and a matrix of either pyrolytic carbon or a combination of resin char and pyrolytic carbon	Various Aircraft Brake Systems Manufacturers and Material Suppliers/USA
1975	CVD CCC structural brake system developed in just 27 months for the Anglo-French Concorde aircraft; it routinely completed normal energy stops of 25.1M ft-lb, overload stops of 31.3M ft-lb, and a rejected takeoff of 51.6M ft-lb of energy	Structural CCC brake was qualified for a commercial aircraft Low wear rate and exceptional safety demonstrated	Super-Temp Company (Brake Discs)/USA Dunlop, Ltd. (Brake Tests)/ENGLAND

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1976	U.S. space shuttle (off of a Boeing 747 aircraft) lands with CVD CCC-lined beryllium brakes	First heavy aerospacecraft flight vehicle successfully braked with CCC frictional materials	BFGoodrich Aerospace/Super-Temp/USA
1976	Anglo-French Concorde commercial aircraft entered service with 2-D CVD PG CCC brake discs	Largest commercial aircraft to use structural CCC brakes Structural CCC brake discs replaced previously selected beryllium brakes CCC brake system reduced aircraft weight by 1400 lb (equal to about 8 passengers) Wear rate less than predicted after six months service	Dunlop, Ltd. (Brake System)/ENGLAND British Airway (Aircraft Flight)/ ENGLAND Air France (Aircraft Flight)/FRANCE
1976	2-D CCC brake discs successfully flight tested on USAF F-16 fighter aircraft	First flight demonstration of 2-D CCC brake discs for a multinational, high-volume production military fighter The three CCC rotating discs and four CCC stationary discs weighed less than one-half that of state-of-the-art steel brakes Normal landings required the CCC brakes to absorb 8.5M ft-lb of kinetic energy; maximum energy landings involved about 20M ft-lb CCC brake discs expected to provide twice the number of landings compared to steel discs	Goodyear Aerospace Corporation/USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1977	2-D CCC discs flight evaluated on commercial Boeing 747 aircraft brake system	Another potential application of 2-D CCC brake discs for very large, subsonic commercial aircraft Projected 1400 lb weight savings compared to steel brakes or equivalent to seven passengers Fourth generation CCC brakes expected to give 6-10 times more life and at one-fourth the cost compared to first-generation (1972) CCC materials	Goodyear Aerospace Corporation/USA
1977	2-D CCC brake discs successfully flight tested on a large commercial McDAC DC-10 aircraft	Another application of 2-D CCC brake discs to very large, subsonic commercial aircraft Increased the potential for retrofitting DC-10 brake systems Annual fuel savings of over 30,000 gallons estimated as a result of weight savings provided by the CCC brake discs (compared to steel)	Goodyear Aerospace Corporation/USA
1977	CCC brake discs developed for the French Mirage aircraft	CCC brake discs became available for a high-performance French military fighter	Societe Europeenne de Propulsion (SEP)/ FRANCE
1977	Four world sources for 2-D CCC frictional materials evaluated to compare aircraft brake performance	Laboratory dynamometer tests, composite property measurements, and nondestructive inspection provided competitive differences between the respective materials	Super-Temp Company/USA Goodyear Aerospace Corporation/USA ABEX Corporation/USA Dunlop, Inc./ENGLAND AF Flight Dynamics Lab/USA
1977	Half-worn CCC brake discs were routinely discarded during brake overhaul	Current practice greatly increased the cost of aircraft per landing Innovative approaches were needed to reclaim partially-worn CCC brake discs	Various Brake Manufacturing Sources/ USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1978	Random fiber CCC friction material in production for F-15 A/C brakes	First operational use of random fiber CCC aircraft brake discs	Bendix Aircraft Brake & Strut Division/ USA
1978	BFGoodrich acquired Super-Temp Company	Corporate commitment to expand the utilization of CCC for A/C braking systems	BFGoodrich Aerospace/Super-Temp/USA
1978	2-D CVD CCC brake discs were undamaged after Anglo-French Concorde aircraft rejected takeoff	Most severe frictional test to date by a commercial aircraft using CCC brake discs Demonstrated the reuse capability of CCC brake discs after a high-temperature RTO incident	Dunlop, Ltd./ENGLAND
1978	2-D CVD CCC brake discs successfully flight tested on the Canadair CL600 Challenger twin-jet aircraft	First executive jet aircraft to fly with CCC brake discs CVD matrix composites provided over 10 times better wear life compared to first-generation resin char CCC materials CCC brakes enabled 100 lb per aircraft weight savings compared to steel brakes 1600 or more landings forecasted for the CCC brake system compared to 400 landings for comparable steel brakes	Goodyear Aerospace Corporation/USA
1978	Gulfstream III successfully flight tested with CCC brake discs	Second western hemisphere corporate jet transport to use CCC brake discs	Goodyear Aerospace Corporation/USA
1978/88	2-D CVI PG densified carbon fabric CCC produced for aircraft brake discs	First production facilities for 2-D CCC aircraft brake disc materials in Asia	Lanzhou Carbon Industry/P.R. CHINA
1978	2-D CCC brake (rotor and stator) discs flight tested on the French military "Mirage 2000" aircraft	First flight of a French military production aircraft with 2-D CCC brake discs	Societe Europeenne de Propulsion (SEP)/ FRANCE
1979	CCC rotor brakes were qualified for the CH47/Boeing Vertol 234 heavy lift helicopter	CCC frictional materials successfully demonstrated in a helicopter brake system	BFGoodrich Aerospace/Super-Temp/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1979	2-D CCC brake discs were successfully tested on the U.S. Navy F-14 aircraft	First application of 2-D CCC brake discs for an advanced Navy fighter aircraft First retrofit use of CCC brake discs in an operational military production aircraft (replaced beryllium) Projected CCC brake life was 750 landings compared to 100-150 landings for previously-used metallic brakes	Goodyear Aerospace Corporation/USA
1980	Establishment of a complete CCC manufacturing facility for production of aircraft brake discs	Production capability was established to compression mold, heat treat, CVD infiltrate, and resin impregnate composite friction materials	Bendix Aircraft Brake & Strut Division/ USA
1980	First launch of a CCC-lined beryllium brake for space shuttle	Fully-operational flight demonstration of U.S. shuttle CCC brakes	BFGoodrich Aerospace/Super-Temp/USA
1980	2-D CCC brake discs and pads used successfully on high-performance racing cars	First operational use of 2-D CCC brakes for Formula 1 racing cars CCC brake discs exhibited more dependable braking performance, marked reduction in pedal pressure, and more consistent braking compared to previously-used materials A new commercial outlet for CCC frictional materials	HITCO (Brake Discs)/USA Team Brabham (Racing Car)/ENGLAND
1981	2-D CVD CCC brake discs performed successfully on a large British commercial aircraft	First flight of BAe 146 aircraft with CCC brake discs	Dunlop, Ltd./ENGLAND
1981	Formula 1 race car became operational with 2-D CCC braking material	Formula 1 race car outfitted with French 2-D CCC brakes	Societe Europeenne de Propulsion (SEP)/ FRANCE

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1982	Half-worn brake discs were machined, CVD welded together, and new clips attached	A new process for reclaiming partially-worn CCC brake discs Cost per brake landing was greatly reduced by using extra-thick discs mixed with partially-worn discs	Dunlop, Ltd./ENGLAND
1982	Boeing/Delta airlines selected 2-D CVD CCC brake discs for the commercial aircraft B-757	3,000 landings anticipated with CVD 2-D CCC brake discs Weight savings of 678 lb/aircraft compared to competitive brake materials Better stopping distance with CCC brake discs	Dunlop, Ltd./ENGLAND
1982	Improved CCC brake discs baselined for the USAF B-1B bomber	Five pairs of CCC brake discs were used in each of the eight brake main landing gear assemblies for a total weight savings of 1,200 lb (compared to an equivalent steel stack) Compared to first-generation CCC materials, the new fifth-generation CCC had 100% higher mechanical properties, wear life increased by 20 times, production costs reduced 10%, and cost-per-landing decreased by 95% Major progress was also achieved in developing CCC wet brake materials	Goodyear Aerospace Corporation/USA
1982	Commercial airbus A-300 aircraft lands with 2-D CCC brake discs	First landing demonstration of 2-D CCC frictional materials for a French airbus aircraft	Societe Europeenne de Propulsion (SEP)/ FRANCE

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1983	Fifth-generation 2-D CCC successfully tested on an SF-340 commercial aircraft	Improved physical property version of original material with increased disc life (by a factor of two)	Goodyear Aerospace Corporation/USA
1983	One U.S. company provided CCC brakes for over 2500 military and commercial aircraft	CCC frictional materials become state-of-the-art for aircraft brakes	Goodyear Aerospace Corporation/USA
1983	Upgraded CCC brake materials used on Formula 1 racing cars	CCC brakes were 30 lb lighter than comparable steel brakes CCC brakes permitted less distance for deceleration and an improvement in acceleration after severe braking	HITCO (CCC Manufacturer)/USA Motor Racing Development/Team Brabham Ltd. (Race Car)/ENGLAND
1983	Eleven Formula 1 race cars used CCC brakes	Increased acceptance of CCC brake materials for high-speed race cars No mechanical failure of CCC experienced	HITCO (CCC Manufacturer)/USA
1984	2-D CCC friction materials fabricated for production of Boeing 767-300 commercial aircraft brake system	First commercial CCC brake system for eight CCC brakes weighed a total of 1500 lb; CCC brake discs provided a weight savings of 870 lb compared to conventional steel friction materials	Bendix Aircraft Brake & Strut Division/ USA
1984	U.S. CCC brake disc manufacturer selected for production of French Airbus A310-300 airliner	First U.S. supplier of CCC brake discs for French commercial aircraft Up to 40% weight reduction anticipated with CCC brake discs compared to steel brakes Up to 5000 landings per brake set anticipated without refurbishment and 10,000 landings with refurbishment Capable of accommodating critical braking conditions during rejected aircraft takeoffs	BFGoodrich Aerospace/Super-Temp/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1984	2-D CVD CCC brake disc system (24 main landing gear wheels) successfully completed ground testing on free world, largest military C-5B transport	Major brake improvements reported to be 400 lb weight savings, $20M lower lifecycle costs and improved operational safety	BFGoodrich/Transportation Products Division/USA
1984	2-D CVD CCC brake disc system successfully flight tested on heavy military C-5A aircraft	CCC brake system judged to be also suitable for use on other military transport aircraft	BFGoodrich/Transportation Products Division/USA
1984	Successful landing of the Boeing 757 commercial aircraft with 2-D CVD CCC brake discs	CCC brake discs performed successfully on a U.S. commercial, long-range aircraft	Dunlop, Ltd. (Brake Discs)/ENGLAND Boeing Airplane Company (Aircraft)/USA
1984	2-D random fiber CCC brake discs were successfully tested on the Fokker 100 commercial jet transport	First commercial short-to-medium haul (100 passenger) twin-jet aircraft to use CCC brake discs Projected 300 lb weight savings with CCC brake discs compared to steel discs	Goodyear Aerospace Corporation/USA
1984	2-D CCC brake discs were baselined for the Swedish advanced JAS 39 Gripen multirole combat aircraft	First foreign fighter to use a U.S. advanced CCC brake disc	Goodyear Aerospace Corporation/USA
1984	2-D CCC brake discs specified for a commercial (8-12 passenger) executive jet aircraft	Increased interest in CCC brake discs for small executive jet transports	Goodyear Aerospace Corporation/USA
1984	CCC brakes used on winning world championship Grand Prix 500 CC motorcycle	Another commercial market for CCC frictional materials	HITCO (Brakes)/USA Honda (Motorcycle)/JAPAN

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1984	2-D CVI PG/carbon (PAN-based) fiber CCC brake (rotor and stator) discs selected for the Airbus Industries A310-300 and for retrofit on A310-200s	Societe Europeenne de Propulsion became major supplier of CCC brake discs for French commercial and military aircraft Carbon brake shipset (8 brakes) weighed about 1100 lb less than similar steel units on the A310-300 derivative	Societe Europeenne de Propulsion (SEP) (Brake Discs)/FRANCE Messier-Mispano-Bugatti (Brake Design)/ FRANCE
1984	CCC materials retrofitted to metallic clutch plates and tested on a dynamometer	Potential application outlet for CCC frictional materials First prototype CCC clutch based on substitution design	Tilton Engineering Inc./USA
1985	Eighth-generation CCC brake discs containing PAN-based carbon fabrics were developed	Competitive attributes and limitations of PAN-based fiber versus pitch-based or rayon-based fiber CCC were quantified	Goodyear Aerospace Corporation/USA
1985	Thick, large-diameter CCC brake discs manufactured by bonding two thinner pieces	Approach for manufacturing CCC brake discs from used, machined parts	Goodyear Aerospace Corporation/USA
1985	2-D CCC structural brake discs provided over 4,000,000 landings on commercial transports	Valuable service and cost per landing data obtained	Messier-Bugatti/FRANCE
1986	Sole supplier of qualified CCC discs for Boeing 747-400 aircraft	Major escalation in use of CCC for commercial aircraft brakes CCC brake shipset weighed about 7,200 pounds compared to 9,000 pounds for a metallic brake system CCC brake discs expected to provide 2,500 to 3,000 landings compared with 1,000 to 1,500 landings for metallic rotors	BFGoodrich Aerospace/Super-Temp (Brake Discs)/USA BFGoodrich/Aircraft Wheels & Brakes Operations (Brake Design)/USA
1986	Qualified CCC brakes for the Embraer AMX aircraft	CCC brakes used with a foreign aircraft	BFGoodrich Aerospace/Super-Temp/USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1986	2-D CCC frictional materials further developed for racing car clutches	CCC clutches for race cars provided improved wear resistance, reduction in moment of inertia, 30-50% reduced flywheel weight and other advantages	HITCO (Clutches)/USA Tilton Engineering, Inc. (Racing Car)/USA
1986	Prostock drag race car used CCC brake/caliper system	2400-lb car stopped from over 124 kmh (200 mph) with an energy absorption rate of nearly 1.6M ft-lb/sec^2	Lamb Components (Brake Designer) HITCO (CCC Manufacturer)/USA
1987	Design and construction of new BFG CCC production facility at Pueblo, Colorado	Scheduled major expansion in CCC brake disc production capacity	BFGoodrich Carbon Products/Aerospace Division/USA
1987	2-D CVD CCC disc material selected for brake retrofit of about 2,000 C-5A military transport aircraft	Major four-year production contract for high volume CCC frictional materials	BFGoodrich Aerospace/Super-Temp/USA
1987	BFGoodrich qualified CCC for Airbus A320 brakes	Continuing escalation in use of CCC for foreign commercial aircraft brakes	BFGoodrich Aerospace/Super-Temp/USA
1987	2-D CVI CCC brake discs manufactured for the French fighter Mirage 2000, the Falcon 900, and the Airbus 300, 300/600, 310, and 320 models	Increased usage of CCC brake discs on French military and commercial aircraft	Carbone Industries/Alsthom Group/ FRANCE Societe Europeenne de Propulsion (SEP)/ FRANCE
1987	Refurbished 2-D CCC worn brake discs flight tested on Saab-Fairchild SF-340 aircraft	First use of refurbished worn CCC brake discs on a commercial aircraft Cost of brake disc ownership reduced by 30%	Goodyear Aerospace Corporation/USA
1987	Grooved CCC disc wear surfaces flight tested on Saab-Fairchild SF-340 aircraft	First demonstration of improved wet rejected takeoff performance of CCC brakes in commercial service	Goodyear Aerospace Corporation/USA
1987	2-D CCC frictional material developed and successfully tested on winning drag racer	New commercial application for frictional CCC Higher performance, lighter weight CCC used for another frictional application	HITCO (Brake Materials)/USA Top Fuel (Drag Racer)/USA

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1987	Two-part oxidation protection system for 2-D CCC flight tested on USAF F-15 A/B military aircraft	Aircraft CCC brake disc life prolonged by a factor of two	Goodyear Aerospace Corporation/USA
1987	Formula 1 race car wins the Detroit Grand Prix with a CCC clutch	Race car CCC clutch had high performance and long life CCC clutch used for over 2000 miles of racing, testing, and qualification The standard metal clutch was discarded after one race or about 180 miles	Tilton Engineering Inc. (Clutch Design)/ USA HITCO (CCC Manufacturer)/USA
1988	2-D CCC friction materials fabricated for McDonnell Douglas MD-11 commercial aircraft brake discs	Largest (2-ft diameter) CCC aircraft brake disc manufactured One hundred pounds of CCC per brake unit	Allied-Signal Aerospace Company/Bendix Wheels & Brakes Division/USA
1988	Embraer AMX CCC brakes in service	CCC brakes used on foreign production aircraft	BFGoodrich Aerospace/Super-Temp/USA
1988	CCC brake discs manufactured for Boeing 747-400 aircraft	CCC baselined for high volume production commercial aircraft brake discs	BFGoodrich Carbon Products (Pueblo)/ USA
1988	Largest (110,000 ft^2) CCC manufacturing plant in the world (Pueblo, CO) becomes operational	Commercial and military aircraft brake disc market warranted establishment of a dedicated production facility Major increase in CCC manufacturing capacity Total investment in plant was $50M Aircraft brake discs remain single largest application for CCC	BFGoodrich Carbon Products (Pueblo)/ USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1988	CCC brake pads evaluated for brake assembly of luxury car	CCC brake pads provided an asbestos-free frictional material CCC pads for front and rear axles of a Mercedes-Benz S-class car was probably the first use in a luxury car Brake disc temperatures in excess of 600°C in mountain driving Low-cost materials and a better understanding of material:performance features were required	Daimler-Benz AG (Brake Design)/ GERMANY Sigri Elektrographit GmbH (CCC Pads)/ GERMANY
1989	Mechanical attachment refurbishment method selected for USAF F-15 and F-16, and the Saab 340 commercial aircraft CCC brake discs	Inexpensive method for extending the life of worn CCC brake discs	Aircraft Braking Systems Corporation/ USA
1989	Bonded-lining refurbishment method selected for Airbus A310 through A340 aircraft CCC brake discs	Original life of CCC brake discs restored Improved brake reliability More expensive than mechanical attachment refurbishment method	Aircraft Braking Systems Corporation/ USA
1989	CCC brake options developed for the commercial Airbus A330 and A340 aircraft	Standard life brakes (1500 landings) were expected to be used on long-range, weight-critical A340 commercial aircraft Heavy-duty brakes (2500 landings) were expected to be used on shorter-route A330 commercial aircraft	Aircraft Braking Systems Corporation/ USA
1989	Heavy-duty CCC brake system developed for USAF F-16 fighter	Improved CCC brake materials helped double the brake life	Aircraft Braking Systems Corporation/ USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	Long-life 2-D CCC brake discs used on USAF B-1B bomber aircraft	Projected CCC brake life was about 900 landings between overhauls CCC brakes were about 1000 lb lighter than equivalent steel brakes	Aircraft Braking Systems Corporation/ USA
1989	CCC brake discs for the U.S. space shuttle orbiter "Discovery" qualified by ground-based landing gear tests	First use of 2-D CCC brake discs for a U.S. space shuttle orbiter landing gear system New carbon braking system was free from dynamic instabilities previously experienced with beryllium brakes CCC brake discs life expectancy estimated to be 10 times longer than previously used beryllium brakes	Air Force Wright Research & Development Center/Flight Dynamics Laboratory/USA
1989	Metal impregnated CCC material was developed for brake linings	Alternate material for high-speed frictional applications	Akebono Brake Industry Co., Ltd./JAPAN
1989	Developed and tested aircraft prototype CCC brake friction material based on nonwoven, near net shape, 3-D preforms with full CVD carbon matrix	First use of 3-D nonwoven preforms, fabricated to near net shape for application to CCC brake discs (patented process)	Allied-Signal Aerospace Company/Bendix Wheels & Brakes Division/USA
1989	All Formula 1 race cars were outfitted with 2-D CCC frictional plate clutches (British Grand Prix)	Extensive use of CCC frictional materials for high-performance racing cars	BP Chemicals (HITCO), Inc./USA
1989	2-D CVD CCC rotor brakes qualified for the V-22 aircraft	CCC frictional materials specified for new military aircraft brake systems	BFGoodrich Aerospace/Super-Temp/USA
1989	Certification of all CCC brakes for space shuttle completed	CCC brakes fully utilized in a structural mode	BFGoodrich Aerospace/Super-Temp/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	BFGoodrich/Pueblo CCC production facility expanded to a 200,000-lb annual capacity	CCC frictional materials demand warranted a major expansion in CCC manufacturing	BFGoodrich Carbon Products (Pueblo)/ USA
1989	2-D CVD CCC brake discs qualified for the French commercial A330 and A340 aircraft brake systems	CCC frictional materials were baseline engineering materials for additional commercial aircraft brake systems Optional CCC brake system designed for 3000 landings with intermediate overhaul every 1500 landings or 5000 landings with intermediate overhaul every 2500 landings	BFGoodrich Carbon Products (Pueblo)/ USA
1989	2-D CCC brake discs fabricated and qualified for the Boeing 737-500 aircraft	CCC friction materials qualified for an intermediate-range commercial aircraft Cost-effectiveness of CCC friction materials were demonstrated for an intermediate-weight commercial transport aircraft	BFGoodrich Carbon Products (Pueblo)/ USA
1990	2-D CCC brake friction materials in fully-worn condition survived maximum energy at 180 kt (900 M ft-lb) refused takeoff of McDAC MD-11 commercial aircraft	Higher performance, lighter weight, and increased safety of CCC friction materials were demonstrated for next-generation jumbo aircraft	Allied-Signal Aerospace Company/Bendix Wheel & Brakes Division/USA
1990	Initial F-16 (Block 50) flight using CCC brakes	Successful flight test confirms CCC brake performance	BFGoodrich Aerospace/Super-Temp/USA
1990	First space shuttle flight of CCC brakes	Structural CCC brakes successful	BFGoodrich Aerospace/Super-Temp/USA
1990	Second Pueblo CCC facility expansion	Annual CCC production capacity increased to 300,000 pounds	BFGoodrich Carbon Products (Pueblo)/ USA
1990	Low-cost, intermediate-density (1.6 g/cm^3) CCC containing nonwoven fibrous reinforcement fabricated for high-speed train frictional components	Low-cost, fast-processed CCC material was evaluated for potential use on high-speed train brake systems	Kobe Steel, Ltd./JAPAN

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1990	2-D CCC friction materials successfully tested on J-7M military aircraft	First prototype CCC brake discs for a P.R. China aircraft brake system	Lanzhou Carbon Industry (CCC Materials)/P.R. CHINA
1990	U.S. space shuttle orbiter "Discovery" lands on earth with a new CCC brake system	First fully-operational U.S. orbiter to use a CCC brake disc system	NASA/USA
1990	2-D CCC reinforced with spun (short) PAN-based carbon fibers used in a variety of aerospace brake disc systems	Low-cost spun carbon fibers used in brake discs of military F-15, F-16, F-18, and C-5B aircraft and NASA space shuttle	Stackpole Fibers Company/USA
1990	Major worldwide producers of CCC materials identified	BFGoodrich Carbon Products, BP Chemicals (HITCO) Inc., and Allied-Signal Aerospace Company/Bendix were major domestic producers of CCC brake discs Societe Europeenne de Propulsion (SEP) and Carbone Industries were major foreign producers of CCC brake discs CCC brake discs constitute more than 90% of the total CCC market	Various World Sources
1991	Random fiber CCC with improved CVD processing was qualified for Airbus A330/340 commercial aircraft brake discs	First demonstration of high-density CCC for modern-day commercial aircraft	Aircraft Braking Systems Corporation/ USA
1991	One-part oxidation protective coating was flight tested on Airbus A330/340 aircraft CCC brake discs	Improved oxidation protection at lower cost with much easier application	Aircraft Braking Systems Corporation/ USA
1991	CCC friction material based on nonwoven near net shape preforms was selected for use on the Boeing 777 brake system	First CCC friction material based on 3-D nonwoven preforms, fabricated to near net shape, and selected for use in a commercial aircraft brake system	Allied-Signal Aerospace Company/Bendix Wheels & Brakes Division/USA
1991	CCC frictional materials were evaluated for secondary braking system of TGV high-speed train	Potential commercial market for CCC materials	Alsthom (CCC Brake Manufacturer)/ FRANCE

TABLE 40 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1991	First five racing car finishers in the U.S. Formula 1 Grand Prix used CCC rotors/ pads	Specialty commercial market for CCC frictional materials	BP Chemicals (HITCO) Inc. (CCC Materials)/USA
1991	Nearly all pro stock, top fuel, and funny-car dragsters used CCC brake rotors and pads	Low volume but important commercial market for CCC frictional materials	BP Chemicals (HITCO) Inc. (CCC Materials)/USA
1991	CCC friction materials designed for secondary braking systems of high-speed trains	First prototype CCC frictional brake materials for high-speed railroad transportation systems	Japan Railway Technical Research Institute/JAPAN
1991	Over one-third of the international commercial transport fleet have Messier-Bugatti carbon brake systems	350 international commercial aircraft were flying with high-performance French CCC brakes	Messier-Bugatti/FRANCE
1991	Over 15,000 carbon discs were furbished for additional use on aircraft brake systems	Cost-effective refurbishment method was developed and applied to structural carbon brake discs	Messier-Bugatti/FRANCE
1991	2-D short carbon fiber (felts and chopped tow)/CVI PG composites were fabricated for frictional applications	Materials development for potential aircraft brake applications	Shaanxi Non-Metallic Material and Technology Institute/P.R. CHINA
1992	CCC brake discs were manufactured for a McDAC MD-90 commercial aircraft brake system	CCC structural brakes were cost-effective for smaller commercial aircraft CCC brakes were designed for 2000 landings minimum CCC brake discs can be refurbished and life extended beyond 2000 landings	Aircraft Braking Systems Corporation/ USA
1992	Prototype CCC test hardware fabricated for Japanese high-speed Mag Lev train	Further commercialization of CCC in new frictional applications	BFGoodrich Aerospace/Super-Temp/USA
1992	29 F-16 block 40 aircraft operational with CCC brakes	Continued CCC high-performance levels in operational fleet	BFGoodrich Aerospace/Super-Temp/USA
1992	F-16 lightweight CCC brakes qualification completed	Another demonstration of effectiveness of CCC brakes	BFGoodrich Aerospace/Super-Temp/USA

TABLE 40 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1992	CCC brakes exhibited significantly-reduced wear rate in commercial service	Commercial service life indicated cost-effectiveness of CCC brakes better than anticipated	BFGoodrich Carbon Products (Pueblo)/ USA
1992	CCC brakes qualified for Boeing 777 commercial aircraft	Continued expansion of market for CCC aircraft brakes	BFGoodrich Carbon Products (Pueblo)/ USA
1993	First flight of the Airbus Industrie A321 commercial aircraft with a CCC brake system	French commercial aircraft used a U.S. CCC brake system and material for its landing gear	Airbus Industrie (Aircraft)/FRANCE Aircraft Braking Systems Corporation (Landing Gear)/USA BP Chemicals-HITCO (CCC Brake Discs)/ USA
1993	All French commercial Airbus transports in production were being equipped with carbon brake systems	CCC brake discs became standard frictional materials for all French large civilian transport aircraft French brake systems company claimed 28% share of the western world civil transport carbon brake market	Messier-Bugatti (Aircraft Brake Systems)/ FRANCE Societe Europeenne de Propulsion (SEP) (CCC Brake Discs)/FRANCE
1993	Certification of CCC brake disc system for large commercial aircraft may exceed U.S. $5M	CCC brake disc certification is very expensive Certification costs are warranted only for high-volume aircraft production	Various Domestic Aircraft Brake Manufacturers/USA
1994	Over 80% of all company aircraft braking systems used CCC brake discs	Majority of medium-to-large aircraft baselined CCC brake discs	BFGoodrich Aerospace/USA
1994	CCC brake system baselined for emergency stopping of a bullet train from a maximum speed of 189 mph	New CCC dry frictional application for high mass ground vehicles	Japan Railway Companies/JAPAN
1994	French Airbus commercial A330 carbon brake discs accommodate 2500 landings/ takeoff cycles before refurbishment	Carbon brake systems capable of 2500 cycles compared to 1000 cycles for comparable steel brakes Carbon brakes offer significant reduction in weight and lower maintenance costs	Messier-Bugatti (Brake Design)/FRANCE BFGoodrich Acrospace (CCC Brake Materials)/USA

TABLE 40 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR FRICTIONAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1994	Russia-USA joint development agreement on new CCC frictional materials	Shared technology may lead to higher performance and lower-cost CCC brakes	NiiGRAFIT/RUSSIA Allied-Signal Aerospace Company (Bendix)/USA
1994	A 33-cm (13-in) diameter CCC brake disc was manufactured in eight hours and had a uniform density of 1.85 g/cm^3 (0.067 lb/in^3)	Fast and economical process may possibly revolutionize CCC brake manufacturing	Textron Specialty Materials/USA
1994	Fully-machined CCC aircraft brake discs cost between $50-200/lb depending upon volume of order	Significant reduction in CCC brake disc manufacturing with greatly increasing volume orders	Various Domestic CCC Manufacturers/ USA
1995	First flight of the Airbus Industrie A319 commercial aircraft with a CCC brake system	Third-generation SEP Sepcarb III CCC brake material had a 75% improved wear rate compared to mid-1980 material Over 1,750 landings were estimated before brake overhaul	Airbus Industrie (Aircraft)/FRANCE Messier-Bugatti (Braking System)/ FRANCE SEP (Brake Discs)/FRANCE

Brake overload stops and rejected takeoff stops demonstrated the material's ability to absorb and dissipate enormous amounts of energy over a very short period of time. Hence total safety was afforded the aircraft passengers even under abnormal braking conditions.

During the mid-1970s CCC friction materials were significantly upgraded, and new aircraft took to the air with these materials. Material candidates were narrowed to about three types of fibrous carbon reinforcements, including (a) woven carbon fabrics, (b) semi-random chopped carbon fibers, and (c) fiber mats with cross-plied reinforcement. Each of these composite reinforcements contained either pyrolytic carbon or a combination of resin char and pyrolytic carbon. The higher-density pyrolytic carbon typically gave lower wear rates. Flight testing continued with new aircraft, including the (a) original B-1 bomber, (b) U.S. shuttle orbiter vehicle, (c) F-16 multinational military fighter, and (d) Hawker Siddeley AV-8A and AV-16A verticle takeoff-and-landing attack aircraft. Over 500 landings were accumulated on the British Super VC-10 commercial aircraft, and over 3,000 landings were logged for F-15 military fighters. Data from these operational landings provided critically needed statistical information on the wear rate of the materials. Six months of Concorde commercial aircraft service revealed a wear rate less than that predicted. Wear rate of F-15 CCC brakes, however, were two to three times higher than predicted. This situation was apparently due to the use of low-density resin char CCC materials and numerous taxi stops encountered during service conditions.

Material upgrading, CCC brake disc prototyping, and flight evaluations continued at a rapid pace during the late 1970s. Fourth-generation CCC frictional materials were developed with about six to 10 times more life and about one-fourth the cost of first-generation materials which appeared about 1970-72. Structural CCC brake discs were prototyped and flight tested for the McDonnell Douglas DC-10 and the Boeing 747 commercial transports. Projected weight savings with CCC brake discs were on the order of 6500 kg (14.3 klb) which provided an annual fuel savings of over 115 kl (30.4 kgal). CCC brake systems were also flight tested on two smaller commercial jets, i.e. the Canadair Challenger CL 600 twin-jet and the Gulfstream III corporate jet transport. The use of CCC brake discs in these aircraft enabled a weight savings of 41-45 kg (90-100 lb) and about twice the number of landings between overhauls compared to heavier steel brakes. Overseas a CCC brake system was flown on a military fighter for the first time. This aircraft was the new French high-performance Mirage 2000 fighter. CCC brake discs also gained favor in retrofitting aircraft brake systems. The U.S. Navy F-14 military fighter, which previously used beryllium brakes, was outfitted with 2-D CCC structural brake materials. This event represented the first use of CCC frictional materials in U.S.

Navy fighter aircraft and the first retrofit of CCC brake discs in an operational military production aircraft. Projected CCC brake life was about 750 landings compared to about 100-150 landings for the previously-used metallic brakes. CCC brake materials also spread to heavy lift helicopters. The material was qualified for the CH47/Boeing Vertol 234 helicopter and successfully tested.

4.8.5.1.3 *The 1980s*

By the early 1980s it was evident to the world that CCC frictional materials were the material of choice for aircraft braking systems. The materials were baselined for the Boeing B-757 commercial airliner. The weight savings was estimated at 308 kg (678 lb) per aircraft, and up to 3,000 landings between overhaul were projected. CCC brake materials were successfully flight tested on three different commercial aircraft including the French Airbus A-300, the British BAe 146, and the Swedish SAAB Fairchild SF-340. Additional material improvements were made to increase the attractiveness of CCC brake discs. Compared to first-generation CCC frictional materials, the new composites had (a) a wear life 20 times higher, (b) twice the mechanical properties, (c) slightly reduced production costs, and (d) about one-half the cost-per-landing. A novel concept for extending the life of CCC brake discs was also generated during the early 1980s. Partially worn CCC brake discs were reclaimed and used. Half-worn brake discs were machined, CVD welded together, and new clips attached. Extra thick CCC discs were mixed with partially-woven discs in the rotor/stator stack, thus enabling CCC brake discs to be used for a longer period of time and with a lower life-cycle cost. A rather interesting but low volume outlet for CCC frictional materials was also developed. 2-D CCC brake discs and pads were successfully evaluated for Formula One race cars. Attributes of the new CCC materials included (a) more dependable braking performance, (b) marked reduction in pedal pressure, and (c) more consistent braking. Within two years 11 Formula One race cars were using CCC brakes.

During the mid-1980s very impressive uses of CCC frictional materials were demonstrated in large commercial and military aircraft. A CCC brake system was qualified for the Boeing 747-400 large commercial aircraft. The brake system cost about twice that of a conventional metallic brake system, but the brake shipset was reduced by 818 kg (1800 lb), and the landings between overhaul were two to three times higher than with metallic rotors. In the military aircraft sector, the big news was the use of CCC brake discs for the free world's largest military transport (C-5B). Based on ground and flight tests, the new CCC brake system was over 182 kg (400 lb) lighter and $20M lower in life-cycle costs compared to a metallic brake system. The entry of CCC brake systems into the commercial short-to-medium haul aircraft market is also worth mentioning. A 2-D CCC frictional material was baselined for

the Dutch Fokker 100 commercial, 100-passenger jet transport. Over 136 kg (300 lb) weight savings were realized with the new CCC brake discs. In the sporting world CCC frictional materials gained increased acceptance. They were laboratory and operationally tested on clutches of race cars, motorcycle brakes, and the brake systems of pro-stock drag race cars.

CCC frictional activities during the late 1980s involved (a) a major expansion of production facilities in both the U.S. and France, (b) continued application of CCC materials to new aircraft, particularly very large aircraft, (c) additional aircraft brake retrofit activities, (d) upgrading of materials performance, and (e) novel brake designs to extend the life of frictional materials. Aircraft production in both the U.S. and France continued to increase, and most of the new aircraft slated for production had baseline CCC frictional materials for their brake systems. BF Goodrich in the U.S. dedicated the world's largest (10,220 m^2, 90, 910 kg), (110,000 ft^2, 200,000 lb annual capacity) manufacturing plant to meet both domestic and overseas orders. In France CCC brake discs were being manufactured for the Mirage 2000 fighter, the Falcon 900, and the Airbus 300, 300/600, 310, and 320 models. CCC brake options were also developed for the Airbus A320, A330, and A340 aircraft. Both standard and heavy-duty aircraft brake designs and materials were developed. Standard-life brakes were expected to provide about 1500 landings for long-range, weight-critical commercial aircraft. Heavy-duty CCC brake systems were designed for about 2500 landings on shorter route commercial aircraft.

CCC materials were also qualified for the Boeing 737-500 intermediate-range commercial aircraft and the new McDonnell Douglas MD-11 large transport. The latter aircraft required the largest (0.61 m, 2 ft diameter) CCC brake discs manufactured to date. About 45 kg (100 lb) of CCC were used in each brake unit. By the late 1980s the 2,000 U.S. C-5A military transports in the U.S. defense inventory were ready for overhaul or redesign. 2-D CCC brake discs were selected as the retrofit material, and a high-volume material delivery contract was initiated. Design efforts on CCC brake systems focused on improving performance and life between overhaul. Brake disc wear surfaces were grooved to improve wet rejected takeoff performance. Two-part oxidation protection materials were also developed for high-performance (high post-braking temperature) brake systems. For the U.S. F-15 A/B military aircraft, brake disc life was increased by a factor of two. Progress continued in extending the life of CCC frictional materials through design approaches. Inexpensive mechanical attachment refurbishment methods were developed, and bond-lining refurbishment methods were also perfected for restoring the original life of CCC brake discs.

4.8.5.1.4 *The 1990s*

During the early 1990s the main emphasis in CCC frictional materials was on (a) new constructions, (b) new manufacturing processes, and (c) life-cycle cost reduction. 3-D nonwoven fibrous reinforcements, based on low-cost PAN-based carbon fibers, were exploited for use instead of higher-cost woven (PAN-based and pitch-based) carbon fabrics. More economical processing methods were also explored, and significant progress was demonstrated. A 33-cm (13-in) diameter CCC brake disc was manufactured in a single eight-hour densification cycle, and the part had a uniform density of 1.85 g/cm^3 (0.0668 lb/in^3). Composite properties are being determined, including the critical frictional coefficients in a variety of environmental conditions. CCC brake disc refurbishment became the major approach for life-cycle cost reduction, since great maturity had been reached in constituent materials costs and composite processing. Dramatic improvements in composite processing may well be on the future horizon, and every effort should be made to develop rapid and economical processes. It is interesting to note that all developing countries in the aircraft manufacturing business have established CCC facilities to provide for future brake needs. For example the People's Republic of China has spent a decade developing appropriate aircraft frictional materials and then used them on their domestically-produced J-7M military aircraft. Eastern European nations, including Russia and the Ukraine, have also developed CCC brake disc materials which are being used in their commercial and defense systems. With the recent downturn in world aircraft orders, most of the near-term future CCC brake disc business will be centered on (a) refurbishing worn discs and (b) replacement parts (spares). The U.S. Boeing 777 large commercial aircraft is one of the last new aircraft of this century. CCC frictional materials have already been qualified for this application and at great expense to the brake systems designer and manufacturer. In the nondefense world the design, testing, and selection of CCC frictional materials for emergency stopping of very high-speed trains was announced. While volume uses may be relatively small, the application represents another impressive and ever-expanding outlet for CCC frictional materials.

4.8.6 Solid Propellant Rocket Motor Components

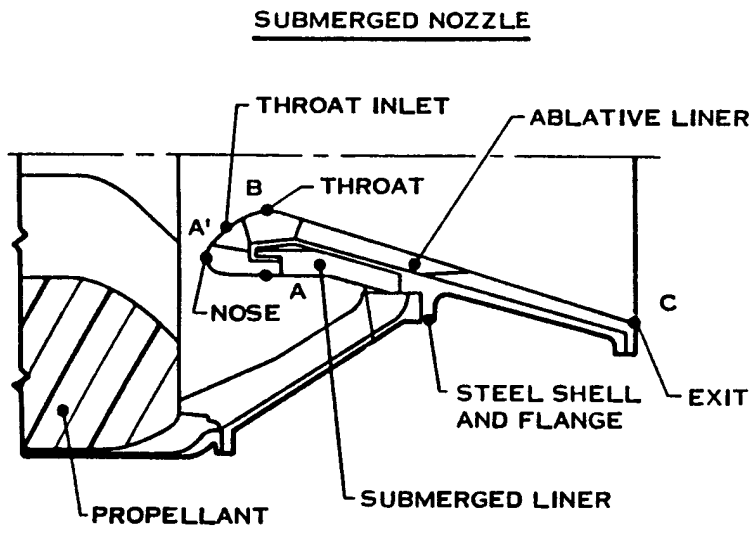
Chemical rocket propulsion systems are classified according to the propellant type, i.e., solid or liquid. Solid propulsion systems are usually called "motors," and liquid propulsion systems are typically referred to as "engines." There are also hybrid propulsion systems in which the fuel is a solid and the oxidizer is a liquid, or vice versa.

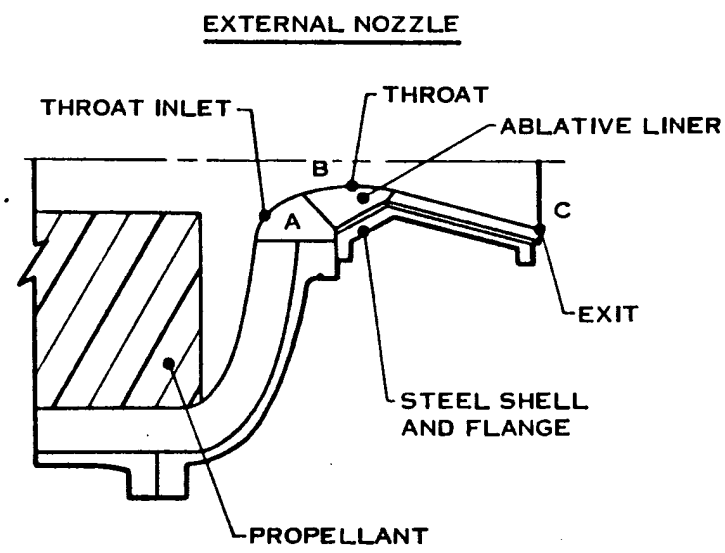
The basic components of a chemical rocket propulsion system are (a) a combustion chamber where propellants are transformed to hot gaseous reaction products, (b) a nozzle to accelerate the hot gas to a high velocity, (c) propellant containers, (d) a method of feeding the propellants into the combustion chamber, (e) an overall structure to support and protect the parts, and (f) various guidance and control devices.

Military solid motors are generally classified as being either tactical or strategic. There are also very large solid motors for expendable space missions, such as the two solid motors on the U.S. Space Shuttle ground-launched propulsion system. Strategic motors are large in size and capable of delivering a weapon a long (intermediate or intercontinental) distance. They are typically either surface-to-surface or underwater-to-surface weapons. Tactical motors represent a very diverse family of motors which are characterized mainly by their size. Their missions vary, such as (a) air-to-air, (b) air-to-surface, (c) surface-to-air, (d) surface-to-underwater, (e) underwater-to-surface, and (f) underwater-to-underwater.

The internal environment of a solid propellant rocket involves severe thermal, mechanical, and corrosive conditions. The range of parameters is quite large, including: (a) temperatures of about 2200-3875°C (2992-7007°F), (b) burning times from 1 to about 120 seconds in either a single pulse, multiple pulses, or boost-sustained firing, (c) pressures of 0.69-34.5 MPa (100-5000 psi), (d) mechanically-erosive alumina particles impacting the surface, and (e) chemically-corrosive oxidizing or reducing gaseous species. Thermal, mechanical, and chemical requirements vary somewhat with the motor (a) propellant chemistry and (b) design, size, and mission. As noted in Figure 18, the throat inlet section experiences high gas pressures and temperatures but relatively low heating and gas velocity. As the hot propellant gases are turned into the nozzle nose section, the heating rate and gas velocity increase significantly. Molten alumina particulates contained in the flow field and high gas-dynamic shear forces cause erosion of the inlet surfaces. Environmental conditions become the most severe in the constricted throat section. Note the large increase in surface heat transfer coefficient which leads to very high heating rates. Firing times range from tens of seconds to several minutes in duration. In addition to the critical thermal conditions noted, the propellant gases may also be highly oxidizing (about 10 percent oxygen species) and slowly vaporize carbonaceous surfaces. Throughout the motor firing it is of paramount importance to limit throat erosion to a predictable and minimal level in order to maintain the design chamber pressure and motor thrust.

The most critical parts of a solid propellant rocket are the nozzle components. Nozzles can generally be categorized as: (a) submerged, (b) external, (c) fixed, or (d) movable. The nozzle is initially convergent to the throat section. Beyond the throat the channel is





LOCATION	GAS PRESSURE (PSI)	GAS TEMPERATURE (F)	GAS VELOCITY (MPH)	ONE DIMENSIONAL CONVECTIVE HEAT TRANSFER COEFFICIENT + SPECIFIC HEAT (H/CP)
A INLET	500	5,500	60	0.08
A' NOSE	485	5,480	160	0.45
B THROAT	398	5,050	735	0.75
C EXIT	10	3,150	2,240	0.05

Figure 18. Schematic of Submerged and External Nozzles and their Environmental Parameters.

divergent, and the flow is accelerated to high supersonic speeds with an attendant decrease in pressure. Details of a nozzle vary with the application. They usually involve: (a) an erosion-resistant throat, (b) high-temperature insulation forward, aft, and behind the throat section, (c) an exit cone, and (d) an outer load-carrying structural material.

4.8.6.1 Nozzle Throats & ITEs

The function of a rocket nozzle throat is to restrict the hot gaseous flow and thereby maintain the chamber pressure for near-constant conditions. No throat recession would enable constant chamber pressure, but all materials are subject to varying degrees of recession due to the high temperature and particulate erosive conditions.

The requirement for improved nozzle throat materials for large rocket motors was due to great advances in solid propellant technology during the 1960s. These new solid propellants greatly increased the prospects for greater missile payload, weight, range, and reliability provided suitable nozzle materials could be developed. The new energetic propellants, however, created a host of materials problems because their environments were associated with (a) much higher combustion gas temperatures, (b) increased wall heating rates, (c) more corrosive and erosive exhaust gases, (d) higher operating pressures, and (e) larger gas-dynamic shear forces acting on the exposed material surfaces. To meet these challenges the U.S. propulsion community originated a complex nozzle design involving (a) ablative phenolic plastic parts for low heat transfer regions, (b) refractory tungsten, silver infiltrated porous tungsten, and polycrystalline graphites for the throat section, (c) metallic materials for structural containment of the individual nozzle parts, and (d) adhesives to bond the many pieces together. Most of the materials developmental activities were focused on obtaining improved erosion-resistant throats. Pyrolytic graphite and codeposited silicon-carbide/pyrolytic graphite-coated graphites were developed. The most popular throat assembly for large tactical and strategic solid propellant motors consisted of thin, multiple pyrolytic graphite washers. Plastic or elastomeric spacers had to be inserted between each washer to avoid material fracture as the insert expanded in response to motor firing. Pyrolytic graphite was thought to be the most acceptable material because it (a) exhibited low erosion rates (0.025 mm/s, 1.0 mil/s) in small-diameter (6.35 cm, 2.5 in) throats, (b) possessed anisotropic thermal conductivity for directional thermal control, (c) survived both hot and cold motor restarts, (d) performed satisfactorily for long firing durations, and (e) exhibited reasonable lifetimes at nozzle chamber pressures less than 13.8 MPa (2.0 ksi). Motor performance was generally acceptable with this type of complex assembly, but it also had inherent design problems and manufacturing scale-up challenges. Up to 20 different nozzle pieces had to be fabricated to high tolerances and then attached with temperature-sensitive adhesives.

Nozzle reliability was thus a constant issue. Hence, new materials were desperately needed to withstand the severe nozzle environment and to simplify nozzle design. CCC materials appeared to have the best prospects for satisfying all of these requirements, and for that reason, various material types were developed and tailored for use in solid rocket motor nozzles.

With the advent of CCC materials, a more reliable throat section became possible. First-generation 2-D CCC materials exhibited lower recession compared to ablative plastics but higher recession when compared to graphites. In addition the 2-D CCC throat materials had poor matrix-dominated mechanical properties. With subsequent development of high-density 3-D and n-D CCC constructions, revolutionary changes in nozzle design and motor performance became possible. Major systems benefits included (a) design simplicity (as little as 3 versus 18 major parts), (b) improved reliability, (c) surface contour control, (d) highly predictable and reproducible performance, (e) weight reduction of at least 10 percent, (f) adaptability to a very wide range of nozzle designs, (g) competitive costs, and (h) availability from several manufacturing sources.

Figure 19 is a schematic of a mid-1980 U.S. space solid-propellant motor. The throat package shown pertains to the first of two solid motors used in the U.S. inertial upper stage to carry payloads of about 2273 kg (5000 lb) from low-Earth orbit of the Shuttle Space Transportation System (STS) to geosynchronous orbit. Note that CCC materials are used for the inlet and nose sections of the throat assembly. A great diversity in materials was used in an effort to obtain the highest possible performance and at the lowest possible weight. In subsequent developments 3-D and n-D CCC materials were used for the integral throat-entrance section of nozzles.

4.8.6.2 Nozzle Exit Cones

The primary function of an exit cone is to control the expansion of hot exhaust gases and deliver the optimum level of thrust for the motor. This basic function must be performed without (a) excessive distortion, (b) structural instability, and (c) component failure.

The exit cone of a solid propellant motor is either (a) fixed, (b) movable, (c) locked-in-place, or (d) extendable. Movable nozzles are preferred for course correction during motor firing. Extendable exit cones (ECCs) are especially useful for upper-stage rockets to maximize thrust and minimize storage length. Small solid propellant rockets typically have a single exit cone of limited length and size. Larger rockets have one or more nozzles and exit

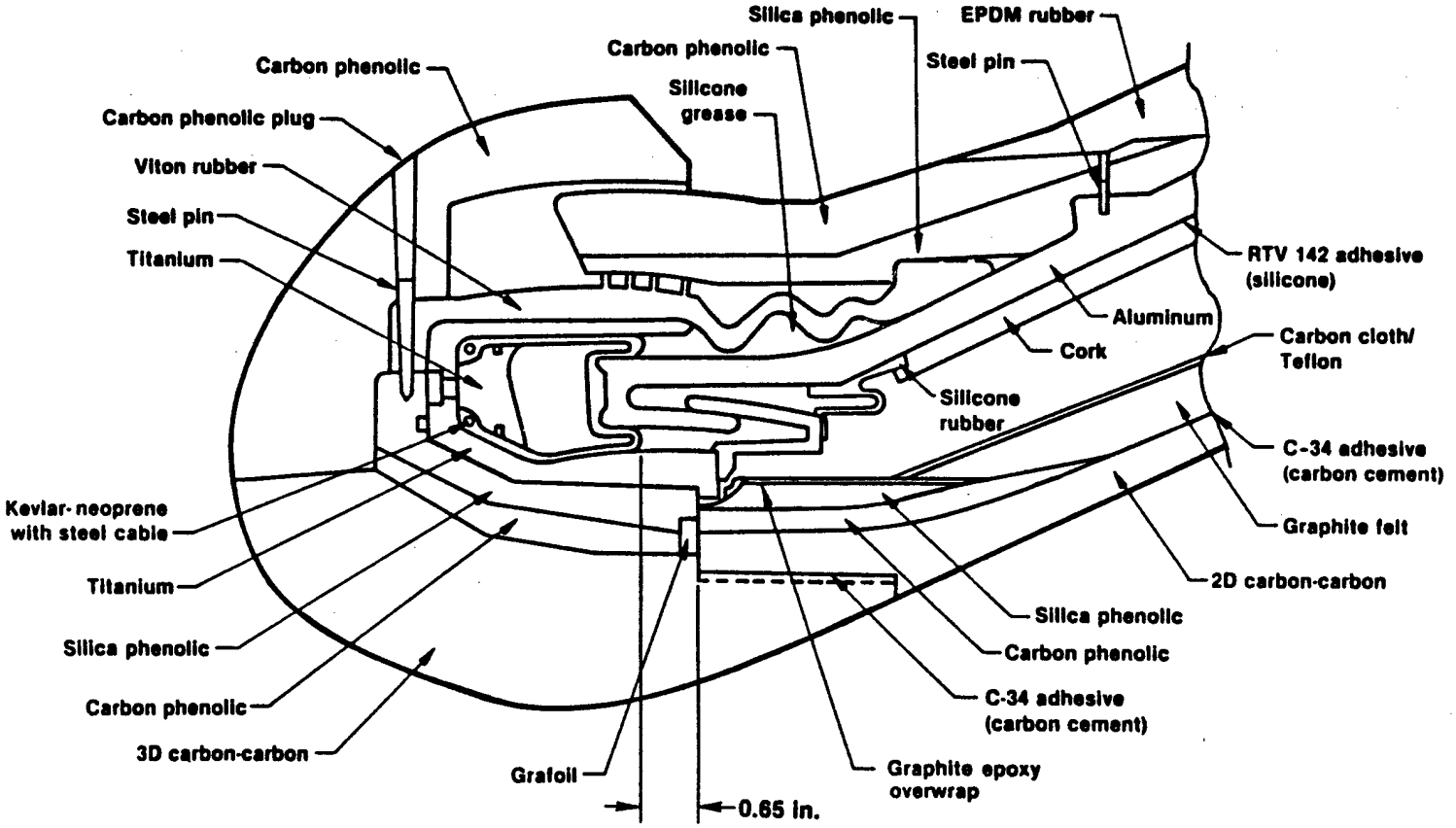


Figure 19. Schematic of a Space Solid Propellant Motor Nozzle Detailing the Assembly Complexity.

cones. Each exit cone is essentially identical to the other, but great variations may be observed in sizes, diameters and wall thicknesses.

The severity of the thermal environment decreases greatly as the propellant exhaust products leave the throat region and expand in the exit cone section of the motor. Other environmental changes include (a) relatively-high gas temperature, (b) flow acceleration to supersonic conditions, (c) sharp decrease in local pressure, and (d) an attendant decline in the surface heating rate.

First-generation motor nozzle exit cones were composed of high-temperature metallics, but with increases in propellant flame temperatures and heating rates, ablative plastic composites became the materials of choice. Composites containing asbestos, glass, silica, quartz, and carbon fiber-reinforced phenolic resins became state of the art. Both 2-D tapewrapped and involute reinforced constructions were widely used. The ablative composites were adhesively bonded to an external metallic structural shell.

The advent of CCC materials provided an opportunity to use higher-performance and lighter-weight composites in motor exit cones. Advanced nozzle designs were also possible in which the CCC material served jointly as the ablative liner and the structure. The single design material (CCC) enabled nozzles with (a) less weight, (b) reduced volume envelope, (c) less assembly complexity, and (d) lower production costs. These results can be directly translated into increased missile thrust performance for range extension or increased payload weight.

CCC composites have many intrinsic properties which lend themselves for uses in solid propellant motor nozzle exit cones. They include: (a) low linear recession, (b) retention of stiffness and strength at high temperatures, (c) low mass density, and (d) low reactivity with the chemical and particulate species of solid propellant gases.

State-of-the-art 2-D CCC materials, when used in a thin, self-supporting structure, have certain limitations. They include (a) the usual low matrix-dominated properties, (b) composite property sensitivity to defects, (c) high costs and long time fabrication, and (d) lack of structural redundancy as in a supported ablative exit liner. Due to the high structural loading of some motor exit cones, they occasionally fail in ground-based motor firings or in actual operational use. Most of these difficulties are due to the use of a threaded cylindrical attachment for the nozzle assembly.

In spite of the occasional failure of 2-D CCC exit cones, these materials have made important contributions to both ground-launched and space rocket motors. Lightweight and thin-walled CCC exit cones have been used successfully on the (a) operational U.S. Peacekeeper Stage III, (b) inertial upper stages (IUS), (c) STAR series of space motors, and (d) other solid propulsion applications.

3-D CCC exit cones may possibly be the answer to the exit cone reliability problem. Numerous types of 3-D and n-D CCC exit cones have been fabricated and motor tested. Figure 20 is a schematic of an advanced solid propellant rocket motor nozzle with a 3-D CCC exit cone. The performance of 3-D CCC exit cones to date has been less than satisfactory. The material has intrinsic fail-safe features, but the need for a thin structure complicates the through-the-thickness reinforcement needed to withstand structural loads. Additional 3-D CCC exit cone concepts will surely be developed, and it is expected that state-of-the-art 2-D CCC exit cones will gradually yield to more reliable 3-D and n-D CCC constructions.

4.8.6.3 Thrust Vector Control Components

The thrust from a solid propellant motor can be vectored with (a) movable nozzles or (b) a thrust vector control (TVC) system. In the latter system hot gases are bled from the motor chamber and injected through the nozzle exit cone wall. A hot gas valve (HGV) is the key component in such TVC systems. It is composed of (a) pintle, (b) outlet nozzle, (c) casing, (d) pintle insulator, (e) valve insulator, and (f) hot gas inlet. Figure 21 is an illustration of a hot gas valve with a blunt pintle.

With availability of high-density, multidirectionally-reinforced CCC materials, the prospects for an efficient hot gas valve design became more of a reality. Prototypes developed by the French SEP organization contained (a) high-density 4-D or 3-D CCC for the pintle and outlet nozzle, (b) high-density 4D CCC for the casing, (c) low-density CCC for the pintle insulator, (d) special 3-D CCC for the valve insulator, (e) insulative silica/phenolic composite for the hot gas inlet, (f) metal actuator rod, and (g) steel housing. Solid propellant tests conducted in both France and the U.S. demonstrated the feasibility of the hot gas valve. These positive tests proved a breakthrough in the HGV challenge, due mainly to the use of advanced CCC materials and a reliable pintle-valve concept. The main problem encountered was a significant amount of alumina deposit on the chamber wall. Additional design work is underway to minimize this problem and improve valving of the highly energetic gases.

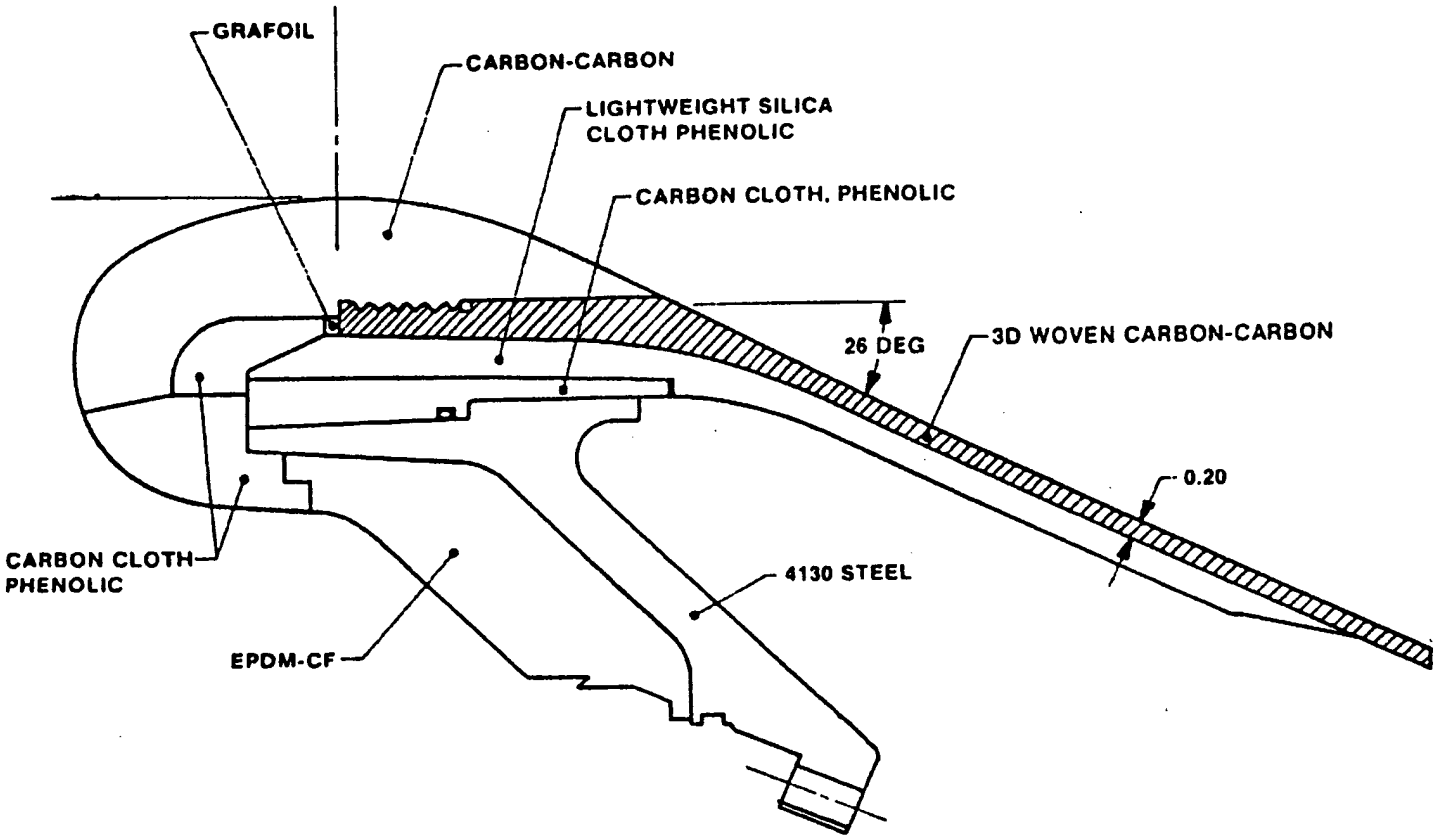


Figure 20. Schematic of an Advanced Solid Propellant Rocket Motor Nozzle.

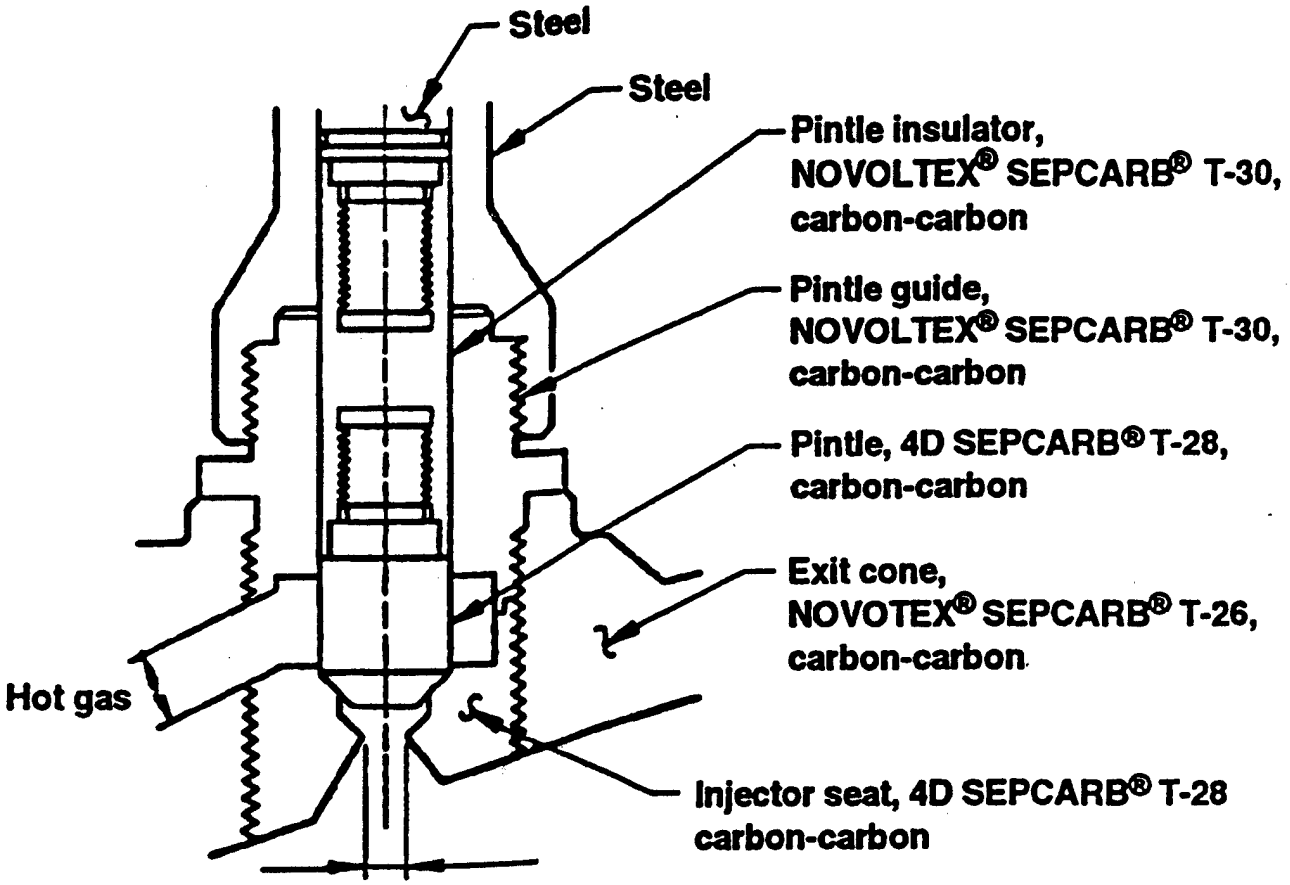


Figure 21. Schematic of a TVC Hot Gas Valve for a Solid Propellant Motor.

4.8.6.4 Blast Tubes

Certain solid propellant motor systems, like anti-aircraft missiles, contain a long blast tube. It is designed to conduct hot gaseous products to a distance nozzle, and in some cases redirect the flow through the nozzle assembly. First-generation blast tubes used heavy tungsten or lightweight ablative plastic composites to contain the corrosive and erosion propulsion gases. Since the newly-available CCC materials had demonstrated low ablation rates in these types of environments, prospects were high that the materials could be used as liners in blast tubes or as insulated blast tubes. Prototypes of these concepts were fabricated and tested. It was demonstrated that solid propellant gases could be turned up to 90° with CCC containment materials. The CCC materials were also prototyped in the form of hot gas roll control valves.

Table 41 lists many of the CCC prototypes developed for solid rocket motor applications and the year of their development. These components include (a) nozzle throats, entrance caps, and integral throat entrance (ITE) sections, (b) TVC hot ball and socket assemblies, (c) fixed and deployable exit cones, (d) hot gas injection ports, (e) hot gas valves and tubing, (f) pintle throats, end caps and shields, (g) insulative throat backup structures, (h) blast tube liners, and (i) other critical components.

4.8.6.5 Chronology

Table 42 lists the chronology of CCC prototypes for solid propellant motors.

4.8.6.5.1 *The 1950s*

Prior to the 1950s rocket nozzle throats were composed of refractory metals like tungsten or brittle ceramics like polycrystalline graphites. By the mid-1950s graphites had gained acceptance as throat materials in small rocket nozzles. It was thought (incorrectly) that much larger diameter graphite and oxidation-resistant graphite billets would be needed for the impending larger diameter solid propellant motors. Accordingly, the U.S. Air Force in 1959 contracted for a $21M program to develop graphite billet sizes up to about 0.76 m (30 in) in outer diameter. This three-year program met its objective, but one-piece, thick-walled graphite nozzle throats routinely cracked during motor firing because thermostresses exceeded the intrinsic properties of the material. The large-diameter graphite nozzle throats were later sectioned to relieve thermally-induced expansion and stress, but very limited success was obtained with this design approach. Large-diameter solid propellant motors designers then began to avoid graphite nozzle throats and focus on pyrolytic graphite. Developmental progress was very slow,

TABLE 41
FIRST CCC PROTOTYPE COMPONENTS FOR SOLID PROPELLANT ROCKET MOTORS

YEAR	PROTOTYPE	ORGANIZATION
1962	Nozzle exit cone	HITCO/USA
1963	Multiple-section, bonded entrance-throat-exit cone assembly	Thiokol Chemical Corporation/Elkton Division/USA HITCO/USA
1963	Nozzle graphite throat insulated with low-density CCC material	Union Carbide Corporation/Carbon Productions Division/ USA
1965	Pintle end cap	San Rafael Plastics Company/USA
1966	Igniter container	San Rafael Plastics Company/USA
1966	Hot gas injection ports for thrust vector control	Thiokol Chemical Corporation/Wasatch Division/USA Union Carbide Corporation/Carbon Products Division/USA
1971	Blast tubes of hot gas roll control valve systems	Thiokol Chemical Corporation/Wasatch Division/USA
1976	Nozzle integral throat-entrance cap (ITE) component	Fiber Materials, Inc.
1976	Thrust vector control hot ball and socket	United Technologies Corporation/Chemical Systems Division/USA Fiber Materials, Inc./USA
1982	Low-cost, autowoven reinforced 3-D CCC nozzle ITE	Avco Corporation/Systems Division/USA
1985	Automatic woven 3-D fibrous graphite-reinforced CCC exit cones	Aerospatiale/FRANCE
1985	Low-cost, short fiber 3-D reinforced CCC exit cones	Societe Europeenne de Propulsion (SEP)/FRANCE
1986	Hot gas valve with pintle, insulator, outlet nozzle and casing for solid rocket motor	Societe Europeenne de Propulsion (SEP)/FRANCE
1991	3-D braided reinforced CCC nozzle exit cone	Albany International Research Corporation/USA U.S. Composites Corporation/USA
1993	Very large, autowoven 3-D reinforced CCC ITE for Ariane 5 launch vehicle	Societe Europeenne de Propulsion (SEP)/FRANCE
1994	Manifolds for solid propellant gas generators	Kaiser Aerotech/USA

TABLE 42

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1962	2-D CCC exit cone fabricated and tested 30 seconds on a solid propellant motor	First 2-D CCC nozzle exit cone for a solid propellant motor	HITCO (Exit Cone)/USA Thiokol Chemical Corporation/Huntsville (Motor Firing)/USA
1963	2-D CCC entrance-throat-exit component fabricated and tested on a solid propellant motor	First 2-D CCC nozzle assembly for solid propellant motors	HITCO (CCC Assembly)/USA Thiokol Chemical Corporation/Elkton Division (Motor Firing)/USA
1965	2-D molded carbon fiber/pitch resin CCC forward exit cone fabricated and motor tested	First large tactical solid propellant motor (SRAM) with a 2-D CCC nozzle part	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA Union Carbide Corporation/Carbon Products Division (CCC Material)/USA
1966/67	2-D molded carbon fiber/pitch resin CCC and 2-D tapewrapped CCC hot gas injection ports fabricated and static motor tested	Largest 2-D CCC components to date for hot gas thrust vector control of large (60 in. and 120 in. diameter) solid rocket motors	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA Union Carbide Corporation/Carbon Products Division (CCC Material)/USA Western Backing Company (Tapewrapped CCC Material)/USA
1968	2-D CCC fabricated for rocket motor nozzle throat	First prototype CCC throat for a tactical (SRAM) solid propellant rocket motor nozzle	Carborundum Company/USA
1968	2-D CCC fabricated and tested for the nose inlet section of a gimballed, thrust vector control (TVC) submerged rocket nozzle	First use of 2-D CCC at the nose inlet of a movable nozzle for a post-boost propulsion system CCC part successfully survived a high oxidizing gas, low pressure, and long burn time (150-300 sec) solid propellant exhaust firing	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA BP Chemicals/U.S. Polymeric (CCC Manufacturer)/USA

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1969	2-D laminated CCC ring fabricated and tested for the throat of a quick-turn tactical solid motor	First use of 2-D CCC throat in a movable nozzle design and exhaust products of low oxidizing gas, high pressure (1700 psi) and short (3 sec) burn time	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA Carborundum Company (Laminated CCC Material)/USA
1970	CCC throat sections fabricated and tested in a solid propellant motor	First demonstration (outside the U.S.) of CCC in solid rocket motor nozzles	Societe Europeenne de Propulsion (SEP)/ FRANCE
1971	Pyrolytic graphite-coated CCC nozzle components successfully fabricated and flight tested	Low erosion of coated CCC material demonstrated in actual flightweight solid rocket motor nozzle	Super-Temp Company (Nozzle Part)/USA AF Space & Missile Systems Organization/ USA
1971	2-D CCC liners fabricated and tested in 90° turns of blast tubes of a hot gas roll control valve system	First 2-D CCC used in blast tubes for control of severe gas/particle erosion	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA Carborundum Company (2-D CCC Material)/USA
1971	2-D involute STAR 17 CCC exit cone designed, fabricated, and successfully test fired in simulated high altitude conditions for 150 sec in an exhaust temperature of 3105°C (5620°F)	One of the first demonstrations that thin-walled (0.065 in.) CCC are suitable for exit cones of space solid propellant motors	Thiokol Corporation/Elkton Division (Exit Cone Design)/USA HITCO (Exit Cone Fabrication)/USA Arnold Engineering Development Center/ AFSC (Motor Firing)/USA
1971	2-D flat laminate CCC rings fabricated and tested in a large (12" dia. I.D.) throat of a submerged nozzle	First large submerged nozzle with a 2-D CCC throat material	Thiokol Chemical Corporation/Wasatch Division (Motor Design & Test)/USA Carborundum Company (2-D CCC Material)/USA Haveg Industries (2-D CCC Material)/USA BP Chemicals/U.S. Polymeric (2-D CCC Material)/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1972/74	2-D laminated CCC rings fabricated and static tested as forward and exit sections of a pyrolytic graphite throat in a TVC submerged nozzle	First production solid propellant motor nozzle with high density (1.8 g/cm^3) 2-D CCC nozzle components developed with PAN-based carbon fiber reinforcement High-density (1.8 g/cm^3) PAN-based carbon fabric CCC and regular density (1.60 g/cm^3) rayon-based carbon fabric CCC demonstrated to be adequate for near-throat regions of large production solid propellant motor nozzles	Thiokol Chemical Corporation/Wasatch Division (Joint Venture)/USA Hercules, Inc./Utah Operations (Joint Venture)/USA
1973	Large CVD pyrolytic graphite-coated 2-D CCC nozzle throat fabricated	First full-scale PG coated CCC throat for solid propellant motor	HITCO/USA
1974	2-D involute graphite (rayon-based) fabric/CCC exit cone fabricated for third stage of U.S. Navy C-4 solid rocket motor	Lightweight CCC exit cones showed high potential for use on upper stages of submarine launched ballistic missiles	HITCO (Exit Cone Fabrication)/USA Thiokol Chemical Corporation/Wasatch Division (Exit Cone Design and Test)/USA
1974	Thin (0.080 in. thick) 2-D involute CCC exit cone designed, fabricated, and test fired at simulated high altitude conditions on a STAR 30 space solid propellant rocket motor nozzle	2-D CCC exit cone performance certified by simulated high altitude motor firing	Thiokol Corporation/Elkton Division (Exit Cone Design)/USA HITCO (2-D CCC Exit Cone)/USA AF Arnold Engineering Development Center/AFSC (High Altitude Motor Firing)/USA

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1975	Joint Air Force program initiated to fabricate and evaluate advanced CCC materials for ITEs of future solid propellant motor nozzles	State-of-the-art pyrolytic graphite washer nozzle throats were complicated, costly, and occasionally failed during firing More severe exhaust of Peacekeeper solid rocket motors required improve materials Most promising CCC materials evaluated for future motor uses Established a methodology for transitioning promising CCCs from development to engineering design Involved 11 domestic suppliers of CCC materials A new and large potential outlet for 3-D CCC materials Air Force and Navy later invested $28M during 1977/81 for 3-D CCC ITE technology	Air Force Materials Laboratory/AFSC/ USA Air Force Rocket Propulsion Laboratory/ AFSC (Motor Tests)/USA Aerospace Corporation (ITE Post-Test Analyses)/USA CCC Materials Suppliers/General Electric, Haveg, Brochier, SAIC, Super-Temp, McDAC, Oak Ridge Y-12 Plant, Union Carbide Corp., Textron Specialty Materials, Edler, and HITCO/USA McDonnell Douglas Astronautics Company (Post-Test Analyses)/USA Southern Research Institute (Properties)/ USA United Technologies/CSD (Nozzle Assemblies)/USA
1976	2-D involute CCC exit cone (25-in. exit diameter) flight tested on a space vehicle motor 7	First flight test of a 2-D CCC motor exit cone	Aerojet-General Corporation (Nozzle Design)/USA
1976	3-D pierced fabric CCC ITEs manufactured	First full-scale nozzle ITE for first-stage motor of AF Peacekeeper (MX) solid propellant missile	Avco Corporation/Systems Division/USA
1976	3-D CCC integral throat-entrance cap (ITE) nozzle parts fabricated	First full-scale prototype ITE parts for upper-stage solid propellant launch vehicles	Fiber Materials, Inc./USA
1976	2-D involute graphite (rayon-based) fabric CCC exit cone fabricated for STAR 48 space solid motor	2-D involute CCC of greater interest for high-performance space solid propellant motor nozzles	HITCO/USA

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1976	4-D CCC nozzle throat successfully fired in a full-scale solid propellant rocket motor	First demonstration of 4-D CCC utility in space solid propellant motors	Fiber Materials, Inc. (Carbon-Carbon Nozzle Throat)/USA Morton Thiokol Corporation/Elkton (Motor Firing)/USA
1976	Over 200 solid propellant rocket motor nozzle parts (up to 300 mm throat diameter) of 4-D CCCs manufactured and successfully test fired in various ground-based test facilities and flight tests	4-D CCC demonstrated adequate performance in a wide variety of solid propellant rocket motor nozzles Two major types (3-D and 4-D) of CCC became available for use in solid propellant rocket motor nozzles	Societe Europeenne de Propulsion (SEP)/ FRANCE
1976	3-D CCC nozzle throat and 2-D exit cone successfully static fired on a STAR 48 solid propellant rocket motor	Demonstrated utility of various CCC materials in large space motor nozzles and exit cones Greatly increased designers interest in CCC exit cones as a lightweight replacement for 2-D carbon fabric/phenolic composite ablative materials	Thiokol Corporation/Elkton Division (Nozzle Design)/USA General Electric Company/Re-Entry & Environmental Systems Division (ITE)/ USA
1976	Thin (0.080 in. thick) low-density (1.40 g/cm^3) 2-D involute CCC exit cone designed, fabricated, and test fired (sea level) on a STAR 48 space solid propellant rocket motor nozzle	Lightweight 2-D CCC exit cone use demonstrated on large space solid propellant motors	Thiokol Corporation/Elkton Division (Exit Cone Design & Motor Firing)/USA HITCO (2-D CCC Exit Cone)/USA
1976	CCC hot ball and socket successfully tested in solid propellant rocket motor nozzle	First ground-based test of an ultra-simple thrust vector control (TVC) nozzle	United Technologies Corporation/Chemical Systems Division/USA
1976	Over 150 CCC nozzle throats successfully evaluated with a range of sizes (0.25-14 in. diameter), motor pressures (500-1400 psi), and burn durations (15-155 sec)	No nozzle throat material failures were observed Fail-safe features of CCC throat materials became obvious	Various Sources/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1976	About one-fifth of pyrolytic graphite nozzle throats failed during engineering development of a launch vehicle propulsion system	Reliability of pyrolytic graphite throats for advanced solid propulsion systems questioned Increased prospects for using 3-D CCC throats in launch vehicle solid motors	Various Propulsion Company Sources/USA
1981	3-D pierced fabric CCC ITE with a 2-D tapewrapped throat support manufactured and tested for large, submerged production rocket nozzle	First production solid propellant motor using a 3-D PAN-based carbon fiber CCC ITE	Thiokol Chemical Corporation/Wasatch Division (Motor Design and Test)/USA Textron Specialty Materials (3-D CCC Materials)/USA
1981	CCC nozzle ITEs and throats baselined for all new U.S. ballistic missile and space motor systems	U.S. Peacekeeper three stages, IUS two stages, Scout third stage, Atlas dual Apogee burn motors, Trident II and IPSM space motors took advantage of CCC performance features	Various Propulsion Company Sources/USA
1982	3-D autowoven preform and CCC fabricated for nozzle exit cones	First demonstration of reliable 3-D CCC for solid rocket motor exit cones	Avco Corporation/Systems Division/USA
1982	Helix wound/pierced fabric and woven conical fabric CCC exit cones fabricated	Alternate material fabrication approaches for producing CCC nozzle exit cones	Avco Corporation/Systems Division/USA
1982	CCC materials developed for valve parts and tubing of solid propellant rocket motors	Excellent hot gas control and insulation of metallic parts demonstrated in new CCC propulsion applications	Societe de Europeenne Propulsion (SEP)/ FRANCE
1982	Lightweight CVD welded CCC membrane nozzle exit cone fabricated and tested	First domestic firing of a French advanced CCC exit cone assembly	United Technologies Corporation/Chemical Systems Division (Motor Firing)/USA Societe Europeenne de Propulsion (SEP) (Exit Cone)/FRANCE
1982	Twenty-nine successful static firings of 3-D CCC ITEs and 2-D CCC exit cones on second-stage (SRM-2) of the inertial upper stage space solid motor	Demonstrated reliability of 3-D CCC ITEs and 2-D CCC exit cones for heavy space solid rocket motor nozzles	United Technologies Corporation/Chemical Systems Division/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1982	Advanced thickness-compliant, thickness-stiffened, and lightweight exit cone concepts were analyzed and promising concepts selected for fabrication	A 3-D pierced fabric CCC and thin membrane CCC concepts were selected for fabrication and motor tests	United Technologies Corporation/Chemical Systems Division/USA
1983/85	Noninvolute 2-D CCC exit cone construction concepts analyzed and demonstrated	Promising CCC exit cone constructions identified and several concepts verified Attempt to extend 3-D CCC ITE technology to thin-walled exit cones	Hercules Aerospace Company/USA
1983	Flight test of 2-D CCC extendable exit cone system and 3-D CCC ITE on AF Peacekeeper third-stage motor	First flight test of strategic missile with CCC extendable exit cone system and 3-D CCC ITE	Hercules Aerospace Company/USA
1983	2-D CVI involute CCC exit cones performed successfully on 18 flight STAR 48 exit cones of the Delta-class PAM-D system	Reliability of 2-D CCC for exit cones increased	Morton-Thiokol, Inc./Elkton Division (Motor Design)/USA HITCO (EC Fabrication)/USA
1983	CCC integral ball and exit cone (hot ball and socket) components successfully tested on a solid propellant motor	First test of a single, integral piece movable CCC nozzle	United Technologies Corporation/Chemical Systems Division/USA
1983	Upgraded and lightweight CCC membrane exit cone fabricated and successfully motor tested	Very high-performance space solid propellant motor nozzle performance demonstrated	United Technologies Corporation/Chemical Systems Division (Motor Firing)/USA Societe Europeenne de Propulsion (SEP) (Exit Cone)/FRANCE
1984	Standardized production, fabrication, processing and quality assurance procedures were established for 2-D involute CCC motor exit cones	Manufacturing specifications established for lightweight, thin-walled nozzle exit cones Fifteen CCC exit cones manufactured in a production environment	Aerojet Strategic Propulsion Company (Exit Cone Design & Management)/USA Haveg-Reinhold (Exit Cone Fabrication)/ USA Kaiser Aerotech (Exit Cone Fabrication)/ USA HITCO (Exit Cone Fabrication)/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1984	CCC component development, sea level testing, and three flight proof tests completed for the strategic missile (Peacekeeper) propulsion systems	3-D CCC ITEs baselined in each of two propulsion stages and 2-D involute CCC extendable exit cones baselined for stage III motor	Air Force Space & Missile Systems Organization/AFSC/USA
1984	2-D involute CCC exit cones failed during space firing of STAR 48 solid propellant motors	Westar 6 and Palapa B-2 satellites stranded in an incorrect space orbit Insurance losses for each satellite were about $75-105M Heavier, ablative 2-D carbon fabric/ phenolic exit cones replaced 2-D CCC exit cones on future STAR 48 motors	HITCO (Exit Cones)/USA Morton-Thiokol Corporation/Elkton Division (STAR 48 Motor)/USA McDonnell Douglas Government Aerospace (Payload Assist Module-PAM)/ USA
1984	PAN-based and pitch-based carbon fabric CCC exit cones successfully tested on a 10,000 lb solid propellant motor	Potential of higher strength and higher stiffness (compared to rayon-based carbon fabric reinforced) exit cones demonstrated	Jet Propulsion Laboratory/California Institute of Technology/USA
1984	3-D CCC ITE advanced development program completed for 1st and 2nd stage Trident-II propulsion systems	3-D CCC throat region materials demonstrated outstanding performance compared to alternate materials	Morton-Thiokol, Inc./Wasatch Division (Joint Venture)/USA Hercules, Inc./Utah Operations (Joint Venture)/USA
1984	Very thin (0.5 cm, 0.2 in.) 3-D CCC "Novoltex" (TM) exit cone test fired for 30 seconds on a solid propellant motor	First French ground test firing of a low-cost high-performance 3-D CCC exit cone	Societe Europeenne de Propulsion (SEP)/ FRANCE
1984	3-D and 2-D CCC materials test fired for nozzle throat and nested, extendable exit cone for improved performance space motor (IPSM)	CCC materials become increasingly attractive for space solid motor throats and exit cone applications	Morton-Thiokol Corporation/Wasatch Division (Motor Design)/USA AF Arnold Engineering Development Center/AFSC (High Altitude Motor Firing)/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1984	2-D CCC exit cone manufacturing experienced high rejection rate in U.S.	About one-fourth of exit cones failed during processing or use Types of defects were identified as delaminations, wrinkles, low-density indications, machining errors, processing anomalies, and inadequate properties Across-the-board improvements required to maximize the acceptability and use of 2-D involute CCC exit cones	Various Sources/USA
1985	Potential of CCC materials assessed for use in tactical solid motors	CCC useful when structural and thermal requirements are critical Significant CCC cost reductions are needed to enhance potential uses	Aerojet Strategic Propulsion Company/ USA
1985	Automatic woven 3-D fibrous graphite/CVD PG CCC exit cone fabricated	3-D CCC constructions extended from nosetips to nozzle exit cones	Aerospatiale/FRANCE
1985	2-D CCC extendable exit cone and 3-D CCC ITE successfully ground tested in advanced solid rocket motors	Advanced CCC materials provided weight savings opportunities for solid rocket motor nozzles Increased confidence in using CCC for medium-to-large solid propellant motor nozzles	Air Force Rocket Propulsion Laboratory/ AFSC (Motor Firing)/USA Textron Specialty Materials (3-D CCC ITE)/USA Hercules Aerospace Division (Design)/ USA Aerospatiale (Fixed Exit Cone & Forward EEC)/FRANCE Kaiser Aerotech (Densification)/USA Kaiser Aerotech (Advanced 2-D Involute EC)/USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1985	High-density, braided 3-D ITE and exit cone successfully static fired on a solid propellant motor	Very low erosion rates were measured Another preform reinforcement scheme for CCC nozzle materials	Albany International (Braided Preform)/USA General Electric Company/Re-Entry Systems Operations (HIPIC Densification)/ USA Morton-Thiokol Corporation/Elkton (Motor Firing)/USA
1985	Three-stage M4 solid rocket motors containing carbon-carbon nozzles entered service on French nuclear submarines	Increased usage of CCC materials in long-range strategic rocket motors	Societe Europeenne de Propulsion (SEP)/ FRANCE
1985	3-D CCC "Novoltex" (TM) throat tested in a solid propellant motor nozzle	First successful test of 3-D "Novoltex" (TM) in a solid propellant motor nozzle throat Lower-cost CCC nozzle throat performed well during 30-second firing	Societe Europeenne de Propulsion (SEP)/ FRANCE
1985	Course autowoven-TM, high-density 3-D CCC exit cone fabricated and successfully tested	First 3-D CCC exit cone fabricated in the U.S. Fail safe features of 3-D CCC nosetips extended to solid rocket nozzle exit cones Identified a need for fine woven reinforcement and a lower-density matrix	Textron Specialty Materials (Exit Cone)/ USA Air Force Rocket Propulsion Laboratory/ AFSC (Motor Firing)/USA
1985/86	3-D CCC integral throat entrances fabricated and successfully tested in advanced solid propellant motors	High-performance solid propellant rocket motor throats demonstrated for potential uses on the Navy Trident D5 and the AF small ICBM	Textron Specialty Materials (ITEs)/USA Morton-Thiokol Inc./Wasatch Division (ITE Firings)/USA Aerojet Strategic Propulsion Company (ITE Firings)/USA

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1985	High percentage of 2-D CCC exit cones on flight-qualified space solid motors survived ground and flight testing	90% of CCC exit cones performed successfully in ground tests 95% of CCC exit cones performed successfully in flight tests Significant improvements required in nozzle design and materials for future high-performance, upper-stage propulsion	Various Propulsion Companies/USA
1986	Thin-walled, 3-D CCC Novoltex-TM exit cone successfully test fired on a Minuteman Stage III motor	New 3-D CCC material for high-performance solid rocket motor nozzles	Air Force Rocket Propulsion Laboratory/ AFSC (Motor Firing)/USA Societe de Europeenne de Propulsion (SEP) (Nozzle Exit Cone)/FRANCE
1986	CCC nozzle successfully test fired on an advanced Pershing II missile	The CCC nozzle reportedly doubled the range of the Pershing IA missile CCC materials technology extended from ICBM to IRBM nozzles	Martin-Marietta/USA
1986	Four CCC "Novoltex-TM" exit cones were fabricated and evaluated by U.S. propulsion companies	3-D CCC "Novoltex-TM" exit cones were candidates for new U.S. ballistic missile solid rocket motors	Society Europeenne de Propulsion (SEP)/ FRANCE
1986	3-D and n-D CCC parts (pintle, pintle insulator, outlet nozzle, and casing) fabricated and successfully tested in a hot gas valve of a solid rocket motor	Breakthrough in hot gas valve technology for thrust vector control of solid rocket motors CCC parts accommodated 2000°C, but previously-used metallic parts were limited to about 1300°C	Societe Europeenne de Propulsion (SEP)/ FRANCE
1987	French 3-D "Novoltex-TM" CCC exit cone successfully test fired at 10 kft simulated altitude on a STAR 30B space solid motor	Successful demonstration of 3-D CCC exit cone for potential space solid motors	Air Force Astronautics Laboratory/AFSC (Motor Firing)/USA Societe Europeenne de Propulsion (SEP)/ FRANCE

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1987	Design, fabrication and test of integrated CCC nozzle and exit cone assembly	Demonstration of CCC ability to replace multi-piece nozzle assembly components with single-piece material structures for weight and reliability gains	Fiber Materials, Inc./USA
1987	Filament-wound 2-D CCC motor exit cones fabricated	Alternate manufacturing process for solid rocket nozzles exit cones	HITCO/USA Hercules Aerospace Company/USA
1987	Production facility established for 3-D woven CCC exit cones and ITEs using both CVD and pitch HIPIC densification methods	First U.S. rocket motor manufacturer to produce own CCC nozzle components	Hercules Aerospace Company/USA
1987	Flight test of Navy Trident II (D-5) missile with 3-D CCC ITEs in nozzle	First U.S. Navy strategic missile with CCC ITE in nozzle	Hercules Aerospace Company/USA
1987	3-D CCC throat successfully tested on 27-in. diameter space solid motor with nozzle moved over 4°	First demonstration of thrust vector control with a space solid motor	Morton-Thiokol Corporation/Elkton Division/USA
1987	More than 200 2-D CCC exit cones used on space solid propellant STAR 30, 37, & 48 rocket motor nozzles	60 2-D CCC exit cones successfully used in flight Two flight and four ground-based static test firings resulted in CCC failures	Morton-Thiokol Corporation/Elkton Division (Exit Cone)/USA BP Chemicals (HITCO) Inc. (Exit Cone Fabrication)/USA
1987	2-D involute CCC critical failure mode was identified for O.D. restrained exit cones of solid rocket motors	Fill direction compression was determined to be CCC critical failure mode during motor firing Across-ply tension and interlaminar stresses generated during CCC processing were also shown to be critical	Morton-Thiokol, Inc./Wasatch Operations/ USA

TABLE 42 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1987/92	CCC hot gas valve fabricated for a nozzle thrust vector control system and successfully tested on a solid propellant motor	Advanced thrust vector control system demonstrated with 3-D and 4-D valve parts	Societe Europeenne de Propulsion (SEP) (Valve)/FRANCE UTC/Chemical Systems Division (Design)/ USA Air Force Phillips Laboratory (Test)/USA
1987	Lightweight 2-D CCC exit cones flight tested without failure on space solid propellant geostationary "MAGE" motor	Increased reliability demonstrated for 2-D CCC on space solid propellant motors	Societe Europeenne de Propulsion (SEP)/ FRANCE
1987	Ultrafine woven 3-D CCC "Novoltex" material evaluated in a solid propellant motor nozzle test	First domestic motor firing of "Novoltex" CCC exit cone	UTC/Chemical Systems Division (Motor Firing)/USA Societe Europeenne de Propulsion (SEP) (Exit Cone)/FRANCE
1988	Automated woven 3-D CCC exit cone successfully test fired on a full-scale third-stage small ICBM solid motor	Autowoven carbon fiber-reinforced CCC technology extended from motor ITEs to exit cones	AF Arnold Engineering Development Center/AFSC (Test Firing)/USA Hercules Aerospace Company (Exit Cone)/ USA
1988	CCC materials developed for nozzle throats and exit cones of solid propellant motors	CCC materials became baseline composites for advanced solid propellant motor nozzles	Nisson Motor Company/JAPAN
1988	High-density (1.90 g/cm^3) 3-D CCC "Novoltex-TM" throat successfully flight tested on a solid propellant motor	First French flight test of a higher-performance CCC nozzle throat	Societe Europeenne de Propulsion (SEP)/ FRANCE
1989	2-D involute CCC exit cones were used on Air Force IUS, Peacekeeper 3rd stage, and space shuttle payload assist module solid propellant motors	2-D CCC materials continue to replace ablative carbon fabric/phenolic resinous composites in solid propulsion nozzles	Air Force Ballistic Missile Office/AFSC/ USA

TABLE 42 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	3-D CVI CCC exit cone failed during its first flight test on a U.S. advanced strategic rocket motor nozzle	Exit cone performance was sensitive to CCC properties CCC properties were sensitive to specific processing parameters employed	Aerojet Solid Propulsion Company (Motor Manufacturer)/USA Societe de Europeenne Propulsion (SEP) (Preform)/FRANCE BFGoodrich Aerospace/Super-Temp (CVI Densification)/USA
1989	3-D CCC ITE manufactured for 120-in. diameter solid rocket motor nozzle of the Ariane V launch vehicle	Believed to be the largest CCC rocket nozzle part fabricated to date for an operational launch vehicle	Societe de Europeenne Propulsion (SEP)/ FRANCE
1990	Fabrication and test of intercepter missile braided CCC exit cones	Demonstration of application of 3-D braided materials for exit cone applications	Fiber Materials, Inc./USA
1990	First launch of Air Force Delta II with GEM strap-on boosters-used CCC ITEs in nozzles (nine strap-on motors per launch)	First ground launch vehicle to use 3-D CCC nozzle ITEs	Hercules Aerospace Company/USA
1990	Flight test of air-launched Pegasus satellite launch vehicle with 3-D CCC ITEs (three stages)	First air-launched booster to utilize 3-D CCC nozzle components	Hercules Aerospace Company/USA
1990	Filament-wound PAN-based carbon fiber tape CCC exit cones in 10 in. diameter	Improved property structure coupled with greatly-reduced labor cost and the potential to scale process to much larger exit cones	Jet Propulsion Laboratory/California Institute of Technology/USA
1990	Rhenium-coated 4-D CCC fabricated and evaluated in the throat and blast tube of solid rocket motors	Coating thickness and adhesion to CCC substrate were critical to successful use	Ultramet (Coating)/USA Thiokol Corporation/Wasatch Division (Motor Firing)/USA
1991	Advanced 3-D braided exit cones were fabricated for rocket motor tests	Alternate 2-D and 3-D braided CCC materials developed for solid motor test evaluations Nonproprietary densification processing was used	Albany International Research Corporation (Preforms)/USA Atlantic Research Corporation (Preforms)/ USA U.S. Composites Corporation (Densification)/USA

TABLE 42 (Concluded)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SOLID ROCKET MOTOR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1991	High-strain, noncommercial polycrystalline graphite qualified as a replacement for 4-D CCC throat material for Mk 111 Tomahawk booster	Bulk graphite materials were lower cost than 4-D CCC materials High cost of reactivating graphite production, obtaining design data and motor firings undoubtedly raised delivered graphite costs to unacceptable (but nonquantified) costs	Atlantic Research Corporation/USA U.S. Navy/USA
1991	3-D automated woven CCC ITE (4000-lb, 8-ft diameter) manufactured for NASA advanced solid propellant rocket motor (ASRM)	Largest prototype CCC ITE fabricated to date Low-recession, high-reliability ITE available for U.S. advanced space transportation systems	Textron Specialty Materials/USA
1991	CCC chamber polar boss fabricated and evaluated in a solid propellant motor firing	First CCC polar boss nozzle component successfully tested	UTC/Chemical Systems Division (Motor Firing)/USA Societe Europeenne de Propulsion (SEP) (Polar Boss)/FRANCE Air Force Phillips Laboratory/SMSC/AFMS/USA
1992	3-D polar woven CCC multiple throat inserts successfully tested over 25 seconds in a high-energy solid propellant rocket motor nozzle	3-D CCC throats successfully test fired in advanced integrated stage solid rocket motors	GenCorp/Aerojet Propulsion Division (Motor Firing)/USA
1993	Large 3-D CCC ITE successfully ground tested in first flightweight Ariane 5 solid rocket motor	Validated use of 3-D CCC for very large solid rocket motors	Societe Europeenne de Propulsion (SEP)/ FRANCE
1994	CCC exit cone for commercial satellite Perigee solid propellant space motor	First P.R. China space motor CCC exit cone CCC materials become state-of-the-art for Asian solid propellant motor exit cones Significant upgrade in Asian CCC applications technology	China Aerospace Corporation/Hexi Company/P.R. CHINA

and as a result they were forced to use ablative graphite fabric/phenolic composites. The latter material proved to be perfectly acceptable, because an appreciable amount of throat erosion could be tolerated without significant chamber decay. The U.S. Titan solid propellant launch motor is but one example of the successful use of ablative plastics for nozzle throats.

4.8.6.5.2 *The 1960s*

Concurrent with the development of first-generation CCC materials during the early 1960s, several CCC prototype components were fabricated and tested for short periods of time on solid motors. These 30-second motor evaluations indicated that CCC had great potential for use in the (a) entrance, center, and exit regions of throats and (b) exit cone regions. Significant increases in material density were required, however, to lower the ablation/ erosion rate and to decrease surface roughness during hot gas exposure. Low-density versions of CCC materials were also evaluated for potential use as an insulator backup in heavy metal nozzle throats. The CCC insulators provided high thermal stability compared to state-of-the-art silica fabric/phenolic composites, but this advantage was negated by the higher thermal conductivity.

During the mid-1960s additional rocket motor screening of new materials was accomplished, and several new prototypes were fabricated for evaluation.

The late 1960s was filled with many activities searching for potential applications of CCC materials. Significant progress had been made in improving material quality and properties, but much remained to be done. The general thought at this time was that CCC materials could potentially replace polycrystalline graphite for many of the solid rocket motor components. In spite of material deficiencies, 2-D CCC materials were tested and used in the very small throat regions of tactical solid motors. A very tiny CCC throat was employed in the U.S. 7.0-cm (2.75-in) diameter folded-fin aircraft-launched rocket. CCC materials were also of interest for use in much larger tactical motors. Ablative plastic materials previously used in the throat region of large short range attack missiles were replaced with pyrolytic graphite and CCC washers. The latter materials had lower erosion rates, excellent thermal shock resistance during pulse heating, and predictable performance. During the late 1960s CCC materials were also used for the first time in movable nozzles. The CCC throat materials proved to be outstanding candidate materials. They were applied primarily for the nose inlet sections of long-burning strategic solid motors.

4.8.6.5.3 *The 1970s*

During the early 1970s the properties of CCC materials appeared to be adequate for increased uses in solid rocket motor components. Several U.S. propulsion companies conducted materials evaluation programs and created new nozzle designs. The materials were demonstrated to have high strength and stiffness at elevated temperatures, low thermal expansion, low density, and reduced potential for gas path leaks in the nozzle. These material properties and characteristics suggested that a designer could create new solid motor nozzles with (a) high reliability, (b) simplicity (fewer parts), (c) fail-safe features (no failures), and (d) unlimited flexibility and scalability to meet a wide variety of future nozzle configurations and sizes. Impediments to using CCC materials in solid rocket motors were many but not technologically limiting. These obstacles included (a) low transverse material properties, (b) some material variability, (c) long manufacturing times, (d) high material costs per pound, (e) need for larger-size parts, (f) more design data, and (g) more complex design procedures.

During the early 1970s the U.S. propulsion companies were heavily engaged in the development of a usable throat material for medium-to-large solid rocket motors. As noted previously pyrolytic graphite washers were the center of focus, but their inconsistent performance prompted other developmental activities. Materials forward and aft of the erosion-resistant PG throat ablated at a faster rate, and this undesirable feature induced greater turbulent flow and motor performance loss. Regular density (1.6 g/cm^3 , 0.058 lb/in^3) rayon-based carbon fabric CCC and high-density (1.8 g/cm^3, 0.065 lb/in^3) PAN-based carbon fabric CCC materials were fabricated in ring sections and placed in the entrance and trailing sections of a PG nozzle throat. Both CCC materials were demonstrated to be adequate. Some of the other important propulsion events involved the development of erosion-resistant throat materials and new motor exit cones. CCC materials were coated with pyrolytic graphite to improve their erosion resistance. In spite of questionable material quality, the coated CCC parts were successfully flight tested in a lightweight solid rocket motor nozzle.

Erosion-resistant throat materials were also of interest to other countries developing long-range ballistic missiles. In France a CCC throat section was fabricated and successfully motor tested. As we shall later see, this was but one event in a long series of impressive French uses of CCC materials for solid rocket motor applications.

During the early 1970s CCC materials also became of increasing interest to the U.S. space propulsion community. Nozzle exit cones were needed that were lighter in weight than available ablative plastic composites. 2-D fabric involute resinous

constructions, which had been used for nozzle applications, were recreated in CCC form by pyrolyzing the plastic composite precursor and then densifying the material. Using this approach thin-walled (0.165 cm, 0.065 in) CCC exit cones were fabricated and successfully test fired in a simulated high-altitude motor firing. The solid propellant exhaust temperature was about 3105°C (5620°F), and the firing time was near 150 seconds. This promising test enabled the space Star 17 motor to baseline 2-D involute CCC materials for the nozzle exit cone. Subsequently, lightweight CCC materials spread to many other space rocket motor designs.

CCC nozzle designers, noted for their conservatism and build-and-test philosophy, now became very intrigued with prospects for using CCC materials in very advanced nozzle designs. One U.S. designer proposed that the entire nozzle assembly could be constructed with CCC materials. This all-carbon nozzle would be a thermally radiating part in which the CCC materials served as both the gas-containment liner and the external structural shell. While such a nozzle was not constructed, it nevertheless catalyzed the thinking of other propulsion designers to examine the prospects of using CCC materials in solid propellant motors.

Blast tubes in solid rocket motors represented yet another interesting application for CCC materials. Up to this point in time, heavy tungsten or lightweight ablative plastics were used to contain the erosive and corrosive gas stream. 2-D CCC blast tubes were successfully fabricated and tested. The new carbonaceous materials were found to be highly resistant to surface shear brought about by turning of the particle-laden gas stream.

The mid-1970s were the most exciting and productive years for applying CCC materials to solid rocket motor nozzles. 2-D CCCs were developed with higher densities, improved structural properties, and greater uniformity. Orthogonally-reinforced 3-D CCC materials with high (2.0 g/cm^3, 0.072 lb/in^3) densities became available for missile reentry nosetip applications. These emerging materials were also of great interest to the propulsion community because their properties were competitive with or exceeded those of polycrystalline graphite. It was postulated that the CCC materials would be suitable for (a) substrates or structural backups for refractory nozzle liners and (b) large nozzle pieces exposed directly to the hot exhaust gases. The major problem was to create 3-D fiber-reinforced CCC materials having cylindrical reinforcement coordinates instead of the available rectangular reinforcement schemes. Secondly, fibrous preforms in large wall thickness and sizes were also required. Both U.S. and French efforts were initiated to solve this problem, and both nations enjoyed some degree of success. The French, however, were entirely successful in developing semiautomated machinery for production of large 3-D cylindrical fibrous graphite preforms. This technology was later exported to the U.S. for use in various defense and space programs. High-density CCC

cylindrical components containing the new 3-D reinforcement constructions and densified with high-pressure pitch infiltration appeared to be the ideal solution for rocket nozzle throats and throat regions.

CCC exit cone materials development and evaluation continued during the mid-1970s. Star 30 and Star 48 space rocket motors with 2-D CCC exit cones were successfully ground tested. The first flight test of a 2-D involute CCC exit cone was completed in 1976.

Overseas, French development and testing of CCC materials was also progressing at a rapid pace. Unlike in the U.S., nozzle throat development centered on high-density 4-D CCC materials. Over 200 nozzle materials with throat diameters up to 30 cm (11.8 in) were evaluated in various ground-based test facilities and in numerous flight tests.

A major U.S. materials development program was initiated in the mid-1970s to obtain CCC materials for large solid rocket motors. This critical program was motivated by (a) a continuing history of PG washer throat failures, (b) continued propellant advances with attendant severe exhaust environments, (c) outstanding properties demonstrated in 3-D CCC nosetip materials, and (d) high prospects for automated weaving of large and thick fibrous carbon preforms needed for composite fabrication. Eleven U.S. CCC materials organizations participated in this development and screening program, and over U.S. $28M was spent in the next few years. Hundreds of 3-D, 4-D, 5-D, and other n-D-reinforced CCC materials were fabricated and their properties measured. Over 150 CCC nozzle throats were successfully test fired without a failure (mid-1970s). Test throat sizes ranged between 0.64-35.6 cm (0.025-14.0 in); motor pressures were between 3.48-9.65 MPa (0.50-1.40 ksi); and motor firing times were between 15 and 155 seconds. Most of the test material constructions were of a 3-D configuration which were woven by a host of different methods. The 3-D PAN-based fibrous carbon reinforcement coupled with high-density, pitch-based coke matrix was found to exhibit the best balance of properties and performance features. 3-D CCC materials were therefore baselined for the throat region of advanced solid propellant motors. Full-scale CCC ITEs were manufactured for the large first-stage motor of the U.S. Peacekeeper (MX) missile and for the nozzles of upper-stage solid propellant motors. CCC materials were also produced in the form of throat inlet rings and for supporting throat sections. The throat support rings were mechanically attached (threaded) to the adjacent CCC exit cone liner, thus marking the first time such an attachment method had been used in nozzle technology.

CCC entrance rings, ITEs, throat supports, and exit cones were fabricated and static test fired for over 150 seconds. These CCC prototypes demonstrated the applicability of CCC materials for long burn space solid motors. A very high expansion ratio (88:1) 2-D CCC exit cone was also manufactured in support of space motor technology. Static firing of this CCC exit cone on the third stage of a Minuteman III solid propellant motor was highly successful. Motor performance was increased by five percent which was equal to the total (performance) gained by all propellant improvements in the previous 15 to 20 years.

High-performance CCC nozzle prototypes were not only available in the U.S, but high-quality parts had also been developed in France. Through cooperative agreements between France and the U.S., French-manufactured nozzle throats and exit cones were evaluated by U.S. propulsion companies. A high-density (2.0 g/cm^3, 0.072 lb/in^3) 4-D CCC ITE and a 2-D involute CCC extendable exit cones were purchased from France, incorporated into a U.S. solid motor, and successfully tested in a simulated altitude space environment. The motor exhibited a very high specific impulse which is noteworthy in the space propulsion business. These evaluation activities demonstrated that (a) high-density 3-D and 4-D CCC materials were suitable nozzle throat materials, and (b) adequate performance was obtained with 2-D CCC exit cone materials provided great care was taken in their manufacturing.

Other high-tech countries developing solid rocket motors took note of the U.S. and French developments in CCC materials. England reported the evaluation of 2-D CCC materials, and the former USSR disclosed developments of 3-D CCC materials.

By the late 1970s many different CCC concepts had been originated and fabricated into appropriate cylindrical specimens for testing. Most of the prototyping efforts involved material scale-up to full-size parts, generating design data on some of these parts, and test firing the remaining parts to confirm analytical predictions of anticipated materials performance. One U.S. manufacturer of CCC materials had already fabricated several hundred CCC propulsion components.

Material scale-up to full-size prototypes was not an easy task and often involved the generation of new preform weaving or assembly equipment, larger processing equipment, and revised processing conditions. Several thick-walled 3-D CCC billets cracked during processing, but with the aid of computer models, the fibrous constructions were redesigned and the processing conditions adjusted to minimize in-process stresses. An overwrap technique was also demonstrated to reduce in-process billet failures, after which no further ITE

prototypes cracked during processing. CCC materials were also prototyped for various production nozzles in which unsatisfactory performance was occasionally encountered. A 4-D CCC nozzle throat was fabricated and successfully ground tested in an Antares II space solid motor. This event was the first static motor test in the U.S. for a 4-D CCC throat material. In the same time frame, a French-manufactured 4-D CCC throat was also successfully test fired. The latter motor firing involved the first nozzle tested with a CCC free-standing ITE. Flight testing of the 4-D CCC throat was later accomplished on an Antares III/Star 31 space solid motor. This test represented the first flight demonstration of a 4-D CCC throat in an operational, upper-stage space solid motor. As a result of these tests the n-D CCC throat material was specified for future nozzle uses in lieu of the presently-used polycrystalline graphite throat material.

4.8.6.5.4 *The 1980s*

By the early 1980s the world propulsion communities were well aware of the great progress made in applying CCC materials to solid propellant rocket motors. The United States had baselined 3-D high-density CCC materials for the ITEs of new ballistic missile and space motor systems including: (a) all three stages of the Peacekeeper (MX) strategic missile, (b) Trident II motors, (c) both stages of the IUS space motors, (d) third stage of the Scout missile, (e) burn motors of the Atlas Dual Apogee space system, (f) improved performance space motor (IPSM), and (g) others. A large number of ground-based motor firings and flight tests had also been logged on CCC materials. From this statistical database, it was apparent that high-density 3-D or 4-D CCC materials could satisfy all or most of the requirements for near-term solid propellant motors. There was increased confidence in using 2-D CCC exit cones based on 29 successful static firings of the second-stage IUS motor and 18 successful flight tests on the Star 48 space motor system. Ninety percent of all 2-D CCC exit cones performed successfully in ground motor firings, and 95 percent of all 2-D CCC exit cones were successfully flight tested. Nevertheless, 2-D CCC exit cone manufacturing left much to be desired in terms of quality, constituent materials and reproducible processes. One-fourth of all exit cones failed during processing or use. This situation was due to many factors such as (a) material delaminations, (b) fabric wrinkles, (c) low-density matrix indications (LDIs), (d) machining errors, (e) processing anomalies, and (f) inadequate composite properties. Efforts were therefore initiated to (a) standardize manufacturing procedures, (b) upgrade constituent materials, particularly woven graphite fabric, and (c) employ quality assurance techniques to screen out questionable materials, composites, and constructions.

In the mid-1980s the use of 2-D involute CCC exit cones for space solid motors took a decided turn for the worst. CCC exit cones on two Star 48 motors

failed during motor firing and stranded very expensive satellites (Westar 6 and Palapa B-2) in incorrect orbits. To avoid any future possible motor exit cone failures, baseline 2-D CCC exit cones were replaced with heavier ablative 2-D carbon fabric/phenolic materials. Needless to say this was a serious step backwards in the use of lightweight CCC materials for space exit cones. In an effort to regain confidence of the propulsion community, a large number of new 3-D CCC concepts were evaluated for potential use. These concepts involved thickness-compliant, thickness-stiffened, and other lightweight constructions. Some of these CCC concepts were reduced to practice and evaluated in motor firings. 3-D braided CCC exit cone materials, for example, provided adequate structural properties and cost savings in manufacturing. Their ablation surface roughness, however, tended to be high due to large matrix pockets. The performance of other 3-D CCC materials also produced mixed results. The major problem appeared to be a low reinforcement content in the thickness direction. The materials generally performed adequately in the thin sections of an exit cone, but structural failure was occasionally experienced in the thicker neck region. Stronger and stiffer in-plane properties of CCC exit cone materials were then realized with the use of PAN-based and pitch-based carbon fabrics. Transverse composite properties, of course, remained essentially the same. Exit cones were fabricated with these improved fabric reinforcements, and they were successfully test fired in a 4.5 kg (10 klb) thrust solid propellant motor. In spite of these successful demonstrations, 2-D CCC exit cones are still baselined with rayon-based carbon fabrics.

Meanwhile in France, a manufacturing method had been perfected for obtaining pseudo 3-D fibrous carbon reinforcements. The fibrous carbon preform was shaped into an exit cone design and densified with pyrolytic carbon. The material was successfully tested for 30 seconds on a solid propellant motor. The exit cone technology was later improved and exported to the U.S. for possible uses in strategic and space motors.

In the late 1980s CCC materials for solid rocket motors took on quite an international character. The U.S. and French organizations were unquestionably leading the world in the uses of CCC materials. Cooperative efforts were initiated between the two countries to (a) evaluate promising materials and (b) share certain propulsion technologies. French-manufactured 3-D and 4-D CCC hot gas valve parts were successfully tested on the thrust vector control system of a U.S. solid propellant motor. Ultrafine woven 3-D CCC Novoltex-TM exit cones manufactured in France were also successfully test fired on U.S. solid propulsion motors. Japan was reported to be manufacturing CCC nozzle throats and exit cones, but no publications could be found in the open literature to confirm their activities. Likewise, the former USSR was known to be engaged in similar propulsion material activities.

CCC materials began to be used with such routine frequency in the throat regions of medium-to-large solid rocket motors that any new development was hardly worth mentioning. Virtually all successes were with 3-D and 4-D constructions. In France the pseudo 3-D-reinforced Novoltex-TM CCC material was successfully flight tested on a high-performance solid rocket motor. To the great credit of French propulsion engineers, a 3-D CCC ITE was baselined for the 3.05 m (120 in) Ariane V solid rocket launch vehicle.

In spite of several very visible failures of CCC exit cones, the materials remained of great interest for use in lightweight propulsion parts of solid rocket motors. CCC exit cones offered the greatest system benefits in space motors and upper-stage motors where weight is a premium. 2-D involute CCC exit cones were baselined for the U.S. Air Force IUS, third stage of the Peacekeeper missile, and the Space Shuttle Payload Assist Module (PAM) solid propellant motors. A review of all space motors up to 1987 revealed that more than 200 2-D CCC exit cones were used on U.S. Star 30, 37, and 48 space rocket motors. Sixty 2-D CCC exit cones were successfully used in flight. Only two CCC exit cones failed in flight, and only four 2-D CCC exit cones failed in static ground-based firings. Post-test evaluation of the failed CCC exit cones revealed that the critical failure mode was restraint of the outer diameter during motor heating. Composite fill direction compression was determined to be the critical failure mode. Cross-ply tension and interlaminar stresses generated during composite processing were also shown to be important. Many material and technology improvements were subsequently made in 2-D CCC exit cone manufacturing in the hope of providing a highly reliable propulsion part. These efforts included (a) improved quality constituent materials, (b) controlled materials processing, (c) expanded design database, (d) better understanding of materials behavior, and (e) increased use of nondestructive inspection techniques for identifying suspect materials. All of these activities tended toward reducing CCC exit cone failures but not to the level required by some of the propulsion systems.

4.8.6.5.5 *The 1990s*

The early 1990s continued in the long tradition of using multidirectionally-reinforced CCC materials for solid rocket motor nozzles. All of the nine strap-on boosters for the U.S. Air Force Delta II system specified 3-D CCC throats in 1990. In addition the Pegasus satellite launch vehicle used 3-D CCC ITEs in all three stages. This event was the first use of 3-D CCC nozzle components for air launched solid rocket boosters.

The 1990s were perhaps the last chapter in the development of large-diameter rocket nozzle throats. With the advent of 3-D CCC throat materials for major

defense solid propellant motors, the question was raised concerning the applicability of the material for future very large motors. 3-D CCC nozzle ITEs had already performed without failure in every previous solid rocket motor application, and hence it offered very high reliability. The materials also had very predictable and low erosion rates. Nozzle designs were available for large motors up to and including the Peacekeeper first stage motor. The only issue remaining was a manufacturing plant capable of producing the required component sizes. The ITE of the Advanced Solid Rocket Motor (ASRM), which was to provide a higher lift capability for the U.S. Space Shuttle, was baselined with 3-D CCC material. Because of the size of the part involved, a new manufacturing facility was designed and built. It contained the largest 3-D processing equipment in the world. The part to be manufactured was composed of a 2.44 m (8-ft) diameter, PAN-based carbon fibrous reinforcement with over 139,000 radial rods and a wall thickness greater than 17.8 cm (7.0 in). The fibrous carbon preform was produced in the U.S. on French-designed and built, fully-automated machinery. The preform was then rigidized, NDE inspected with computed x-ray tomography, and low pressure/carbonization (LOPIC) processed with pitch and resin to reach full density. The first ASRM ITE was completed in the fall of 1991 and weighed over 1818 kg (4000 lb), the largest CCC part ever manufactured in the world. At this point things began to fall apart. NASA began to have second thoughts about the performance gains versus risks and costs of using 3-D CCC nozzle throats. Later the ASRM motor ITE was reduced from a production program to a developmental program. Eventually, the entire ASRM program was a victim of U.S. budget cutting and cancelled. Meanwhile in France the large 3-D CCC ITE for the Ariane 5 launch vehicle was successfully motor tested on the ground. In view of the above, there is little doubt that 3-D CCC ITEs can provide reliable and reproducible performance and at affordable costs.

By the early 1990s CCC materials had only been used sparingly in tactical solid propellant motors. Inexpensive polycrystalline graphite throats and ablative plastic composites generally fulfilled the nozzle needs. A number of larger tactical solid motors were designed with CCC throats, including the Mark 111 Tomahawk booster. Then in a strange turn of events, the U.S. Navy decided to qualify a high-strain polycrystalline graphite for the Tomahawk booster nozzle. The high-strain graphite was previously developed for strategic missile nosetips, but due to the superiority of 3-D CCC materials for this application, the material was never baselined in a strategic system. Up to this point the 4-D CCC throat had performed satisfactory but was higher in bulk material costs. Nevertheless a considerable amount of funds was expended to reactivate the graphite manufacturing plant, obtain needed design data, and perform motor firing tests. When considering total materials development and qualification costs

along with life-cycle costs, it is not apparent that polycrystalline graphites are superior to state-of-the-art CCC materials for large tactical solid motors.

Additional pioneering achievements in CCC materials for solid rocket motors will likely be few and far between during the remainder of 1994. Solid motor developments for defense purposes was greatly curtailed as the "Cold War" ended. Commercial uses for solid propellant motors, especially in the space satellite business, will continue and increase with time. Ground-launched and space motor business, then, likely hold the key for future application outlets of CCC materials in solid propellant rocket motors.

4.8.7 Liquid Propellant Engine Components

Liquid propellant engines have been developed as the basic propulsion for (a) rockets, (b) satellites, (c) guided missiles, (d) aircraft, (e) research devices, and (f) other types of vehicles. They have provided thrust levels ranging from a few ounces for satellite orbital control to many hundreds of thousands of pounds for Earth-launched vehicles. Liquid propulsion is characterized by (a) a high state of development, (b) relatively complicated systems design, (c) capability for repeated operation, (d) long firing times, and (e) the specific propellants employed. Their uses are based on many selection criteria including (a) operational mission, (b) performance, (c) reliability, (d) minimum weight, (e) logistics, (f) economics, (g) availability, (h) maintainability, (i) mobility, and (j) others.

Liquid propulsion systems are generally classified as either (a) primary or (b) secondary. Primary propulsion systems tend to be very large and generate an enormous amount of thrust for many minutes in duration. They are used on multi-stage vehicles which are propelled from the Earth-to-space or Earth-to-Earth. The engine typically consists of (a) a thrust chamber (injector, combustion chamber, and nozzle), (b) propellant tankage, and (c) a feed mechanism including a secondary power sourece, plumbing, and regulatory devices for propellant transfer. Secondary propulsion systems are designed around a thrust chamber. This unit consists of a cylinder, a throat, and a nozzle. Liquid oxidizer and fuel are injected into the cylinder and then combusted with the aid of an igniter or burned spontaneously in the presence of each other (hypergolic). Thrust chambers are used in a wide spectrum of secondary propulsion applications, such as (a) attitude control and stabilization of satellites and flight vehicles, (b) coplanar and interplanar orbit changes, trajectory corrections, (c) rendezvous, (d) docking, (e) lunar and planetary landings, (f) retrofiring for reentry or stage separation, (g) mission abort, and (h) gas generation. Engines for secondary propulsion employ many of the same cryogenic and storable

bipropellants as used in primary propulsion, but in addition they may burn a liquid monopropellant like 90 percent hydrogen peroxide.

The combustion of liquid propellants creates high-temperature products of low molecular weight. Combustion gas temperatures range from about 1093°C (2000°F) in gas generators to over 3930°C (7106°F) in very advanced propulsion systems. The widely-used cryogenic hydrogen and oxygen fuel has a combustion temperature of 2767°C (5012°F). Most of the liquid propellant systems form highly oxidizing species, like water and carbon dioxide. The notable exception is fluorinated combustion products. In any event the hot gas flow is highly turbulent, and the local pressure is numerically great. Heat is thus transferred at a high rate to the walls of the combustion chamber, nozzle, and adjacent parts. Various cooling techniques have been developed to cope with this heating problem. They are based on (a) absorptive, (b) dissipative, and (c) mass transfer cooling systems. More specifically, they include (a) regenerative cooling, (b) inert heat sinks, (c) ablation, and (d) combinations of these techniques. Regenerative cooling is the most widely-used form of cooling for liquid propellant engines. It is an absorptive technique in which heat transferred to the chamber wall is conducted internally to an actively regulated flowing fluid (propellants). Despite its great complexity in design and manufacturing, regenerative cooling has proven to be quite reliable.

Unprotected CCC materials have very limited potential uses in chemical propellant engines. This situation is due to the highly-oxidizing exhaust products formed from most liquid propellant systems. The ablation rate for unprotected CCC materials indicates that it has an unacceptable surface recession in the temperature regimes of the thrust chamber through the throat and exit nozzle until a reasonably low temperature is reached. Nevertheless, it has been demonstrated that CCC liners for thrust chambers can significantly decrease the erosion rate of ablative thrust chambers. Secondly, CCC parts have exhibited very low erosion rates in hot species from fluorinated propellants.

CCC materials with enhanced oxidative stability (protected CCC) appear attractive for use in upper-stage and satellite propulsion systems. Protected CCC materials have been successfully tested in various oxidizing gases. The materials were coated with either (a) dense graphite like pyrolytic graphite, (b) carbides like silicon carbide, or (c) metals like columbian. The materials have performed adequately in both supported and free standing structural shapes (like nozzle extension skirts), exhibited low erosion rates, and survived thermal shock conditions associated with engine restarts. Engine designers feel that coated CCC materials are not satisfactory for most liquid propulsion systems, especially in (a) extended motor firings, (b) high

motor pressures, and (c) high combustion temperatures. Perhaps the greatest shortfalls are not in materials performance, but rather in available design approaches and databases.

In more recent times materials developmental efforts have shifted away from coated CCC materials and toward intrinsically oxidative-resistant hybrid material systems. Carbon fiber-reinforced silicon-carbide composites have exhibited lower oxidative losses, relatively high strength, and some degree of brittleness. The silicon-carbide matrix protects the oxidation-susceptible carbon fiber, but unfortunately the ends of the fibers are exposed and will vaporize in hot oxidizing environments. The French SEP has fabricated a hybrid CCC exit cone for the third stage of their heavy lift Ariane rocket. The exit cone was 1.0 m (39.4 in) long, 0.94 m (37 in) in outer diameter, and weighed 25 kg (55 lb). The weight savings versus conventional metallic parts was about 10 kg (22 lb).

To summarize, state-of-the-art CCC materials are expected to find only limited applications in liquid propellant engines. When used in a straight substitution design, the CCC materials do not generally offer any significant advantages. The materials exhibit high erosion rates if uncoated or high costs if coated (compared to ablative plastic composites and metals). From a thermochemical point-of-view, refractory metallics and ceramics will usually outperform CCC materials unless structural requirements, reliability, and potential weight savings are of great importance. The best near-term prospects for use appear to be in radiation-cooled nozzle extensions of spacecraft engines. In this application the nozzle extension would be attached to a regeneratively-cooled nozzle. The coated CCC material would offer significant weight advantages and possibly cost advantages. The coated CCC materials are expected to become more competitive in the future as developments yield (a) thinner structural composites, (b) higher temperature and more reliable coatings, and (c) lower-cost materials.

Table 43 lists the first reported CCC prototypes developed for components of liquid propellant systems. These applications have involved (a) liners for ablative and regeneratively-cooled thrust chambers, (b) extension skirts for nozzles, (c) combustion chambers, (d) flame-holders, (e) nozzle throats, (f) missile elevons, (g) turbine wheels, and (h) others.

4.8.7.1 Chronology

Table 44 lists important CCC prototyping events associated with liquid propellant engines.

TABLE 43
FIRST CCC PROTOTYPE COMPONENTS FOR LIQUID PROPELLANT ENGINES

YEAR	PROTOTYPE	ORGANIZATION
1964	Free-standing (large) thrust chamber	San Rafael Plastics Company/USA
1965	Liner for a small ablative plastic thrust chamber	North American Aviation/Rocketdyne Division/USA
1966	Free-standing (small) thrust chamber	The Marquardt Company/USA
1968	Throat section for a halogenated propellant engine	North American Aviation/Rocketdyne Division/USA
1970	Integral combustion chamber-exit cone for a rocket ramjet	McDonnell Douglas Astronautics Company-East/USA
1971	Liner for a regeneratively-cooled thrust chamber	San Rafael Plastics Company/USA Aerojet Liquid Rocket Company/USA
1978	Flameholder for a rocket ramjet	UTC/Chemical Systems Division (CSD)/USA
1982	Thrust chamber for a bipropellant pulse engine	Rockwell International Corporation/Rocketdyne Division/USA
1984	Nozzle (high expansion) extension skirt	HITCO/USA Chromalloy Research & Technology Division/USA UTC/Pratt & Whitney Engineering Division/USA
1985	Structural elevon fin for missile guidance control	LTV Aerospace & Defense Company/USA
1988	Nozzle chamber liner and throat for a restartable, fluorinated engine	Aerojet TechSystems Company/USA
1988	Very small, free-standing spacecraft thrust chamber	Rockwell International Corporation/Rocketdyne Division/USA
1991	Bearings for a cryogenic liquid propellant pump	Societe Europeenne de Propulsion (SEP)/FRANCE

TABLE 44

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR LIQUID PROPELLANT ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1964	Full-scale, 2-D CCC thrust chamber fabricated	First CCC prototype for a radiation-cooled, liquid propellant thrust chamber	San Rafael Plastics Company/USA
1965	Full-scale, 2-D resin char CCC propulsion liner tested	First CCC prototype liners for Apollo liquid propellant, 100-lb thrusters (attitude control rockets)	North American Aviation/Rocketdyne/ USA
1965	Full-scale 2-D CCC mixing baffles and throats fabricated	First CCC prototype parts for high-performance hybrid motors	San Rafael Plastics Company/USA
1966	Low recession, subscale CCC 2-D thrust chambers fabricated	CCC compatibility with high-temperature fluorinated propellant exhaust gases demonstrated First prototype CCC thrust chamber for high specific impulse liquid fluorine/hydrazine propellant engines	Aerojet-General Corporation/USA
1966	2-D carbon (rayon-based) fabric/CVI PG matrix nozzle thrust chamber fabricated and tested	Full-scale (100-lb thrust) engine chamber for liquid propellant engine of spacecraft attitude control system	The Marquardt Company (Test)/USA Raytheon Company (Thrust Chamber)/ USA
1968	2-D CCC throat hot fired (160 seconds) in an ablative thrust chamber using an advanced engine	Demonstrated low erosion of CCC in halogenated propellant exhaust gases	Rockwell International Corporation/ Rocketdyne Division/USA
1968	Large 2-D carbon (rayon-based) fabric/CVI PG matrix nozzle thrust chamber fabricated and tested	Free-standing, full-scale (3000-lb thrust) engine chamber for high-energy fluorinated propellant space engine	The Marquardt Company (Test)/USA Raytheon Company (Thrust Chamber)/ USA
1970	Uncoated and coated 3-D CCC thrust chamber specimens fabricated	Subscale integral thrust chambers available for testing in rocket ramjet exhaust environments	McDonnell Douglas Astronautics Company-East/USA

TABLE 44 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR LIQUID PROPELLANT ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1971	2-D tapewrap graphite (rayon-based) fabric/resin-pitch carbon matrix CCC liner fabricated and hot tested for a regeneratively-cooled FLOX-methane thrust chamber	Novel passive-active thermal protection scheme for liquid propellant engine thrust chambers	Aerojet Liquid Rocket Company (Design & Test)/USA San Rafael Plastics Company (Liner Fabrication)/USA
1973	PG-coated CCC thrust chamber material successfully evaluated in 2204°C (4000°F) N_2O_4/amine exhaust	Demonstrated utility of coated CCC for long-duration, multiple restart liquid propellant engines	The Marquardt Company/USA
1978	CCC rocket ramjet flameholder fabricated	One of the first applications of CCC materials for rocket ramjet propulsion systems	UTC/Chemical Systems Division/USA
1979	Carbon-carbon composite survived 120 seconds in extremely high propellant exhaust temperatures	CCC potential demonstrated for space storable, long burn, liquid fluorine-hydrazine thrust chambers	HITCO (Thrust Chamber)/USA Jet Propulsion Laboratory (Chamber Test)/USA
1979	Rocket engine prototype 2-D CCC thrust chamber was designed, fabricated, characterized, and test fired (200 seconds) in 3620°C (6550°F) fluorine/hydrazine propellant exhaust	Space storable, liquid propulsion technology was demonstrated for application to future planetary propulsion systems	FMI, Inc. (Chamber Densification)/USA Southern Research Institute (Chamber Properties)/USA Jet Propulsion Laboratory/California Institute of Technology (Chamber Design & Test)/USA
1979	Full-scale, 2-D CCC combustion chamber fabricated	First uncoated CCC integral combustion chamber-nozzle for rocket-ramjet propulsion evaluation	McDonnell Douglas Astronautics Company-East/USA
1981	Silicon-carbide coated 3-D CCC successfully tested in 2149°C (3900°F) oxidizing propellant exhaust and 1000 psi pressure	Coated CCC potential was demonstrated in severe oxidizing-exhaust products of liquid propellant engines Designers interest increased in coated CCC for liquid propulsion components	Aerojet Strategic Propulsion Company/ USA

TABLE 44 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR LIQUID PROPELLANT ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1981	Full-scale, pyrolytic graphite-coated 2-D CCC combustion chamber fabricated	First prototype coated CCC for liquid propellant rocket ramjet application	McDonnell Douglas Astronautics Company-East/USA
1982	Coated (silicon-carbide) and uncoated 3-D and 4-D CCC thrust chambers evaluated in liquid bipropellant pulse engine exhaust	Demonstrated high dimensional stability of coated and uncoated CCC during long-duration, low-pressure pulsed firings	Rockwell International Corp./Rocketdyne Division/USA
1984	3-D and 4-D CCC and other carbonaceous materials evaluated in rocket ramjet exhaust environments	CCC materials have sufficient durability and strength for potential uses in rocket ramjets	McDonnell Douglas Astronautics Company (Nozzle Materials)/USA
1984/85	Silicon-carbide coated 2-D contoured engine nozzle extension successfully fabricated and tested (1220 sec) for a large (shuttle) liquid propellant engine	First prototype, uncooled skirt extension for very large liquid hydrogen-oxygen propellant engine Another potential use of oxidation-resistant CCC for liquid propellant engines	UTC/Pratt & Whitney Engineering Division (Cone Design and Testing)/USA HITCO (CCC Nozzle Extension)/USA Chromalloy Research & Technology Division (Coating)/USA Southern Research Institute (Nondestructive Evaluation)/USA
1985	Full-scale CCC missile elevon fin fabricated and tested	First structural elevon fin for missile guidance control	LTV Aerospace & Defense Company/ USA
1988	2-D CCC nozzle throat and 3-D CCC chamber liner was fabricated for a restartable, fluorinated propellant engine	CCC materials and parts became available for evaluation in advanced space engines	Aerojet TechSystems Company/USA
1988	Columbium coated CCC chambers were fabricated for a very small, lightweight, 150-lb thrust engine	Smallest, yet full-scale, CCC thrust chamber for a space maneuvering operations	Rockwell International Corp./Rocketdyne Division/USA
1989	Carbon fiber-reinforced silicon-carbide matrix hybrid composite was fabricated and successfully tested	First structural, oxidation-resistant hybrid composite for a liquid fueled rocket engine	Societe Europeenne de Propulsion (SEP)/ FRANCE

TABLE 44 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR LIQUID PROPELLANT ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1990	Triaxially braided CCC exit cone successfully tested on high-performance storable liquid propellant rocket engine	CCC materials experience low erosion in hot halogenated exhaust products Thin-walled braided CCC suitable for engine exit cone or thrust chamber liner	Aerojet Propulsion Division/USA
1991	Bearings fabricated for a cryogenic pump	Demonstrated frictional characteristics of CCC materials at very low temperatures	Societe Europeenne de Propulsion (SEP)/ FRANCE
1992	2-D thin-walled CCC thrust chambers fabricated for space maneuvering vehicle propulsion	2-D CCC materials exhibited performance advantages for small propulsion components Low-cost threaded attachment methods were demonstrated	Kaiser Aerotech/USA

4.8.7.1.1 *The 1960s*

During the 1960s the United States has been heavily involved in the development of advanced propulsion systems, particularly those suitable for use in space. New and improved materials were needed for higher-performance engines and new duty cycles. CCC materials looked attractive for some applications because of their high-temperature properties even though the materials were (a) porous, (b) structurally weak, (c) susceptible to oxidative losses, (d) difficult to manufacture in desired sizes and shapes, and (e) quite expensive. Nevertheless, rather impressive prototypes were developed and successfully tested. The first pioneering effort involved a full-scale, 2-D CCC thrust chamber for a radiation- cooled liquid propellant thrust chamber. This 1964 event was quickly followed with the development of a low recession liner for the small attitude control rockets of the U.S. Apollo system. Up to this point in time, the silica fabric-reinforced phenolic plastic composite liners exhibited fabric melting and removal by gas-dynamic shear and high-temperature vaporization conditions. The thrust chamber was redesigned to include (a) a CCC liner of 2-D carbon fabric with either resin char or pyrolytic graphite matrix to accommodate the flame front, (b) an overwrap of silica fabric/phenolic composite for insulative purposes, and (c) an outer metallic shell to accommodate the mechanical loads. This three-layered material thrust chamber worked rather well. It greatly increased the interest of the U.S. propulsion industry and the exploration of additional CCC uses. Meanwhile in space engine developments much attention was being given to the development and use of highly halogenated liquid propellants. Engines using these propellants exhibited very high specific impulse which is greatly desired in lightweight space engines. The ultrahigh temperatures associated with these propellants created significant materials problems, but it was found that CCC surfaces receded at a very low rate in these combustion gases. For that reason there was a flurry of activity to fabricate and test various CCC components in fluorinated propellant space engines. Both subscale and full-scale thrust chambers were manufactured with rayon-based carbon fabric and either resin char or pyrolytic graphite matrix. A free-standing CCC chamber was successfully fabricated for a 3000 lb thrust engine. Engine throats were also produced and successfully tested for 160 seconds.

4.8.7.1.2 *The 1970s*

CCC materials development, prototyping, and testing for high-performance space motors continued on into the 1970s. One 2-D CCC thrust chamber prototype was fabricated and tested for 200 seconds in 3620°C (6550°F) exhaust products from fluorine/hydrazine propellants. This prototype demonstrated the applicability of CCC materials for space-storable, liquid propulsion engines, which were needed for future planetary exploration.

Rocket ramjets were also becoming important in the late 1970s. Subscale and full-scale combustion chambers (including the nozzle) were fabricated and tested, and ramjet flameholders were also produced with CCC materials. The composites exhibited significantly less material loss compared with conventional ablative plastic composites, but due to the high through-the-thickness thermal conductivity, the CCC thrust chamber had to be either (a) radiation cooled or (b) insulated somehow from the remaining metallic structure.

4.8.7.1.3 *The 1980s*

The availability of new CCC materials in the 1980s greatly increased their prospects for uses. CCC materials were coated with columbium and successfully tested in a very small, 150-lb thrust engine intended for use in space maneuvering operations. 3-D and 4-D CCC materials were fabricated into full-size thrust chamber configurations and coated with (a) pyrolytic graphite, (b) silicon carbide, or (c) a higher-temperature hafnium carbide. Some of the prototypes were successfully evaluated in long-duration, low-pressure pulsed firings of space bipropellant engines. The most impressive prototype demonstration, in the opinion of the author, was the fabrication and extended testing of a very large nozzle extension. A contoured engine nozzle extension of 2-D CCC was silicon carbide coated. This translating CCC nozzle was about 50.8 cm (20 in) in length with an exit plane diameter of approximately 117 cm (46 in). The translating coated CCC nozzle section was test fired for over 80 minutes in a restart mode using an upgraded U.S. shuttle liquid propellant engine. This was the first CCC prototype for high-performance, liquid hydrogen-oxygen engines. The nozzle skirt extension remained fully functional during the test firings. It served as a radiation-cooled (nonregeneratively cooled) and lightweight component of the engine system.

4.8.7.1.4 *The 1990s*

The attractiveness of using oxidation-protected CCC materials for liquid propellant components waned in the 1990s. In spite of many successful prototype fabrication and evaluation efforts, not a single CCC part moved from the test and evaluation stage to production. The total area was re-examined in the early 1990s in an effort to quantify the benefits of CCC materials and focus on the best near-term prospects. With the downturn in U.S. defense funding, the prospects for using CCC in production liquid propellant engines appear even dimmer. The prospects of using hybrid carbon-ceramic or all-ceramic composites appear more attractive. It is anticipated that many of the uncoated and coated CCC prototypes evaluated to date will be re-examined in terms of hybrid compositions. World efforts are apparently being led by French companies, who have already manufactured and tested many

hybrid and all-ceramic propulsion parts. This field of technology apparently needs a more systematic and coordinated effort to establish the attributes, limitations, and future potential of CCC and competitive materials for liquid propellant engines. Continued prototyping is critical to future developments.

4.8.8 Gas Turbine Engine Components

An air-breathing propulsion system that derives its thrust from a jet of hot gases is known as a gas turbine engine or jet engine. This type of device burns its fuel (kerosene or kerosene-based mixture) in the airstream that powers the engine. Air flows through the gas turbine's inlet and is compressed. The high-pressure air flows to the combustion chamber where it is mixed with fuel and ignited. The newly-formed combustion products expand and rush at high velocity through the turbine and exhaust nozzle. The turbine is connected by a shaft to a compressor and rotates it. In some engine types the turbine also powers a propeller or fan. The principle of a gas turbine engine is relatively simple, but its design and manufacturing are complex.

4.8.8.1 Types of Engines

Aircraft gas turbine engines are routinely categorized as either (a) man-rated or (b) limited-life, i.e. expendable. Aircraft that have humans aboard employ man-rated engines. Both commercial and military aircraft use man-rated gas turbine engines. Limited-life engines are generally a single-mission engine, like that required for a subsonic cruise missile.

Limited-life gas turbine engines are a scaled-down version of conventional aircraft engines. However their volume and weight are at a premium. The engines have a single mission and operate for up to 15 hours, but they must be restarted occassionally to demonstrate readiness.

Supersonic combustion-ramjets (scramjets) are yet another type of jet engine. The engine is designed for very high Mach number winged flight vehicles. Air in the engine inlet is not slowed all the way to subsonic speeds prior to entry into the combustor. The air temperature and pressure remain low, and the fuel is burned with less dissociation.

4.8.8.2 Engine Material Requirements

Engine materials are exposed to severe operational and conventional environmental conditions. These parameters involve (a) subzero, high, and cyclic temperatures, (b) thermal shock, (c) thermal gradients, (d) reactive and oxidizing combustion products,

(e) stresses of varying magnitudes, (f) vibrations, (g) acoustical loading, and (h) shearing high-velocity gases. Maximum gas temperatures are about 750-1550°C (1382-2822°F). The materials are subjected to thermal shock conditions during engine starts. The materials also experience high thermal gradients during engine start and changes in engine power settings. The combustion gases are highly oxidizing due to the presence of oxygen, water vapor, carbon monoxide, carbon dioxide, and nitrous oxides. Gas velocities may be up to about 1.2 km/s (4.0 kft/s) which impose gas-dynamic shearing forces on the hot flow surfaces. These forces are high in any section that changes the direction of the hot gases. Structural loads are typically carried by high-temperature metals if possible. In the case of an engine turbine, however, stresses are numerically high due to the centrifugal forces of the rotating component. Finally, acoustical loads are present and may give rise to acoustical fatigue problems.

Higher-performance and fuel-efficient gas turbine engines are possible by increasing the (a) turbine inlet temperature (TRIT) and (b) cycle overall pressure ratio (OPR). State-of-the-art nickel superalloys are limited to a maximum use temperature of about 1150°C (2102°F), and refractory metals used in static engine structures are acceptable to about 1650°C (3002°F). Since gas temperatures may exceed the service temperature of metallic engine materials, various forms of cooling have been developed. These cooling schemes reduce the efficiency of the engine. Uncooled metallic parts may experience warpage or surface oxide destruction. There is thus a pressing need for higher temperature, lightweight structural materials for new engine designs.

Gas turbine engines for commercial and military aircraft have many common requirements. Military planes are more demanding in terms of performance and specialized flight features like (a) maneuverability, (b) high acceleration/deceleration, (c) vertical takeoff and landing, and (d) low observability. Gas turbine engines for commercial aircraft must be very reliable because they are man-rated. Engine durability is also a major requirement, and between 500 and 2000 hours of operational use are needed between major overhauls. Other features include (a) high fuel efficiency, (b) noise suppression, (c) low maintenance, (d) improved thrust-to-weight ratio, and (e) lower initial and life-cycle costs.

Many systems benefits could be derived with the use of new and improved materials in gas turbine engines. The machines could be made (a) lighter, (b) more fuel efficient, (c) smaller in size, and (d) higher in thrust-to-weight ratio.

4.8.8.3 Potential CCC Material Uses

Protected CCC materials appear to have many attributes being sought by designers of gas turbine engines. These benefits are essentially fivefold, including: (a) reduction in design complexity, (b) ultrahigh temperature capability without cooling, (c) reduction in weight and size, (d) potential for lower life cycle costs, and (e) an extensive domestic industrial base for manufacturing parts. The high-temperature stability of protected CCC materials is similar to that of conventional refractory metals but vastly superior to nickel superalloys. CCC substrates have adequate strength and stiffness at elevated temperatures, but their matrix-dominated properties tend to be low. The materials have excellent thermal shock resistance, provided the coating is firmly anchored to the CCC substrate. Protected CCC materials can also accommodate thermally-induced stresses and local hot streaks. Their expansion coefficients are low, thus making it easier to withstand axial and transverse gradients. The protected CCC materials have high stiffness; hence, part deflections under loading are smaller. Facesheet buckling is thus of lower probability. Design complexity can be reduced by (a) elimination of or reduced dependence on cooling, (b) reduced part counter, and (c) easier component assembly. Significant weight reductions can also be realized in both the component and the system. Low mass density leads to low-weight parts, and this feature is especially important in rotating components where high centrifugal stresses must be accommodated. Protected CCC materials are about 75 percent less dense than nickel superalloys and 80 percent less dense than refractory metals. Protected CCC part costs are presently higher than those fabricated with metals. This situation is due mainly to the high cost of the coating and the limited volume production of parts to date. Unlike most metals, protected CCC materials are not strategic materials, and they are available from numerous domestic sources.

Protected CCC materials exhibit certain limitations for use in gas turbine engines. The maximum use temperature is restricted by the external coating. Current material systems are used up to 1540°C (2804°F) for long periods of time. Durability of the cracked coating and the underlying oxidation protection materials are also of concern. The best available material systems have lasted over 1000 hours in laboratory oxidation tests, but at least twice this life is required for man-rated gas turbine engines. Protected CCC part costs are presently about 3-4 times that of metallic components, mainly due to the expensive coating employed. Adequate inspection techniques to assure component quality and to identify parts for removal are yet another design concern. Field repair techniques are in their infancy. Great improvements are needed to extend the life of in-service components. Finally, all of the matrix-dominated properties tend to be low, thus restricting part design.

Protected CCC materials used in gas turbine engines have been primarily a multilayered 2-D composite. This type of composite is rather complex in chemical composition and construction. Substrate materials are composed of a high-strength carbon fabric and an oxidation-inhibited carbon matrix. This composite is overlaid with a glass-forming substance and possibly other specialty layers. Surrounding the entire protected CCC substrate material is a ceramic coating of silicon carbide or silicon nitride. Limited experience has also been gained with 3-D CCC, but their uses have been restricted by (a) coating nonuniformity, (b) poor distribution of particulate inhibitors in the matrix, and (c) high cost of the fibrous reinforcement.

Protected CCC parts have been considered for variable noncritical parts of both man-rated and limited-life gas turbine engines, as noted in Figures 22 and 23. Many of the parts shown in the schematics have been designed using a metal-to-CCC substitution approach, fabricated to existing part tolerances, and tested in both laboratory conditions and actual gas turbine engine environments. Most of the developmental efforts accomplished to date have involved (a) low stressed parts, (b) low risk parts in conventional and 2-D nozzle exhaust systems, and (c) stationary components. Impressive results have also been obtained with coated CCC rotating parts, but developmental progress has been hampered by (a) high stress fields, (b) need for high-tolerance parts, and (c) complex configurations. At present the advanced composites are not cost/risk competitive with conventional metallic materials. Domestic gas turbine engine manufacturers have essentially abandoned further development of protected CCC components because of (a) oxidative losses during temperature cycling, (b) moisture absorption by the protective sealant constituents, and (c) limited ability to predict its service life. In an effort to partially circumvent the oxidation problem, hybrid composites are being developed. These materials are based on an oxidation-resistant ceramic matrix like silicon carbide which has been reinforced with strong and stiff carbon fibers. In oxidizing environments the composites have exhibited low mass loss, but the exposed ends of the fibers are preferentially oxidized. At the present time the domestic gas turbine community is attempting to circumvent the oxidation limitation of engine materials by prototyping with all ceramic composites. Materials developmental progress has been very limited, and many problems uncovered in previous protective CCC materials have resurfaced in the ceramic fiber matrix-reinforced composite developments. The common need for an external protective coating is but one example.

The future of protective CCC materials for gas turbine engines obviously lies in continued improvements in material performance and cost factors, and a design-to-use approach for components.

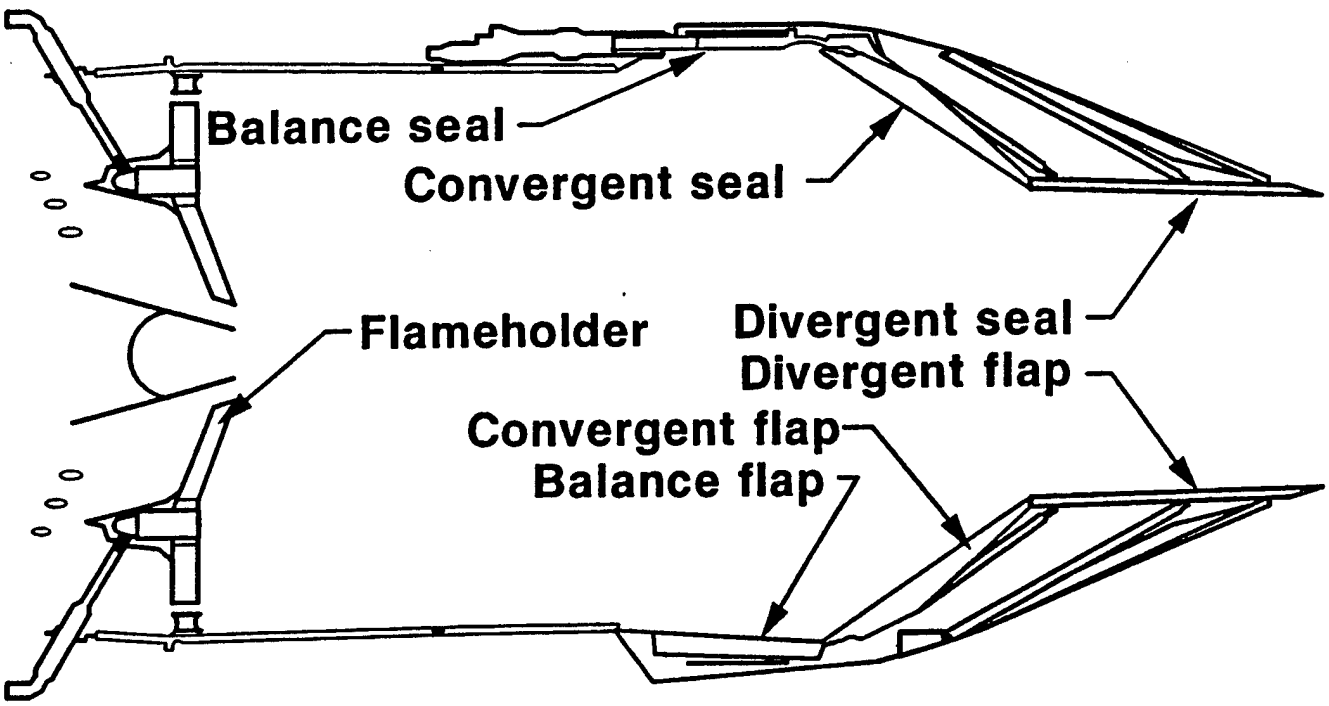


Figure 22. Potential Applications of Coated CCC Parts in Man-Rated Gas Turbine Engines.

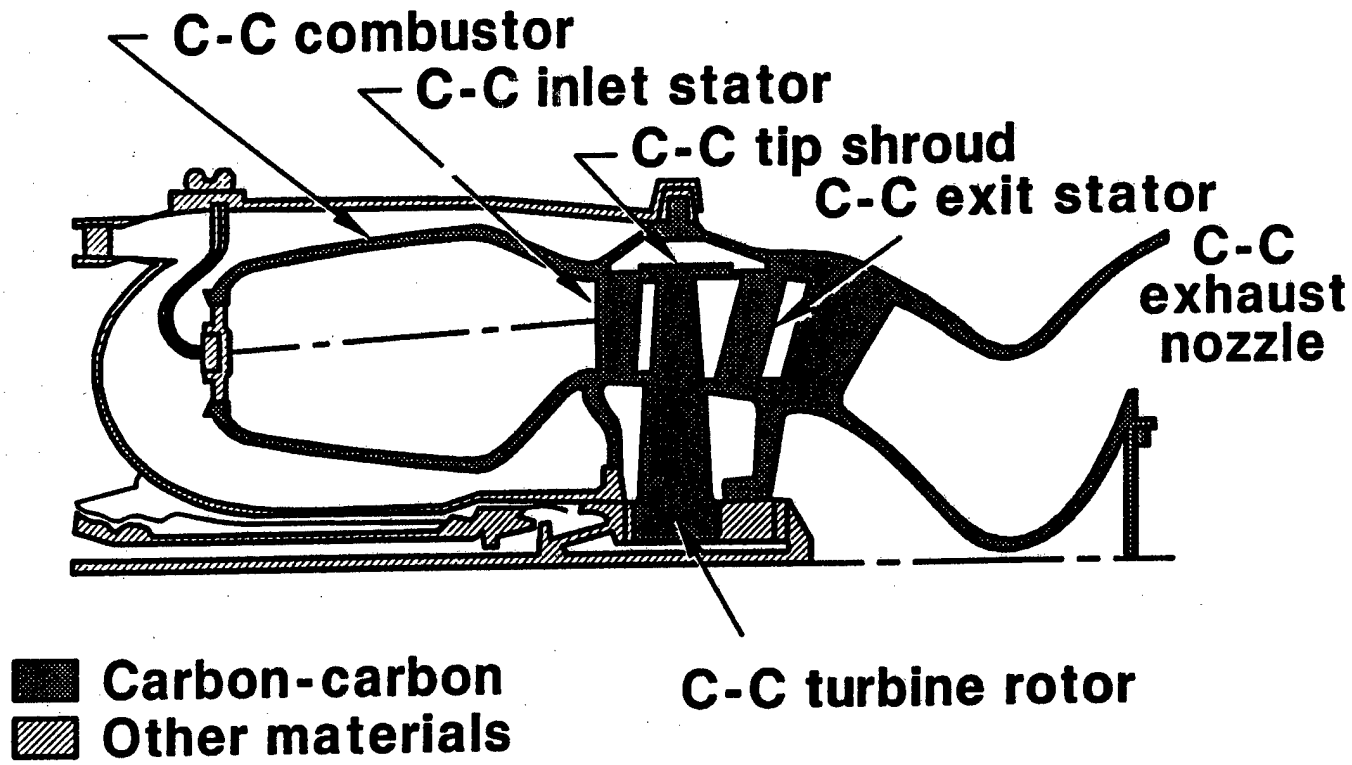


Figure 23. Potential Applications for Coated CCC Parts in Limited-Life Gas Turbine Engines.

Table 45 lists various protected CCC components which have been fabricated along with the first year these pioneering events took place. Application prototypes have included many parts for (a) axisymmetric nozzles, (b) 2-D nozzles, (c) turbine wheels, (d) combustion chambers, and (e) hot gas ducting and shielding.

4.8.8.1 Chronology

CCC prototypes for future uses in gas turbine engines are listed in Table 46.

4.8.8.1.1 *The 1970s*

The first prototype CCC component for a gas turbine engine was fabricated and tested in the early 1970s. A thermal protective overwrap material was being sought for engine combustors which would provide temporary containment of hot gases in the event of a burnthrough. Ablative plastics were found to provide several minutes of protection, sufficient to permit the pilot to shut down the faulty engine. CCC materials demonstrated even better burnthrough protection, but due to fabrication difficulties and high costs, the materials never went beyond the prototype stage.

In the late 1970s protected CCC materials development had progressed to the point where it was possible to consider them for gas turbine engine uses. The first components fabricated were for the low-stressed, low-risk parts in the aft section of axisymmetric nozzles. Full-scale parts for flaps, seals, and liners of man-rated engines were fabricated with silicon carbide-coated 2-D CCC materials. These materials were originally developed for the U.S. space shuttle orbiter and later found to be acceptable for first-generation engine CCC prototypes.

4.8.8.1.2 *The 1980s*

Having passed the first hurdle of fabricating close tolerance-protected CCC parts, the attention of the man-rated turbine engine community turned to real service evaluation. Numerous parts were ground-tested in a production military engine. Over 716 hours of total engine time were accumulated on some of the components. In another section of the gas turbine engine, the possibility of using protected CCC rotors was under investigation. A small rotor was successfully fabricated and cold-spun tested up to 9.1 km/s (30 kft/s) without failure. This test verified the structural integrity of substrate CCC material, but additional follow-on efforts were needed to coat the parts and retest at high-temperature conditions.

TABLE 45
FIRST CCC PROTOTYPE COMPONENTS FOR GAS TURBINE ENGINES

YEAR	PROTOTYPE	ORGANIZATION
1970	Combustion chamber overwrap	Federal Aviation Agency/National Aviation Facility Experimental Center/USA
1978	Axisymmetric nozzle flaps, seals, and liners	Vought Corporation/USA
1980	Hot gas ducts for V/STOL engines	NASA Lewis Research Center/USA
1982	Axial bladed rotor	Vought Corporation/USA
1982	Nozzle stationary inlet vanes	Vought Corporation/USA
1984	Combustor for limited-life engine	LTV Aerospace & Defense Company/USA Williams International/USA
1984	Axisymmetric nozzle tailcone	LTV Aerospace & Defense Company/USA
1985	Rotor (blade-disc) blisk	General Electric Company/Re-Entry Systems Operations/USA
1985	Exhaust structural thermal shields	BFGoodrich Aerospace/Super-Temp/USA
1987	Sidewalls for a 2-D nozzle	Science Applications International Corp./Materials Sciences Operation/USA
1987	Annular flameholders	Science Applications International Corp./Materials Sciences Operation/USA Rolls-Royce, Inc./ENGLAND
1987	Combustor for a carbon slurry fuel engine	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA Williams International/USA
1988	2-D nozzle flaps and seals	General Electric Company/Aircraft Engines/USA LTV Aircraft Products and LTV Missiles & Electronics Groups/USA Rohr Industries, Inc./USA Chromalloy American Corp./Chromalloy Research & Technology/USA Midland Materials Research/USA UTC/Pratt & Whitney Government Engine & Space Propulsion/USA

TABLE 46

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1970	CCC overwrap protection demonstrated for J-47 gas turbine engine combustion chamber	New protection approach for high-temperature components of man-rated aircraft engines	Federal Aviation Agency/National Aviation Facility Experimental Center/USA
1978	Silicon-carbide coated 2-D CCC parts fabricated for potential using on gas turbine engines	First full-scale flaps, seals, and liners for man-rated gas turbine engine tests	Vought Corporation (Parts)/USA
1981/85	CCC turbine rotor blisk was fabricated	First blade-disc (blisk) single piece CCC turbine engine part manufactured Increased interest in use of CCC for rotating parts of gas turbine engines	General Electric Company/Re-Entry Systems Operations/USA
1982	CCC axial rotor (5.3 in.) survived 30,000 rpm spin test	Provided increased interest in ORCCC materials for rotating parts of limited-life gas turbine engines	Williams International/USA
1982	Coated CCC nozzle vane successfully tested for five hours at 1343°C (2450°F) in a burner rig	Provided increased interest in ORCCC for static turbine engine parts	Williams International/USA
1983	Full-scale silicon-carbide coated CCC flap liners and nozzle vanes fabricated	Demonstrated potential uses of oxidation-resistant 2-D CCC in gas turbine engine nonrotating parts	LTV Aerospace & Defense Company/ USA
1983	Silicon-carbide coated CCC divergent seals survived 716 hours of cyclic heating in an F-100 gas turbine exhaust nozzle	Weight savings from 30-40% less than Columbium alloy liners Demonstrated potential of oxidation-resistant CCC for low-stress, nonrotating man-rated turbine engine parts Demonstrated utility of silicon-carbide coated CCC as a (metallic) substitution material for gas turbine engine designs	LTV Aerospace & Defense Company (Seals)/USA UTC/Pratt & Whitney Aircraft Group (Design & Test)/USA

TABLE 46 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1984	Silicon-carbide 2-D CCC combustor parts fabricated and successfully tested in a full-scale F-107 turbine engine	First demonstration of a full-scale prototype part for a limited-life, gas turbine engine	LTV Aerospace & Defense Company (Coated Combustor Parts)/USA Williams International (Turbine Engine Tests)/USA
1984	Coated 2-D CCC tailcone fabricated for engine evaluation	First prototype ORCCC tailcone for gas turbine engine testing	LTV Aerospace & Defense Company/ USA
1984	Full-scale coated CCC axial rotor successfully tested at 1149°C (2100°F), 17 minutes and 45,000 rpm in turbine engine exhaust	First prototype ORCCC rotor survived ground testing in an actual gas turbine engine	Williams International/USA
1985	Silicon-carbide coated aircraft external structural panels fabricated for AV-8B aircraft	First full-scale coated CCC part for ducting gas turbine engine exhaust	BFGoodrich Aerospace/Super-Temp/USA
1985	CCC turbine rotors demonstrated	High-speed rotor components fabricated and spun tested; results showed analytical capability to accurately predict spin capability	Materials Sciences Corporation/USA Fiber Materials, Inc./USA General Electric Company/Space Division/ USA
1985/92	Turbine engine nozzle ORCCC components manufactured and successfully tested in acoustic and hot dynamic environments	Engine components including full-scale nozzle liners ground tested in gas turbine engine environmental conditions	Rohr Industries, Inc. (Design)/USA General Electric Aircraft Engines (Test)/ USA
1986	Torque drive demonstration of ELITE bi-conic attachment	Successful testing of bi-conic attachments subelement demonstrated ability to transmit torque in engines	Allied-Signal Aerospace Company/Garrett Engine Division/USA
1986	Full-scale (15 in. dia.) lightweight CCC turbine wheel successfully fabricated and spun at high speeds (28 kft/s) and high temperature (1760°C)	CCC materials offer potential for rotating components in expendable gas turbine engines CCC wheel was one-fourth weight that of superalloys Fabrication of complex CCC configuration was successful	LTV Aerospace & Defense Company/ USA

TABLE 46 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1986	Silicon-carbide coated CCC combustor component successfully tested at 1343°C (2450°F) for 163 minutes in a gas turbine engine	First prototype ORCCC combustor for limited-life gas turbine engines	Williams International/USA
1987	Whirlpit demonstration of ELITE CCC gas engine turbine rotors	Successful Whirlpit demonstration established feasibility of CCC design at high structural loading levels	Allied-Signal Aerospace Company/Garrett Engine Division/USA
1987	Coated CCC combustor fabricated and successfully tested in a carbon slurry fuel engine	ORCCC potential demonstrated for advanced propellant engines	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA Williams International (Combustor Design & Test)/USA
1987/91	Divergent flap fabricated and successfully tested in an F-110 gas turbine engine	Thick section structural ORCCC nozzle component prototype	Rohr Industries, Inc. (Design)/USA Science Applications International Corp. (Fabrication)/USA General Electric Company/Aircraft Engines (Test)/USA
1987	Coated ORCCC convergent nozzle component fabricated and successfully tested in 2-D turbine engine	Potential of ORCCC composites for moderately-stressed, high-temperature, man-rated turbine engine nozzle components was demonstrated	Science Applications International Corp./ Materials Sciences Operation (CCC Substrates & Coatings)/USA Rolls-Royce, Inc./ENGLAND Rohr Industries, Inc. (CCC Substrate Components)/USA General Electric Company/Aircraft Engines (Test)/USA

TABLE 46 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1987	Coated ORCCC sidewall nozzle component was fabricated and successfully tested in a gas turbine engine	The potential of ORCCC materials for moderately-stressed, high-temperature, man-rated turbine engine nozzle components was demonstrated	Science Applications International Corp./ Materials Sciences Operation (CCC Substrates)/USA Rohr Industries, Inc. (CCC Substrates)/ USA Chromalloy American Corporation/ Research & Technology Division (Coating)/USA General Electric Aircraft Engines (Tests)/ USA
1988	Silicon-carbide coated inlet nozzle vanes fabricated and tested in a gas turbine engine	Fabricated nozzle vanes having a complex shape, twisted configuration, variable thickness, and high tolerances	Carbon-Carbon Advanced Technologies (C-CAT) (Vanes)/USA LTV Aircraft Products and LTV Missiles & Electronic Groups (Vanes and Coating)/USA Chromalloy American Corporation/ Chromalloy Research & Technology (Coating)/USA Teledyne CAE Turbine Engines (Testing)/ USA
1988	Demonstration of 3-D CCC rotor blade	Application of CCC materials integrated into high-temperature propulsion structure	Fiber Materials, Inc./USA
1988	ORCCC sidewall, convergent flaps, and divergent flap successfully tested in an advanced gas turbine engine 2-D nozzle	ORCCC parts for noncritical components demonstrated in an advanced gas turbine engine	General Electric Aircraft Engines (Nozzle Design)/USA NASA Lewis Research Center (Altitude Engine Tests)/USA
1988	Low-pressure CCC gas turbine blades developed	Analyzed specified material designs which were subsequently fabricated and tested in a hot aircraft engine	Materials Sciences Corporation/USA General Electric Company/Aircraft Engines Business Group/USA

TABLE 46 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1988	Coated 2-D CCC axisymmetric exhaust nozzle flap liners, and divergent flaps successfully evaluated with an aircraft turbine engine at full-augmentation conditions	Manufacturing and evaluation program revealed coated CCC potential for noncritical gas turbine engine applications Large reduction in the amount of cooling air required by CCC nozzle Improved engine thrust vectoring and thrust reversing capabilities are needed to improve aircraft maneuverability and reduce takeoff and landing distances	UTC/Pratt & Whitney Government Engine & Space Propulsion/USA
1988	CCC divergent flap and reverser vane designed for advanced turbine engine 2-D exhaust nozzle	Increased confidence in the potential use of coated CCC for advanced gas turbine engine nozzle parts	UTC/Pratt & Whitney Government Engine & Space Propulsion/USA
1988	Coated 2-D CCC components successfully evaluated for over 4,300 total engine test hours	Coated 2-D CCC components appear competitive with certain coated Columbium gas turbine engine parts	UTC/Pratt & Whitney Government Engine & Space Propulsion/USA
1988	Coated CCC combustor component successfully tested at 1371°C (2500°F) for 669 minutes in a gas turbine engine	Full-duration ORCCC life demonstrated for limited-life gas turbine engine combustor	Williams International/USA
1989	ETEC CCC turbine rotor design	Aerodynamic design included radial element blades to minimize potentially damaging interlaminar stresses in a 2-D CCC turbine rotor	Allied-Signal Aerospace Company/Garrett Engine Division/USA
1989	Silicon-nitride coated 2-D CCC aerovanes fabricated	First prototype silicon-nitride coated 2-D CCC aerovanes for advanced gas turbine engine applications	HITCO (2-D Substrates)/USA United Technologies Research Center (Parts Coating)/USA
1989	Superior performance of silicon-nitride coatings demonstrated in hot (1540°C) gas exhaust environments	Silicon-nitride coated 2-D CCC integral bladed rotor exhibited potential for turbine engines Alternate oxidation-resistant coating demonstrated for CCC	HITCO (2-D Substrates)/USA United Technologies Research Center (Parts Coating)/USA

TABLE 46 (Continued)
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	Silicon-nitride coated 2-D CCC aerovanes fabricated	First prototype silicon-nitride coated 3-D CCC aerovane components for advanced gas turbine engine applications	Fiber Materials, Inc. (Substrate)/USA United Technologies Research Center (Part Coatings)/USA
1989	Coated 2-D CCC divergent flaps successfully tested for 150 hours in gas turbine engine exhaust environments	ORCCC capabilities demonstrated for long-life, noncritical turbine engine part	General Electric Aircraft Engines/USA
1989	Coated CCC panels successfully tested in severe gas turbine engine exhausts	ORCCC potential demonstrated for future V/STOL turbine engine applications	NASA Lewis Research Center/USA
1989/91	3-D reinforced ORCCC turbine blades manufactured using matched tooling and successfully demonstrated	Low-pressure turbine engine blades became available for gas turbine engine tests First successful demonstration of an ORCCC blade component on a high-temperature, rotating gas turbine	Rohr Industries, Inc./Refractory Technology Aerospace Components (Fabrication)/USA General Electric Company/Aircraft Engines (Design & Test)/USA
1989/90	Coated 2-D CCC thrust vectoring vanes fabricated for tests on military experimental aircraft	Silicon-carbide coated CCC thrust vectoring vanes fabricated with significant weight savings over heavy superalloys First flight of a military aircraft (X-31 enhanced fighter maneuverability - EFM) with coated CCC thrust vectoring vanes Two X-31 EFM aircraft flown with three thrust vectoring vanes each and for 30 to 50 hours	Sigri Elektrographite GmbH (Vanes)/ GERMANY Rockwell International (Aircraft Test Flights)/USA MBB (Aircraft Test Flights)/GERMANY
1989	Silicon-nitride coated carbon fiber-reinforced silicon nitride matrix composite rotor hot spun for 15 minutes at over 50.000 rpm and 1540°C (2804°F)	Ceramic-coated hybrid composite components demonstrated useful in aeropropulsion environments	Societe de Europeenne Propulsion (SEP) (Rotor Substrate)/FRANCE United Technologies Research Center (Rotor Coating)/USA Williams International (Hot Spin Test)/ USA

TABLE 46 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	Coated 2-D CCC reverser vane fabricated and tested in large gas turbine engine	First prototype turbine engine reverser vane for a man-rated gas turbine engine	UTC/Pratt & Whitney Government & Space Propulsion/USA
1989	Coated 2-D CCC rotor successfully tested at 1500°C (2732°F) and 53,000 rpm in a gas turbine engine	Performance of ORCCC material at higher temperatures and higher speeds in a rotating application demonstrated	Williams International/USA
1989	Silicon-nitride coated 2-D CCC aerovanes successfully tested in a combustor rig for five hours of multiple cycles	Coating provided both oxidation and hot gas erosion protection Coating had excellent adherence to substrate and did not degrade substrate mechanical properties Rapid heating to 1500-1800°C and subsequent cooling test conditions were accommodated Silicon-nitride coated CCC has potential for use on axial turbojet engine components	Williams International (Combustor Rig Tests)/USA United Technologies Research Center (Coating)/USA BP Chemicals (Hitco) Inc. (then known as HITCO) (Substrate)/USA
1990	ORCCC flaps tested in a gas turbine engine accelerated test reached a 2000-hr simulated life	Demonstrated that CCC oxidation protection was adequate for preventing catastrophic failure by oxidation	Science Applications International Corp./ Materials Sciences Operation (CCC Substrates)/USA American Corporation/Chromalloy Research & Technology Division (Coating)/USA General Electric Aircraft Engines (Tests)/ USA
1990	Fine-woven, high-density (1.7 g/cm^3) CCC turbine wheel with thin blades integrally woven into the rotor was fabricated	Complex CCC architecture fabricated for potential use in turbine wheel applications	Toho Rayon Company, Ltd./JAPAN

TABLE 46 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1990	Silicon-carbide coated 2-D CCC two-dimensional nozzle parts successfully ground tested in an advanced gas turbine engine	Potential material for use in advanced 2-D nozzles of gas turbine engines	UTC/Pratt & Whitney Government Engine & Space Propulsion/USA
1990	CCC coating technique was developed and demonstrated for gas turbine engine ORCCC parts	Repaired CCCs were suitable for additional service in gas turbine engines	UTC/Pratt & Whitney Government Engine & Space Propulsion/USA
1991	Coated 2-D CCC flap successfully tested in a gas turbine engine for 1300 engine hours, over 5100 afterburner cycles, and 2100 equivalent flight hours	Coated 2-D ORCCC material demonstrated for longer service in advanced F-110 gas turbine engine	General Electric Aircraft Engines (Flap Design & Test)/USA Science Applications International Corp./ Materials Sciences Operation (Inhibited CCC Substrate)/USA Chromalloy American Corporation/ Chromalloy R&D Division (Coating)/ USA
1991	2-D CCC parts fabricated and evaluated in high-speed rotating environments	Interest in using CCC materials for rotating parts of gas turbine engines	Mitsubishi Heavy Industries, Ltd./JAPAN Mechanical Engineering Laboratory/ JAPAN
1991/92	Thick (1.6" to 4") 2-D and 3-D ORCCC turbine engine rotor wheels manufactured	ORCCC rotor wheels available for gas turbine engine testing	Rohr Industries, Inc./Refractory Technology Aerospace Components/USA
1991	Multidirectionally-reinforced CCC turbine engine rotor blades fabricated and spin tested at over 12,000 rpm	Full-scale prototype rotor blade demonstrated for gas turbine engines	Textile Technology, Inc. (Preform)/USA Rohr Industries, Inc./Refractory Technology Aerospace Components (Densification)/USA General Electric Aircraft Engines (Rotor Blade Tests)/USA
1992	ETEC CCC gas turbine engine demonstration	First successful demonstration of a CCC axial turbine rotor in a turbojet engine	Allied-Signal Aerospace Company/Garrett Engine Division/USA

TABLE 46 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR GAS TURBINE ENGINE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1992	SiC coated CCC specimens survived over 500 hours in AFWAL cycle oxidation testing	Coated CCC viable for limited-life application at temperatures in the range 2500-3000°F	BFGoodrich Aerospace/Super-Temp/USA
1992/93	Silicon-carbide coated 2-D silicon-carbide fabric/pitch-resin char ORCCC flaps fabricated and successfully ground-tested in an advanced (GE F414) turbine engine	Hybrid (ceramic-carbon) composites exhibited a long life in a high-performance turbine engine Hybrid composite flaps weighed 15% less than comparable metallic flaps	BP Chemicals (Hitco) Inc. (Engine Flap)/ USA General Electric Aircraft Engines (Engine Test)/USA
1992	Full-size coated CCC turbine rotor demonstrated in stoichiometric fuel turbojet engine	Durability of coated CCC adequate for missile engine turbines, major weight reduction, enables high Mach cruise speed	LTV Aerospace & Defense Co./USA

In the mid-1980s many more protected CCC prototypes were tested. Full-scale CCC combustor parts were fabricated and engine tested. The silicon carbide-coated CCC prototypes performed without difficulty. Several hours of restart testing were eventually accumulated on the parts. Perhaps the only real problem encountered was overheating of other turbine engine parts due to reduced cooling air in the protected CCC combustor. The prospects for using protective CCC materials in the static combustor and aft nozzle sections appeared rather good at this time, so other areas of application were investigated. One of the most impressive developments concerned the fabrication and laboratory testing of a CCC rotor. A coated CCC turbine wheel about 5.9 cm (15 in) in diameter was spun up to 8.54 km/s (28 kft/s) and at a maximum temperature of 1760°C (3200°F). The rotor survived and showed little effects of the thermal and stress environments. These tests indicated that protected CCC materials could survive high-stress fields at high temperatures. This was the capability being sought in upgraded verticle takeoff and landing aircraft (V/STOL), where hot exhaust gases have to be ducted and come into contact with the aircraft structure. Coated CCC protective shields were fabricated for use in the vicinity of exhaust gases.

During the late 1980s many integrated materials development and evaluation programs were underway. Much progress had been demonstrated, but there were still issues associated with the use of protected CCC materials in advanced gas turbine engines. Were any available materials suitable for use in any existing gas turbine engine part? What were the prospects for using state-of-the-art protected CCC materials for retrofit parts and in lieu of conventional metallic components? What material deficiencies needed upgrading and to what extent? Should substitution design be abandoned in favor of more promising design-to-use approaches? What additional resources and time were required to achieve any needed improvements?

Major advancements were made in the late 1980's concerning (a) materials performance upgrading, (b) additional testing of axisymmetric and 2-D nozzles, and (c) fabrication and evaluation of new prototypes. In the area of materials development, the technology of silicon nitride coatings was applied to substrate CCC materials and evaluated in the form of rotors and aerovanes. Results were impressive. One prototype rotor was hot spun at over 50 krpm and 1540°C (2804°F) to demonstrate its high thermal stability and load-carrying capability. 3-D reinforced CCC rotors were also fabricated to assess their performance features versus conventional fabric-reinforced substrate materials. The biggest opportunity for protected CCC materials presented itself in the form of thrust vectoring 2-D nozzle components. New nozzle designs were being considered, and this was an opportunity for

protected CCC materials to be evaluated in a design-to-use mode. Full-scale parts were made for the 2-D nozzle flaps and sidewalls. Performance of the flaps was satisfactory but not competitive with metallic parts. The sidewalls, however, were adequate in performance and offered substantial weight savings. Meanwhile in the axisymmetric nozzle parts testing, protected CCC components survived over 800 hours including many hours at maximum augmentation and many thousands of afterburner lights and nozzle actuations. Several new prototypes were also fabricated and tested including (a) annular flameholders and (b) inlet nozzle vanes. The first flight test of a coated CCC part in a gas turbine engine also took place during the late 1980s. Silicon carbide-coated CCC thrust vectoring vanes were flown on an advanced military aircraft, and up to 50 hours were logged with the parts.

4.8.8.1.3 *The 1990s*

The early years of the 1990s involved additional CCC prototype testing, defining the material and design limitations, and assessing the potential of the material for future production applications. Hybrid ceramic composites became available, and the interests of the engine community shifted away from protected CCC materials to newly-available materials. Engine flaps of coated 2-D silicon carbide fabric-reinforced carbon-matrix composites were fabricated and tested in an advanced turbine engine. Prototype articles of carbon fiber-reinforced silicon carbide-matrix composites were also manufactured and evaluated. Further prototyping and evaluation activities will eventually reveal the potential of each type of material for future gas turbine applications.

4.8.9 Missile Vehicle Components

A strategic missile reentry vehicle (RV) is designed to transport a weapon over very long distances (up to 10,000 km, 6215 miles). Missiles containing the RVs are usually launched from the ground or underwater, and then propelled out of the atmosphere with a multi-staged solid motor or liquid propellant engine system. Up to 10 or more RVs are carried on the upper stage propulsion bus, and each RV can be independently targeted to a different location on Earth. Only the RV reenters the Earth's atmosphere at the target area. Initial reentry velocities are very high, i.e. on the order of 4.6-7.6 km/s (15-25 kft/s). Ballistic RVs (BRV) after launch will travel unpowered on a ballistic trajectory. Its path is influenced only by external forces, such as (a) gravity, (b) atmospheric friction, and (c) weather conditions. Maneuvering reentry vehicles (MaRV) contain aerodynamic control systems on board to fly in the reentry atmosphere on a nonballistic or guided trajectory.

A reentry vehicle consists of various subsystems such as (a) nosetip, (b) impact fuse, (c) arming and fusing, (d) thermal/structural protection, (e) antenna, (f) spin stabilization, (g) warhead, and (h) related components. The thermal/structural protection is composed of (a) external heatshield, (b) aft cover, and (c) underlying structure.

RVs are typically placed on top of the missile propulsion system. They may be exposed to the atmosphere, but it is more conventional to place an aerodynamic shroud around them for protection during the launch phase. In the latter case the RV experiences only the mechanical launch loads. Any particulate matter in the atmosphere or nuclear blast loads are accommodated by the shroud. Once out of the Earth's atmosphere, the shroud is removed and the RV is exposed to the space environment. Space environmental effects are minimal because of the short flight time. However, the RV may be exposed to the destructive effects of x-rays or laser energy during the exo-atmospheric flight. Following this flight stage, the RV reenters the Earth's atmosphere. The RV external surfaces are exposed to extreme conditions of temperature, heating, pressure, and sometimes particulate matter. The environmental conditions vary primarily with the (a) vehicle configuration, (b) location on the vehicle, and (c) initial RV velocity and entry angle. The stagnation and sonic point on the RV nosetip experience the most severe environment. During early reentry into the Earth's atmosphere, air slows the RV and the kinetic energy of the vehicle is transformed into thermal energy of the surrounding environment. Convective and radiative heating from the boundary layer produce severe thermal and mechanical conditions including (a) surface temperatures up to 4200°C (7592°F) for nonmelting materials and (b) cold wall heating rates up to 6512 cal/cm^2-s (24,000 Btu/ft^2-s) and stagnation pressures up to about 21.3 MPa (210 atm). All of the environmental parameters change constantly during atmospheric reentry because the RV continually decelerates until weapon detonation. As the RV approaches its Earth target, the frontal external surfaces may encounter particles such as (a) ice crystals, (b) rain, or (c) dust from a previous nuclear explosion on Earth. Particle erosion can be quite severe because of the high velocities associated with the encounter. The effects are most deleterious in the nosetip section because (a) there is little mass to accommodate the environmental effect and (b) asymmetrical shapes may be generated. Nosetip changes, whether they are thermally- or particle erosion-induced, influence the vehicle drag by changing the nosetip drag contribution and by altering the afterbody flowfield. As the vehicle drag is altered, attendant trajectory changes are experienced such as range and velocity. In other words, nosetip erosion or ablation may cause (a) component failure, (b) reentry short of the target, or (c) reentry dispersions with loss of vehicle accuracy. Compared to the RV nosetip, the environmental parameters associated with the heatshield and aft cover are quite benign. The heatshield, however, occupies a large area of the RV. Mass loss and uniform release of the ablated material is generally attained

by proper control of the material composition and construction. Hence thermal/structural materials used on RVs must (a) protect the internal payload from severe heating and (b) retain as much of the original configuration and mass as possible during atmospheric reentry or an encounter with various weapons effects.

4.8.9.1 Nosetips

RV nosetips have different designs, heat protection modes, and materials. First-generation IRBM nosecaps were blunt in configuration, employed the heat sink principle, and were constructed of a thick metallic shell. In 1958 an ICBM test vehicle containing an ablative plastic composite nosecap successfully completed a 3100-km (4988-mile) ballistic flight. As more streamlined nosetips were developed, both ablative plastics and polycrystalline graphites were used to accommodate the more severe thermal conditions. These passively-cooled nosetip materials were preferred for operational missiles because of (a) design simplicity, (b) relatively high performance, (c) large number of available materials, and (d) low costs. The major limitation of the ablative plastics was their high recession rate during heating. The major limitation of polycrystalline graphites was their tendency to exhibit thermostructural failure due to thermally-induced stresses. Actively-cooled nosetips based on water coolant and porous metallic materials were also developed and successfully flight tested. They have not been extensively employed because of design complexity and high weight. Ultimately, the two-decade search for a high-performance nosetip material ended with the development of 3-D CCC materials. It has been reported that the U.S. employs 3-D CCC nosetips on all of its latest missile reentry systems. Other countries are known to have flight tested CCC materials, and they may possibly be using them on operational missile reentry systems.

CCC materials possess many attributes for use on strategic missile RVs. Most of these attributes have been previously discussed, but several features are worth repeating. The CCC materials have exceptional thermal stability and exhibit only minor mass losses in ultrahigh heating environments. 3-D CCC nosetips have survived advanced reentry trajectories with less than 2.54 cm (1 in.) total recession. Similar nosetips constructed of ablative plastics recede up to 17.8 cm (7 in). The CCC materials are mechanically strong and stiff, especially at high temperatures associated with reentry. The composites are thus capable of accommodating high axial and lateral loads. Hypervelocity particle erosion resistance is also good which provides an all-weather capability. The CCC materials have very high resistance to nuclear weapons effects including blast and x-ray environments. About the only concerns are the high cost of the materials and long production times.

CCC nosetips have been fabricated with 2-D, 3-D, 4-D, 5-D, and other n-D reinforcement constructions. 3-D CCC nosetips with orthogonally-oriented reinforcements are the most popular. Fine-weave orthogonal and fine-weave pierced fabric constructions are but two examples. Figure 24 illustrates a number of 3-D and n-D nosetip material constructions. Coarse-weave 3-D CCC contains relatively large yarn or tow fiber bundles with a large spacing between the bundles. Fine-weave 3-D CCC materials are manufactured with smaller diameter tow or yarn bundles, and the bundle-to-bundle spacing is much closer. These materials exhibit relatively smooth surfaces during ablation. High axial 3-D CCCs have a high percentage of continuous reinforement in the axis of the nosetip. These materials exhibit high bend stiffness and can accommodate high lateral loads. 3-D pierced fabric CCC materials utilize woven fabric in lieu of X and Y tows or yarns. This specific material construction enables faster assembly of the fibrous graphite preform, and hence lower cost billets. High symmetry CCC materials are reinforced with 4-D or other n-D constructions. This type of material exhibits more balanced properties in all directions, but its total reinforcement content is generally lower than other forms of 3-D materials.

4.8.9.2 Heatshields

Adjacent to and trailing the reentry nosetip is a large heatshield section. The heatshield covers most of the external surfaces of the RV. Its primary functions are to (a) insulate the underlying structure and internally-contained payload and (b) maintain its original configuration with minimum mass loss. Because of its large size, heatshield weight and influence on reentry aerodynamics are important considerations. RV heatshields have been constructed with heatsink metallics, various ablative composites, and CCC materials. The generally preferred heatshield is composed of a multilayered construction or an integrated heatshield-structure. Multilayered heatshields contain an external ablator, an underlying adhesive layer, and a structural metal to carry the transmitted loads. An integrated heatshield-structure is composed of 3-D ablative plastic and capable of providing both thermal protection and load-carrying capabilities. CCC heatshields have significantly higher through-the-thickness thermal conductivities compared to ablators, and for that reason they are used only for specialized purposes. Their applications are associated with certain features like (a) retention of the original heatshield configuration and thickness during reentry, (b) generation of little ablative species which influence radar return from the vehicle trailing wake, and (c) ultrahigh resistance to nuclear weapons effects.

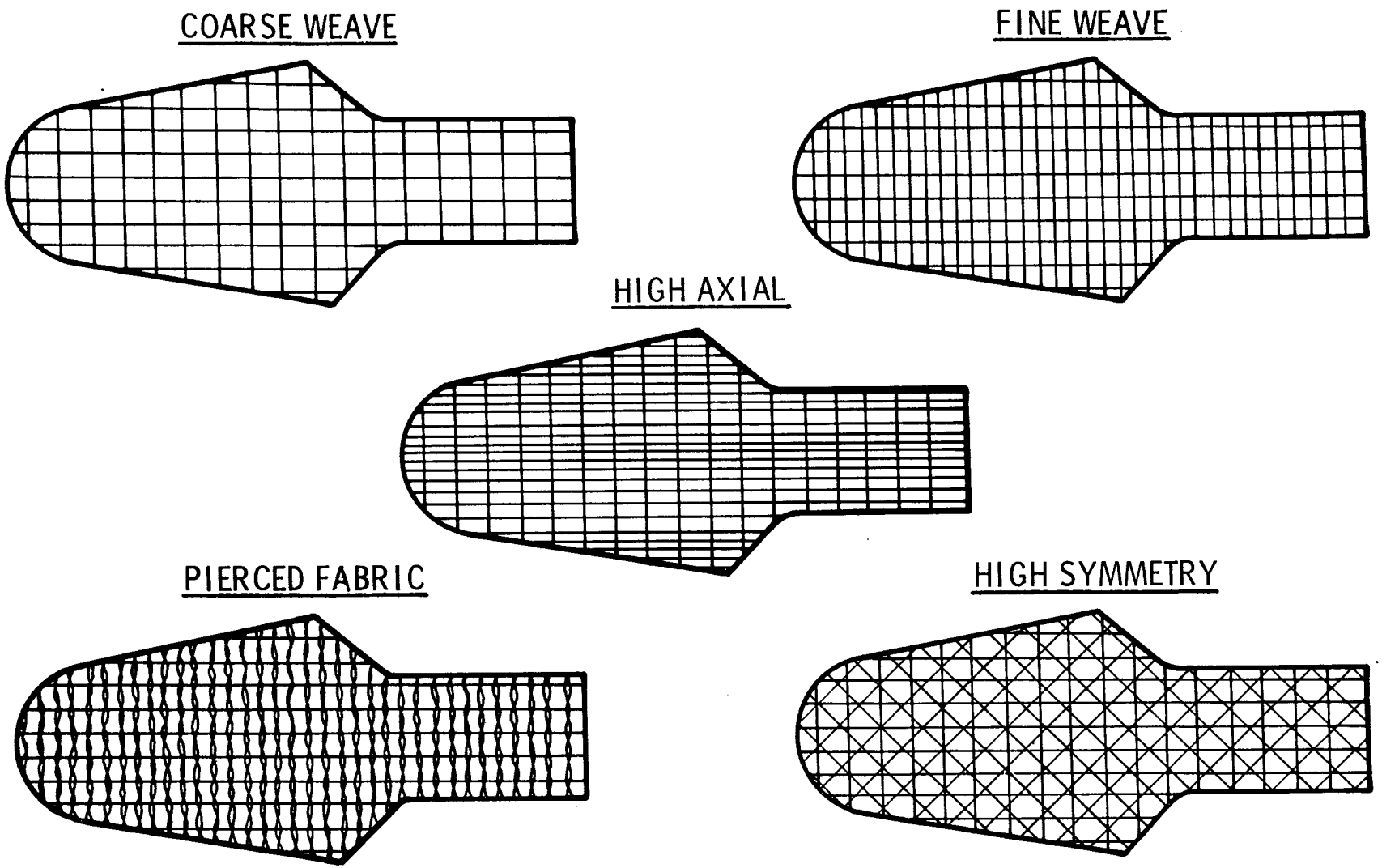


Figure 24. Schematics of 3-D and n-D Fibrous Preforms for Missile Reentry CCC Nosetips.

4.8.9.3 Aft Covers

CCC materials have also been used for the aft cover of the RV. When used in conjunction with a CCC nosetip and heatshield, they enable the design of an all-carbon reentry vehicle.

To summarize, major missile reentry systems benefits have been achieved with the use of CCC materials. The benefits have been particularly noticeable in the area of RV nosetips, and for that reason CCC materials are of interest to all countries that now possess or are developing long-range missile systems. The major systems benefits are (a) increased RV survivability, (b) higher accuracy, (c) higher performance, and (d) an all-weather operational capability.

4.8.9.4 Chronology

Table 47 gives the various CCC prototypes that were developed in support of very high-speed missiles and the first year these articles were fabricated. These prototypes include (a) nosetips, (b) heatshields, (c) aft covers, and (d) x-ray shields.

Table 48 lists a chronology of CCC prototype activities for hypervelocity missile systems. Virtually all of the entries are domestic; few details have been published on non-U.S. activities.

4.8.9.4.1 *The 1960s*

In the United States the Atomic Energy Commission Laboratories were seeking to develop a high nuclear hardness, all-carbon missile reentry vehicle. Polycrystalline graphites were state-of-the-art for missile nosetips, but carbonaceous heatshields and aft covers were not available. To accommodate this need CCC heatshields were developed. The CCC heatshields were very promising, but their high through-the-thickness conductivity necessitated the use of an insulative material between the heatshield and the underlying metallic structure. A low-density, all-carbon insulative material was therefore developed and used successfully. The material was later productionized for uses in high-temperature furnaces, HIPIC units, and other applications.

By the late 1960s two types of CCC heatshields were manufactured in RV sizes. The 2-D CCC heatshields were composed of continuous carbon filament-reinforced carbon matrix composites. Pseudo 3-D CCC heatshields were composed of

TABLE 47

FIRST CCC PROTOTYPE COMPONENTS FOR VERY HIGH-SPEED MISSILES

YEAR	PROTOTYPE	ORGANIZATION
1963	RV graphite nosetip substrate insulator	Union Carbide Corp./Carbon Products Division/USA
1966	RV structural heatshield	Union Carbide Corp./Oak Ridge Y-12 Plant/USA
1967	RV heatshield substrate x-ray absorber	LTV Aerospace Corporation/USA
1968	RV nosetip - shell construction	Atomic Energy Commission/Sandia Laboratories/USA
1973	RV nosetip - plug construction	Air Force Materials Laboratory/USA
1973	Antiballistic missile (ABM) nosetip	Fiber Materials, Inc./USA
1975	RV shape stable, plug nosetip	Acurex Corporation/Aerotherm Division/USA
1983	RV aft cover	Textron Specialty Materials/USA

TABLE 48

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR MISSILE VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1963	Low-density (1.1 g/cm^3) CCC insulator material bonded to polycrystalline graphite missile shell nosetip	Thermally-stable insulator developed for potential use on missile shell nosetips	Union Carbide Corp./Carbon Products Division/USA
1966	Full-scale, filament-wound (0-90°) CCC missile heatshield fabricated	First prototype CCC missile heatshield available for testing	Union Carbide Corp./Oak Ridge Y-12 Plant/USA
1967	Full-scale, CVD PG/chopped fiber composite frusta fabricated	Candidate material for missile reentry vehicle heatshields	Union Carbide Corp./Oak Ridge Y-12 Plant/USA
1968	Full-scale 3-D PG/felt CCC missile heatshield manufactured	First prototype CCC heatshield for evaluation on strategic reentry missiles	Super-Temp Company/USA
1968	3-D needled fibrous (rayon-based) graphite felt/CVI PG matrix CCC missile heatshield survived IRBM earth reentry test	First missile flight test of a CCC heatshield Lowest ablative material recession demonstrated in a high aerodynamic heating environment	Super-Temp Company (Missile Heatshield)/USA
1969	Full-scale, 2-D filament-wound (rayon-based) graphite/CVI PG CCC frusta heatshield fabricated	First flightweight CCC heatshield for missile reentry vehicles	AEC-Sandia Laboratories/USA
1969	2-D filament-wound (rayon-based) graphite/ CVI PG and 3-D carbonized rayon felt/CVI PG heatshields survived ground-based, simulated reentry thermal tests in a rocket motor exhaust	Outstanding thermal shock and thermal resistance of CCCs demonstrated in ground test facilities	AEC-Sandia Laboratories (CCC Heatshields)/USA General Electric Company/Re-Entry & Environmental Systems Division (Tests)/ USA
1970/71	High-density (1.83 g/cm^3) 3-D orthogonal fine-weave CCC exhibited high shape stability in a high-pressure air arc test facility	High-density and fine-weave 3-D CCCs offer high potential for missile nosetip uses	McDonnell Douglas Astronautics Co.-East (Tests)/USA Fiber Materials, Inc. (Fibrous Preform)/ USA McDonnell Douglas Astronautics Co.-West (Preform Densification)/ USA
1970	2-D filament-wound graphite/CVI PG and 3-D carbonized needled felt/CVI PG CCC heatshields survived IRBM flight tests	Flightworthiness of two diferent CCC heatshields demonstrated by actual missile reentry tests	AEC-Sandia Laboratories/USA

TABLE 48 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR MISSILE VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1970	3-D orthogonal fibrous carbon/resin char CCC frustum manufactured	First full-scale prototype 3-D CCC heatshield for Air Force strategic missile reentry vehicles	Avco Corporation/Systems Division/USA
1971	3-D graphite fiber needled felt/CVI PG CCC heatshields successfully tested for the third and fourth time in earth reentry flight tests	Repeatable performance of CCC heatshields was demonstrated by actual reentry flights	AEC-Sandia Laboratories/USA
1972	2-D graphite filament-wound/CVI PG CCC heatshield successfully flight tested in a more severe ICBM-like trajectory	Repeatable performance of a medium-size CCC heatshield/vehicle design	AEC-Sandia Laboratories/USA
1973	Missile nosetip design with a CCC plug was patented	First use of CCC in a plug nosetip design Baseline design for later 3-D CCC missile reentry nosetip Patent rights assigned to Secretary of Air Force (U.S. Patent 3,724,386)	Air Force Materials Laboratory/AFSC/ USA
1973	Coarse-woven 3-D intermediate-density CCC nosetip successfully flight tested	First CCC missile nosetip to survive an IRBM range	Avco Corporation/Systems Division (Nosetip)/USA Defense Nuclear Agency (Flight Test)/ USA
1974	Full-scale 3-D needled felt/CVI PG CCC heatshield successfully tested in an ICBM flight	First full-scale CCC heatshield to survive an ICBM reentry environment Greatly increased missile designer's confidence in CCC heatshields	AEC-Sandia Laboratories/USA
1974/75	3-D CCC nosetip materials instrumented, tested in AFFDL 50MW facility and performance features analyzed	Post-test analyses revealed many material construction:processing:performance relationships Identified importance of small-diameter yarns, small yarn-to-yarn spacing and high matrix density	Aerotherm Division/Acurex Corporation/ USA

TABLE 48 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR MISSILE VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1974	Largest 3-D orthogonal reinforced CCC frusta manufactured	First full-scale (22 in. O.D., 65 in. long) 3-D CCC heatshield for advanced ballistic missile tests	Avco Corporation/Systems Division/USA
1974/78	Source selected for production of ballistic missile 3-D CCC nosetip materials	Competitive bidding on nosetip materials manufacturing saved USAF $25 million	Avco Corporation/Systems Division (Nosetip Manufacturer)/USA
1974	Shell nosetips machined from an intermediate density (1.6 g/cm^3) 3-D CCC billet	3-D CCC nosetips in conventional missile nosetip design available for flight tests	General Electric Company/Re-Entry & Environmental Systems Division (Nosetip Preparation)/USA Avco Systems Division (3-D CCC Billets)/USA
1974	Intermediate-density, coarse-woven 3-D CCC nosetips successfully flight tested over an intercontinental (ICBM) range	Outstanding performance of 3-D pierced fabric and 3-D orthogonal CCC missile nosetips demonstrated compared to state-of-the-art polycrystalline graphites and 2-D carbon fabric/phenolic resin composites	Air Force Space & Missile Systems Organization/USA
1975	Chemical vapor infiltration (thermal gradient process) used to densify 60-in. long filament-wound frusta	Full-scale CCC heatshields available for missile re-entry flight tests	Union Carbide Corp./Oak Ridge Y-12 Plant/USA
1976	Full-scale 3-D needled felt/CVI PG CCC heatshield successfully flight tested on a high ballistic coefficient reentry vehicle simulating a full ICBM trajectory	CCC heatshield successfully tested in a "worst case" ICBM temperature-pressure-time reentry flight environment	AEC-Sandia Laboratories/USA
1976	First flight of the Aerotherm shape-stable nosetip	CCC nosetip developed for higher accuracy missile reentry vehicles	Acurex Corporation/Aerotherm Division/ USA
1976	Full-scale CCC nosetips were evaluated in hot exhaust of a benzonitrile/oxygen-fueled rocket motor	Ablation and thermostructural response of CCC nosetips experimentally determined	Air Force Rocket Propulsion Laboratory/ USA

TABLE 48 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR MISSILE VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1977	3-D CCC shell nosetip models were instrumented, tested in the AFFDL 50MW facility, and performance compared to similar graphite nosetips	Alternate nosetip design validated for missile reentry systems Outstanding thermostructural behavior of 3-D CCC demonstrated Polycrystalline graphite shell nosetips thermostructurally failed under similar conditions	General Electric Company/Re-Entry & Environmental Systems Division (Nosetip)/USA Air Force Flight Dynamics Laboratory (Ground Tests)/USA Acurex Corporation/Aerotherm Aerospace Systems Division (Instrumentation & Data Analysis)/USA
1978	High-density, 3-D CCC plug nosetip successfully flown an ICBM distance on a large ballistic reentry vehicle	First flight demonstration of high-density, 3-D fine-weave	Air Force Space & Missile Systems Organization/ AFSC/USA
1978	3-D CCC plug nosetip selected for the Minuteman Mark 12A reentry vehicle	First U.S. ICBM nosetip application for 3-D CCC	Air Force Space & Missile Systems Organization/AFSC/USA
1979	Design, fabrication, and ground testing of erosion-resistant, shape-stable RV nosetips	First CCC capable of surviving hypervelocity nosetip reentry in ice/dust/particulate environments	Aerotherm Corporation/USA
1979	High-density (1.85-1.90 g/cm^3) 3-D CCC evaluated in air arc heater and rocket engine exhaust facilities	Increased P.R.C. development of 3-D CCC and screening for potential reentry vehicle and solid propellant rocket motor applications	Beijing Research Institute of Materials & Technology/P.R. CHINA
1981	3-D CCC plug nosetip selected to retrofit the Minuteman III, Mark 12 reentry vehicles	Second U.S. ICBM nosetip application for 3-D CCC 3-D CCC exhibited lower ablation and greater shape stability compared to state-of-the-art carbon fabric/phenolic composite	AF Space & Missile Systems Organization/AFSC/USA
1982/85	3-D CCC plug nosetips successfully flight tested on advanced maneuvering reentry vehicles	3-D CCC intrinsic properties adequate to survive high (bending) maneuvering stresses	AF Space & Missile Systems Organization/AFSC/USA

TABLE 48 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR MISSILE VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1983	3-D CCC plug nosetip selected for the Peacekeeper Mark 21 reentry vehicle	Third U.S. ICBM nosetip application for 3-D CCC	AF Ballistic Missile Office/AFSC/USA
1983	High bend stiffness, 5-D pierced fabric billets fabricated	First high-performance CCC for maneuvering reentry vehicle nosetips	Textron Specialty Materials/USA
1984	First MX (Peacekeeper) ICBM flight with full complement of 10 reentry vehicles containing 3-D CCC nosetips	3-D CCC nosetips contributed to improved missile accuracy and survivability	AF Ballistic Missile Office/AFSC/USA
1985	41 3-D pierced fabric CCCnosetips successfully flight tested on Peacekeeper Mark 21 reentry vehicles	First phase of Peacekeeper flight test program completed 3-D CCC nosetip contributed to high reentry vehicle accuracy	AF Ballistic Missile Office/AFSC/USA
1986	Over 1,400 3-D CCC nosetips procured for U.S. operational missile forces	3-D CCC materials replaced polycrystalline graphite and 2-D carbon fabric/phenolic resin composites for missile nosetip	AF Space & Missile Systems Organization/AFSC/USA
1990	4-D CCC nosetip successfully flight tested on an advanced maneuvering reentry vehicle	n-Directionally-reinforced CCC exhibited high performance in a structurally-demanding missile reentry environment	AF Ballistic Missile Office/AFSC/USA
1990	5-D fine-weave pierced fabric CCC nosetip successfully flown on maneuvering reentry vehicle	High-performance CCC demonstrated for advanced missile reentry systems	Textron Specialty Materials/USA

needled felt-reinforced PG matrix composites. Both types of CCC materials were satisfactory, but the pseudo 3-D CCC material appeared to offer the greatest promise in terms of (a) fabrication ease, (b) directional properties, and (c) properties to accommodate changing service environments.

4.8.9.4.2 *The 1970s*

Heatshield activities, under the sponsorship of the U.S. Atomic Energy Commission, were continued in the early 1970s. Two types of CCC heatshields were flown on IRBM trajectories in May and June 1970, and they survived without any problems.

The concept of a 3-D orthogonal CCC material was originated in the U.S. in the early 1970s. 3-D orthogonal quartz fiber-reinforced phenolic composites were previously developed to obtain materials with higher interlaminar shear strength. Such materials were found to have considerable potential for missile nosetips and heatshields. With the advent of high strength, intermediate-modulus graphite yarns and tows in the early 1970s, the 3-D orthogonal-reinforced phenolic composites were recreated in the form of 3-D orthogonal graphite fiber-reinforced phenolic composites. These composites had better ablation resistance than quartz fiber/phenolic materials, and hence some effort was expended in evaluating their potential for missile nosetips. The breakthrough in missile nosetip materials came in the early 1970s when the Air Force Materials Laboratory funded the Avco Corporation to develop a 3-D orthogonal-reinforced carbon matrix composite. The concept of "pyrolyzed plastics" was applied to the 3-D carbon/phenolic materials, and the resultant porous all-carbon material was further densified with resin char. The first-generation 3-D orthogonal CCC materials were of an intermediate density. The fiber bundles contained between 2000 and 10,000 continuous filaments, and the reinforcement construction was a coarse weave. These advanced materials appeared suitable for missile nosetip uses. After an abbreviated ground test program, the first- generation 3-D CCC material was successfully flight tested over an IRBM distance. Upgraded 3-D CCC materials were later developed. These composites had higher densities and a finer- weave construction. The second-generation 3-D CCC materials exhibited very attractive properties and performance in ground-based tests. Consideration was therefore given to the design of new missile nosetips. Conventional polycrystalline graphites were replaced with 3-D CCC in shell nosetip designs. The new nosetips were stronger and did not fail thermostructurally during simulated reentry heating. The shell nosetip design quickly gave way to a new plug nosetip construction. This type of nosetip contained a central plug of CCC material with its trailing stem insulated with carbon fabric/phenolic composite. The CCC plug nosetip was extensively tested in ground-based facilities and found to (a) have high dimensional stability and (b) satisfy all of the other demanding requirements.

During the mid-1970s, 3-D CCC materials continued to be improved. Emphasis was given to both 3-D orthogonal and 3-D pierced fabric constructions. Design data were generated on the two materials, and they were extensively tested in very high-pressure air arc heaters, rocket exhaust facilities, and underground nuclear events. From all of these ground-based tests, it appeared that coarse-woven, intermediate-density 3-D CCC nosetips would perform satisfactorily. During the first ICBM flight, however, the 3-D CCC material unexpectedly exhibited a high ablation rate and nosetip destruction. This fateful event caused the missile systems designers to quickly lose interest in 3-D CCC materials. The U.S. defense community now faced a dilemma. If it abandoned the 3-D CCC materials development, all of the previous investment would be essentially lost. If it reverted to the use of polycrystalline graphites, only slight improvements in thermostructural capability could be realized by the use of new, high strain-to-failure graphites. Systems and test engineers reasoned that the coarse-woven 3-D CCC material developed a rough ablating surface, induced boundary layer transition from laminar to turbulent flow at higher altitudes, and thereby greatly increased the heating rate to the nosetip material. This hypothesis enabled the problem to be attacked by the materials community. A ramp heating test was devised for the AF 50 MW air arc heater, and the boundary layer transition heating of test nosetip materials was studied. These and other ground-based test results demonstrated the importance of (a) smaller-diameter fibrous bundles, (b) closer spacing of the fibrous bundles, and (c) higher density pitch-based carbon matrices. Within a short period of time, a new generation of high-density, smooth ablating surface 3-D CCC materials were developed for nosetip uses. In spite of these successes, many individuals in the U.S. defense community felt that the use of 3-D CCC materials imposed too great a risk, and efforts should continue on upgrading the properties of polycrystalline graphites. These efforts were supported primarily by the U.S. Navy. Several grades of higher strain-to-failure graphites were (a) developed, (b) design data generated, (c) ground and flight tests conducted, and (d) a manufacturing plant established to obtain several thousand billets of materials .

During the mid-1970s, missile reentry in other than clear air became a major concern for RV designers. It was known that the interaction of hypervelocity particles with nosetip materials caused high erosion. Ice crystals, rain, or dust in the target area could thus induce nosetip shape changes or destruction. A shape-stable CCC nosetip concept was generated, developed, and successfully flight tested. The new nosetip construction was designed to maintain the original nosetip configuration regardless of thermal, erosive, or nuclear environmental parameters.

Also during the mid-1970s, efforts continued on the development of CCC missile heatshield materials. Some doubt was voiced concerning the need for such materials, but efforts were continued to place the technology "on the-shelf." A manufacturing technology program produced a full-scale 3-D orthogonal CCC frustrum for demonstration purposes and to obtain design data. At this point in time, the U.S. had three different CCC heatshields ready for use. They were: (a) the previously flight qualified 3-D needled felt/PG matrix composite, (b) the flight tested filament-wound carbon fiber/PG matrix composite, and (c) the newly-available 3-D orthogonal CCC material. In the years to follow, missile systems requirements never became sufficiently demanding to warrant the use of CCC heatshields. Thus closed a long chapter in the development of CCC missile heatshields.

During the late 1970s all of the nosetip materials developmental work came together in the successful flight of an ICBM missile. The nosetip material was constructed of a 3-D orthogonal-reinforced, fine-woven fibrous carbon reinforcement and a high-density, pitch-based carbon coke matrix. It was the answer to the missile nosetip problem which had existed so many years. The new 3-D CCC material was selected as the baseline for the new Mark 12A RV nosetip. This material selection constituted the first use of 3-D CCC material for an operational ICBM RV. Overseas, foreign organizations were also interested in and developing 3-D CCC materials. It is interesting to note that the P.R. China had developed a high-density, 3-D CCC material in the laboratory and was screening it for potential nosetip and nozzle applications.

4.8.9.4.3 *The 1980s*

In the early 1980s a large number of ICBM reentry tests were conducted on the newly-available 3-D CCC materials. No material failures were encountered over a wide range of reentry conditions. Because of this outstanding material performance, 3-D CCCs were chosen to retrofit the operational Minuteman III Mark 12 RVs. The existing carbon- fabric/phenolic composite nosetips were removed, and new high-performance 3-D CCC plug nosetips replaced them. Equally important, the U.S. Air Force also chose the 3-D plug CCC nosetip as the baseline for its new Peacekeeper Mark 21 RV.

MaRVs were also being developed to evade terminal interceptor missiles during the final phase of a reentry trajectory. The 3-D CCC plug nosetip was successfully flown on a MaRV flight path and withstood the high lateral forces due to manuevering. An improved MaRV nosetip material was also fabricated for the first time. It was composed of a 5-D pierced fabric construction and pitch-based coke matrix.

During the mid-1980s 3-D pierced fabric and 3-D orthogonal CCC nosetip materials were successfully flight tested on many different occasions in support of their future uses on operational missile forces. Over 41 3-D CCC nosetips were tested on the Peacekeeper Mk 21 RVs. Many more nosetips were flight evaluated for other missile systems. Manufacturing of the 3-D pierced fabric CCC nosetip material became routine, and over 1400 billets were manufactured.

4.8.9.4.4 *The 1990s*

By the early 1990s 3-D CCC materials had matured greatly, and they were being used on all of the U.S. Air Force operational strategic missile reentry systems. The same materials showed promise for use on maneuvering reentry systems, but other material systems were also being evaluated. Successful flight tests were conducted with 4-D and 5-D fine-weave, pierced fabric CCC materials. With these flight tests the chapter was closed on the long search for an acceptable RV nosetip material.

4.8.10 Aerospaceplane Components

Advanced transportation systems are being developed for low-cost acquisition and utilization of space. These systems utilize an aerospaceplane (hypersonic winged glider) to fly from Earth-to-orbit and back. Their missions are primarily scientific in nature, but some concepts have potential military purposes. Most of the space transportation systems are or will be manned, reusable, and intended to inject payloads into Earth orbit at an expense of about $2000/kg ($909/lb) compared to the current price of about $10,000/kg ($4,545/lb).

Aerospaceplanes reach the upper levels of the Earth's atmosphere and space by two major types of propulsion systems, i.e. expendable vertical launchers or their own unique air-breathing engines. Expendable rockets are or will be used for the (a) U.S. space shuttle orbiter, (b) Soviet Buran, (c) French Hermes, and (d) Japanese Hope. A second class of hypervelocity gliders are to be launched and recovered from national territory. They are designed to be economically viable and cost only a fraction of the expense of expendable launchers. They will take off and land horizontally, with a minimum of turnaround time, on any part of the globe. Several examples of these winged flight vehicles are the: (a) U.S. National Aero-Space Plane (NASP), (b) British Hotol, (c) German Sanger, and (d) French H-Star. Each nation will thus have access to their national space assets without relying on a foreign launch system.

Aerodynamic surfaces of hypersonic flight vehicles are exposed to sustained periods of heating and high temperatures. Three types of passive thermal protection systems have

been developed for these types of flight vehicles including: (a) heat sinks which store the incoming thermal energy, (b) ablative thermal protection systems which dissipate heat by material decomposition and reradiating it to the environment, and (c) insulative systems which reradiate nearly all of the heat to the environment. Passive insulation systems have been found to be the most weight efficient and generally the safest for manned flight vehicles. Protected CCC and hybrid carbon composites (like carbon fiber-reinforced silicon carbide-matrix composite) offer the greatest possibilities for meeting all materials requirements. Protected CCC materials have already been used in operational flight vehicles, and hybrid carbon composites are being considered for future generations of aerospaceplanes. The systems benefits to be derived with these very high-temperature materials are (a) flightweight vehicle due to the low material density and its high strength and stiffness over a wide temperature range, (b) a larger flight envelope with materials capable of accommodating higher service temperatures, (c) reusability for low life- cycle costs, and (d) material versatility and growth potential to meet systems upgrading needs without the development of a totally new class of materials.

Current operational aerospaceplanes and the major ones being considered for the future are discussed in the following text. Emphasis will be given to those flight vehicles requiring protected CCC and hybrid carbon composites for thermal protection uses.

4.8.10.1 U.S. Space Shuttle Orbiter

The space shuttle is part of a U.S. space transportation system. Shuttle missions are generally of two categories, i.e. attached payloads or satellites. An example of an attached payload is the Spacelab module which carries a wide variety of experiments in the very low-to-zero gravity. Satellites are also delivered to space with the space shuttle. They are parked in low-Earth orbit and later retrieved, or they are boosted to a higher orbit with their own propulsion system. The space shuttle was originally designed to place payloads weighing up to 29,500 kg (64.9 klb) in a 185-km (607-kft) Earth orbit and return about 11,400 kg (25.1 klb) from orbit. The space shuttle flight system consists of the (a) U.S. $1.8 billion reusable orbiter, (b) three space shuttle main engines, (c) external propellant tank, and (d) two refurbishable solid fueled rocket boosters. The orbiter carries a manned crew of four to seven along with various payloads. It can remain in orbit for up to about 10 days or longer. The orbiter is launched vertically with a rocket and, after its mission in space, lands horizontally like an airplane. The key to low-cost operation is the reusable orbiter, which is configured as a double delta aircraft and about the size of a U.S. medium transport aircraft such as the DC-9.

The manned orbiter returns from space at an initial hypersonic velocity. During flight in the atmosphere, all of the aerodynamic surfaces are subjected to heating and high temperatures. A thermal protection system of heat protective materials is used because of geometric and thermal constraints.

The orbiter's thermal protection materials requirements are quite demanding because of the diverse environmental conditions and the high safety factor used in the design of manned vehicles. The main heat protective material requirements are: (a) retain the original aerodynamic shape during the entire mission, (b) reproducible strength levels up to 1650°C (3002°F) which are sufficient to withstand flight loads without additional support structure, (c) adequate stiffness to resist buckling from launch loads, airloads, or large thermal gradients, (d) low thermal expansion to limit thermally-induced part deflections and facilitate attachment to metallic structures, (e) oxidation resistance sufficient to maintain original properties without significant degradation, (f) maximum tolerance to foreign object and particle impact damage, (g) resistant to vibro-acoustical loads, (h) long fatigue life, (i) smooth aerodynamic surfaces, (j) low outgassing in space vacuum conditions, (k) fabricable with state-of-the-art methods to yield high-tolerance parts, and (l) reusability for about 50-100 missions.

Coated CCC materials are used to protect the orbiter's surfaces that experience the highest entry temperatures. This portion of the vehicle's thermal protection system consists mainly of the nosecap, wing leading edges, metallic attachments, internal insulation, and interface tiles. The nosecap and leading edges form structural fairings which transmit aerodynamic loads to the forward bulkhead or wing spar through discrete mechanical attachments. Both the nosecap and wing leading edges are precision parts. Close tolerance parts are necessary to avoid perturbations and gaps which interfere with aerodynamic flow and to insure that heated air does not penetrate into the structure. The attachment fittings are made of heat-resistant metals and are arranged to accommodate structural displacement caused by thermal expansion. The metallic attachments and adjacent aluminum structure are protected from excessive temperatures by internally-contained, low-density insulation. Figure 25 illustrates the main thermal protection system used on the operational U.S. space shuttle orbiter.

Five shuttle orbiters have flown over 30 successful Earth-to-orbital missions. Hence, they have a proven thermal protection system. Each orbiter contains about 95 parts of protected CCC material. The heat-protective material is composed of a graphite fabric-reinforced resin coke matrix which has been coated with silicon carbide and internally protected with tetra-ethyl orthosilicate. Total weight of the various parts is about 1700 kg (3740 lb) which is about 20 percent of the total thermal protection system weight. The protected CCC parts cover

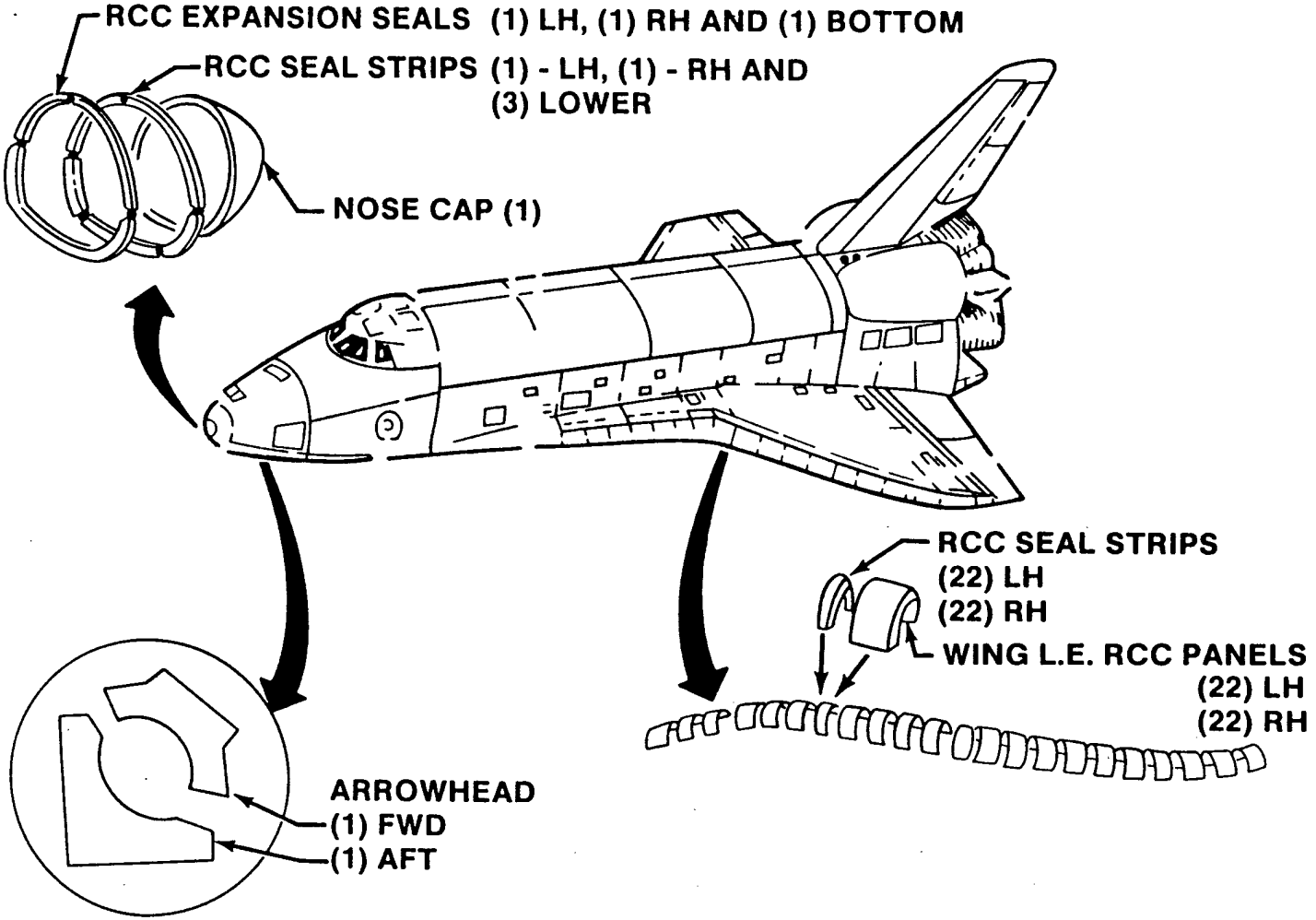


Figure 25. Schematic of the U.S. Orbiter Nosecap and Leading Edge Structural Subsystems (LESS).

a total vehicle area of about 38.3 m (411 ft) which is about 3.4 percent of the total aerodynamic surfaces. The nosecap contains (a) one large nosecap section, (b) a T-seal strip divided into three segments, and (c) an expansion seal divided into three segments. On each of the two wing leading edges, there are 22 panel segments and 22 interpanel seal strips. Aft of the nosecap is a two-piece underbody chin panel which replaced fragile ceramic tiles. The chin panel was retrofitted to the Columbia orbiter, and it will also be used on the newest orbiter Discovery. A two-piece arrowhead section of protected CCC material is used to shield the strut fastening the orbiter to the external propellant tank.

Heat-protective materials for the U.S. space shuttle orbiter were fixed in the early 1970s. Consequently, protected CCC materials were used only where no other material would satisfy the mission requirements. During the following two decades, much progress has been demonstrated in new materials, fabrication knowhow, and design. To take advantage of these new technologies, NASA has been carrying out component trade studies and fabricating other orbiter components to demonstrate (a) performance improvements, (b) weight savings, and (c) cost reductions. Had the orbiter been designed in the early 1990s, it is possible that it would also contain protected CCC materials for its (a) body flap, (b) ailerons, (c) rudders, and (d) other parts. Some of these components have been prototyped and tested, but with the unexpected destruction of the Challenger orbiter in January 1986, all hopes faded for using new technology. Nevertheless, a stronger nosecap has been fabricated. High-strength PAN-based carbon fabric was substituted for the previously-used rayon-based graphite cloth. This gain in structural performance was negated (to some extent) by increased composite material thermal conductivity. Hence, added insulation and changes in the attachment structure were needed. An orbiter body flap (speed brake) was also designed but not fabricated. This advanced vehicle control surface potentially offered many advantages, including (a) weight savings of 1360 kg (3000 lb), (b) higher temperature capability, (c) enlarged velocity-entry angle flight trajectory, (d) improved stiffness, (e) greater resistance to buckling, and (f) longer fatigue life.

In assessing all of the impressive applications for protected CCC materials, it is apparent that the use of ceramic-coated CCC thermal protection material for the U.S. space shuttle orbiter was an achievement of extraordinary proportions. In the early 1960s, ceramic-coated CCC materials became a reality thanks to the creative efforts of Chance Vought Corporation and the sponsorship of the U.S. Air Force Materials Laboratory. The materials technology at that time was represented by only small button specimens, yet screening tests suggested capabilities for future aerospacecraft surfaces. To the great credit of NASA, the coated CCC material was selected for further development, scaled-up to full size components, ground

tested, and used on the operational orbiter. From small laboratory specimens to full-size parts took only nine years, quite an accomplishment by any standard.

The advent of coated CCC materials enabled the U.S. orbiter to achieve several benefits not possible with other forms of thermal protection materials. Protected CCC materials permitted the orbiter to (a) operate in a much larger flight envelope (velocity-entry angle), (b) exhibit cost-effective performance with a reuse capability, (c) avoid complex actively-cooled systems, (d) lower vehicle weight, and (e) increase reliability.

4.8.10.2 Russian Buran

The former Soviet Russian Buran (Siberian snowstorm) or VKK (Vozdushno Kosmicheskiy Korabl: air-space-ship) was the second type of aerospacecraft to fly successfully. The Buran was launched in orbit by the versatile launch vehicle "Energia." It was qualified for a single mission, unmanned, and landed on a runway after completing two Earth orbits. This was the first automatic landing of an aircraft-like spacecraft on a runway. The flight, nevertheless, demonstrated the correctness of the Buran's conceptual design, onboard systems, and thermal protection system. Future flights, if any, will carry a crew of two to 10 astronauts, and the mission may last up to 30 days. The Buran was originally designed to deliver up to 27,300 kg (60 klb) of payload into a 250-km (155-mile) circular orbit and return from orbit to Earth with a payload up to 18,200 kg (40 klb). The Buran made its orbital debut in November 1988.

The Russian Shuttle orbiter is reportedly constructed of aluminum with some steel and titanium and covered with thermal protection materials patterned after that of the forerunner U.S. space shuttle orbiter. Although few details have been published, it is reasonably firm that the Russian Buran has a nosecap and wing leading edges of coated CCC material. It was reported that the Buran orbiter nosecap involved two sections. A dome section made up the primary nosecap, but behind the dome were curved sections about 0.31-0.91 m (1.0-3.0 ft) that encircled the outer circumference of the central dome. Both the nosecap and the leading edges were composed of coated CCC material which was exposed to temperatures up to about 1600°C (2912°F). Based on visual observations the wing leading edges appeared to be smaller than similar components of the U.S. space shuttle orbiter. However the Russian leading edge components were apparently not the precision articles used on the U.S. orbiter. Interviews with Russian space engineers revealed that the first Buran flight involved hot plasma entering between the CCC wing leading edge and the thermal protection tiles on the underwing surface. A small

section of the wing's thin aluminum wall was melted, but the problem should be easily fixed for future Buran flights.

4.8.10.3 French Hermes

The French designed glider spacecraft is known as "Hermes." It is being developed by the European Space Agency (ESA) together with European team nations. The objective of the Hermes aerospaceplane is to provide Western Europe with an independent man-into-space capability. Hermes is configured for both manned and unmanned space operations, but astronauts will be used only when required. Manned missons are envisioned for servicing the European Columbus free flying laboratory or the U.S. Freedom space station. The Hermes is being designed for a crew of three and a cargo capacity of 3000 kg (6.6 klb). Its maiden flight is scheduled in the year 2002 followed by a manned mission with European astronautics in 2003.

The hot locations on the French aerospaceplane Hermes will require the use of protective CCC materials. These aerodynamic surfaces include the (a) nosecap, (b) leading edges, (c) fins, (d) elevons, and (e) body flap. Service temperatures up to 1600°C (2912°F) may be reached. Protected CCC components are the baseline material, but rapid progress in hybrid carbon fiber/silicon carbide-matrix composites may result in these materials being used for selected locations.

Large test parts have already been manufactured and tested. A 0.6 scale of the nosecap and a large carbon/silicon carbon section representative of a fin main box have been fabricated. Protected CCC leading edges have also been manufactured and cycled many times up to 1550°C (2822°F). Peak temperature testing at 1730°C (3146°F) has also been performed to evaluate coating response during possible abort conditions.

4.8.10.4 Japanese Hope

The Hope reusable space transportation system is intended to be propelled into space with the Japanese launcher H-II which is now under development. After performance of its space mission, Hope will fly hypersonically through the Earth's atmosphere to a national (Japanese) landing runway. Hope is designed to stay in space up to 100 hours. There are several missions that the Japanese mini-shuttle could accomplish. Hope could possibly extend the service life of satellites in orbit through periodic checks, repairs, etc. Hope could place equipment and technology experiments into orbit on a timely basis. Thirdly, Hope could supplement the U.S. Space Transportation System by ferrying supplies to the future U.S. space

station Freedom. It is estimated that Hope would likely be capable of transporting 2.2 Mg (4.84 klb) into geosynchronous orbit (GEO). The H-II booster would also be capable of transporting up to 10 Mg (22 klb) to space. The aerospaceplane is intended to retrieve up to 954 kg (2.1 klb) from space and return it to a national landing site. Japan presently intends to build two Hope aerospaceplanes and launch two cargo missions per year to an orbiting space station(s).

The Hope aerospaceplane will experience severe aerodynamic heating during hypersonic flight through the Earth's atmosphere, somewhat similar to other flight vehicles of this type. Temperatures may approach 1700°C (3092°F) on the wing leading edges and slightly lower temperatures on the nosecap and wingtip fins. Protected CCC materials appear attractive choices for these areas, and scaled articles are being fabricated and tested to determine their suitability. It appears that coated CCC materials will be used for the vehicle nosecap and wing leading edges. Figure 26 is a schematic of the nosecap. Like in the U.S. space shuttle orbiter, the nosecap is composed of a coated 2-D CCC material and an adjacent CCC thermal protection system on the underside of the vehicle frontal section. Similar CCC materials or hybrid carbon composites will also be needed for other high- temperature parts, like the (a) tip fins, (b) elevons, (c) rudders, and (d) body flap. Protected CCC materials are expected to be used on about 45 m^2 (417 ft^2) of the Hope, where temperatures of about 550-1300°C (1022-2372°F) are anticipated.

Since the Hope thermal protection materials are being developed and fabricated two decades after the U.S. space shuttle orbiter, the advantages of new materials technology can be incorporated into the flight system. The Hope protected CCC materials will likely be based on woven PAN-based carbon (not rayon-based graphite) fabric with a combined resin char and pitch coke carbon matrix. Multiple layers of silicon carbide will be CVD onto the CCC substrate. A thermal stress relief layer will be used between the outer coating and the CCC substrate, and composed of a diffusion-conversion layer of silicon carbide. Microcracks in the surface ceramic coating will be sealed with an overcoat of silica.

Several subscale protected CCC parts have been fabricated to date. These components included (a) an integral skin-stringer panel simulating a prime structural member of the aerospaceplane, (b) a nosecap having a small radius of curvature, and (c) a leading edge component. These articles were to demonstrate fabrication feasibility, not operational capabilities.

The subscale Hope nosecap had a diameter of 38 cm (15 in) and a height of 20 cm (7.9 in). Peripheral CCC panels used around the nosecap contained pitch-based carbon

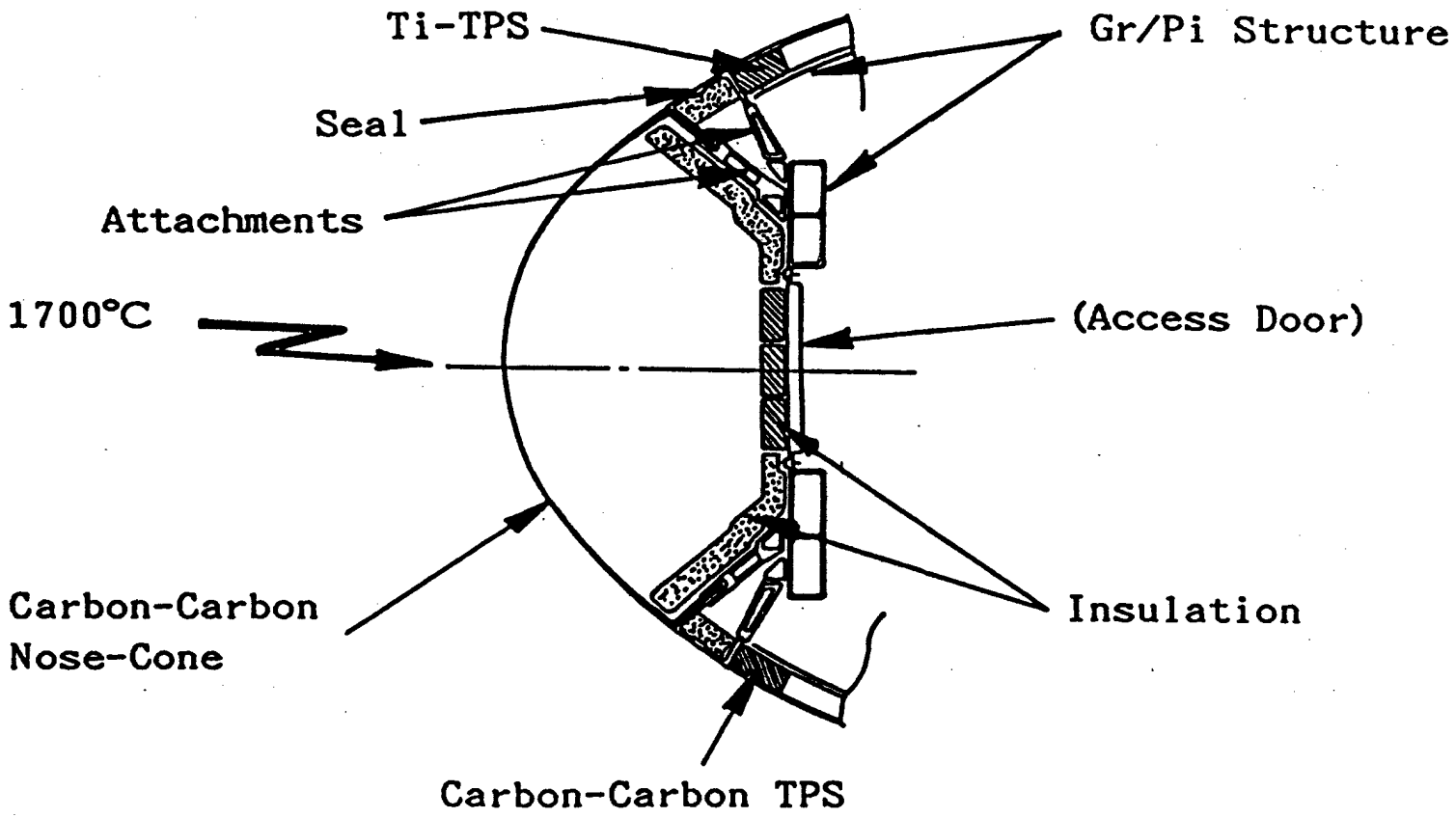


Figure 26. Thermal Protection Concept for the HOPE Orbiter.

fabric. This was probably the first time a pitch-based CCC material was used for thermal protection of an aerospaceplane component.

The structural panel demonstration item was also of great interest because it represented the first use of protective CCC materials in ultralightweight thermal protection systems. The thermal protection panel consisted of (a) thin protected CCC panel, (b) four sets of posts and fasteners to support the CCC panel, and (c) fibrous insulation. Initial laboratory testing indicated that the protective CCC insulative panels were capable of reducing surface temperatures from 1300°C (2372°F) to a lower level compatible with the use of carbon fiber-reinforced polyimide structures. The panels also survived Hope operational environments such as acoustic vibration, mechanical vibration, and impact loads.

The critical thermal protection system for the unmanned Hope space shuttle will be verified with an 864 kg (1900 lb) Orex parabolic vehicle. The Orex will be placed in a single 454 km (280-mile) circular orbit. A braking rocket will then fire, and the vehicle will descend into the atmosphere at the same angle and velocity as the Hope aerospaceplane. The Orex experimental vehicle has an outer diameter of 3.4 m (11.2 ft) and a depth of 1.46 m (4.8 ft). The central nosecap is a partial sphere with a curvature of 1.35 m (4.4 ft). It is reported to be the largest co-cured CCC disc in the world. Surrounding the nosecap are 24 CCC thermal protection tiles.

4.8.10.5 National Aero-Space Plane (NASP)

The NASP program is a major U.S. aerospace initiative with the goal of developing and demonstrating a piloted flight vehicle (X-30) about the size of a Boeing 737. The X-30 is intended to take off horizontally like an airplane, fly into low-Earth orbit, dock with a space station, and then return to Earth, landing like an airplane. This single-stage-to-orbit will be powered with air-breathing liquid hydrogen-fueled ramjet/scramjet engines. The flight vehicle will be fully reusable with support requirements and turnaround times between flights far less than those of the operational shuttle orbiter.

The X-30 flight vehicle will experience considerable aerodynamic heating and high surface temperatures during ascent, atmospheric cruise, and reentry flight. Thermal protection materials requirements are not presently firm because of the evolving X-30 mission and available developmental funding. Protected CCC materials are expected to play a role in the design of X-30 spacecraft.

Thermal protection materials requirements for NASP are significantly greater than the U.S. space shuttle orbiter. The NASP materials should have (a) temperature capability up to 1650°C (3002°F), (b) low density, (c) sufficient strength and stiffness to accommodate low aeroloads, (d) high resistance to acoustic loading up to about 135 db, (e) long life of 150 thermal cycles, (f) no or low outgassing in space vacuum, and (g) compatibility with casual hydrogen.

Protected CCC materials are thermally efficient, lightweight, and passively-cooled solutions for a portion of the X-30 thermal protection system. The baseline materials have not been published in the literature, but it is anticipated that protected CCC materials may be used on the most intensely heated areas. These vehicle locations include (a) nosecap, (b) wing leading edges, and (c) forward fuselage. The remainder of the flight vehicle will likely be based on hot radiative metallic structures. Metal-matrix composites being developed are expected to be used, but some added form of heat protection may be necessary to reduce temperatures to acceptable levels. Various schemes are being evaluated. One promising design approach involves the use of thin protected CCC panels mechanically attached to an underlying metallic load-bearing structure.

To assess the utility of protected CCC materials for the X-30 flight vehicle, a number of full-scale components have been designed, fabricated, and ground tested. One such prototype involved the elevon control surface section. This flight-weight, full-scale component was 1.0 m (3.25 ft) wide, 1.4 m (4.6 ft) long, and 0.35 m (1.16 ft) at the forward leading edge and tapered at the trailing edge. The test component was actually a truncated section of a conceptual control surface economically sized to avoid expanding existing manufacturing facilities. It contained 14 major pieces of CCC materials. Advanced materials and manufacturing processes were used, including PAN-based carbon fabrics and rapid pyrolysis cycles. Identical CCC panels with integral rib stiffeners were first fabricated. The top and bottom panels were then attached by a secondary bonding technique to form the shell of the test component. The article was trimmed, drilled, and pyrolyzed again. The elevon contained a metallic torque tube with 10 CCC ring collars. Attachment of the rib-to-torque tube ring fittings was accomplished with coated CCC bolts and nuts. Conventional metallic fasteners could not withstand the anticipated service temperatures. The prototype elevon was significant because it was the first (a) known large structural component designed and built with advanced protected CCC materials and (b) structural application of protected CCC fasteners in a large CCC structure.

A very impressive protected CCC structural element for the NASP Program was fabricated about 1990. It was the largest prototype structural CCC panel ever

assembled. The coated CCC panel was formed from two 1.0 m (40 in) by 1.74 m (68.5 in) curved coated CCC panels which were joined together with coated fasteners. The protected CCC structural panel had about three times the temperature limit of conventional titanium and weighed about one-third as much as a similar titanium structure. The protected CCC panel was subjected to thermal and mechanical stresses simulating about 200 NASP earth-to-orbit-to-earth flight cycles. Temperatures during tests were as high as 1650°C (3002°F).

The major issues associated with the use of protected CCC materials for the X-30 vehicle are at least threefold. Life requirements are the first concern. All parts are intended to be nonrefurbishable and serve from 50 to 100 missions. Shuttle orbiter-protected CCC components can be removed and returned to the factory for recoating during lengthy turnarounds between flights. Components containing coating chips, which have occurred in the hangar, have been routinely returned to manfacturing for recoating. The X-30 is designed for minimum time on Earth, and all maintenance must be quickly accomplished. The second major concern involves certification for a manned vehicle. Ground certification involves a very large database to predict performance. The life of the part has to be precisely predicted, but present technological capabilities do not permit this, and nondestructive inspection techniques for assuring quality are not well developed. A third major concern involves the historic design experiences with structural CCC components. Unprotected CCC materials have performed admirably in high-temperature, low-stress, short-time applications. Attempts to use these materials in a more structurally-demanding mode, like space rocket motor exit cones, have sometimes resulted in materials failure. Much less is known about the structural behavior of protected CCC materials and components. Materials designed for the shuttle orbiter 100 mission life would likely survive about 25 to 30 NASP thermal-mechanical cycles. The development of a fail-safe coating system for CCC structural materials would go far towards improving a designer's confidence in long-time uses of structural-protected CCC materials. Even if NASP or derivatives never take flight, the program has added innovations to the material science and application of CCCs. Technology transition is already underway, and it is expected that the return-on-investment will be large.

4.8.10.6 Hypersonic Boost Glide Vehicle

Aerospaceplanes have been used for peacetime space transportation systems, but they can also be designed for military applications. One such vehicle type is the aeromaneuvering glider or boost glide vehicle. Its mission is to deliver a weapon over great distances, with a short delivery time, and survive in the target area by various maneuvers. The boost glide vehicle flies primarily in the upper atmosphere and under full aerodynamic control. It is the fastest atmospheric delivery system known for strategic missions.

Aerodynamic heating of the hypersonic aerospace glider occurs throughout the flight trajectory, with surface temperatures depending upon the vehicle velocity, altitude, and location on the glider. Temperatures are typically quite high, and protected CCC materials may be needed for the entire frontal section of the glider.

4.8.10.7 Single-Stage-to-Orbit (SSTO) Vehicles

Future aerospaceplane designs may involve rocket-powered, single-state-to-orbit (SSTO) launch systems. A fully reusable SSTO flight vehicle, like that shown in Figure 27, would have the capability for return-to-launch-site, abort-to-orbit, or down-range abort maneuvers in the event of launch vehicle single or dual main engine shutdown. Such a flight vehicle would have greatly enhanced abort capabilities for a space transportation system (STS), and possibly could avoid future catastrophic events like that of the U.S. Challenger accident. Flight vehicles would strongly resemble the space shuttle orbiter, except for the added wings needed for aerodynamic lifting purposes. It is expected that coated CCC materials would be the leading materials for both the vehicle nosecap and leading edges.

Full-scale protected CCC hot structures for the hypersonic glider have been fabricated and tested in the U.S. One such test article represented the first 1.02 m (40 in) section of a hypersonic gliding body. The structure was ground tested up to 1371°C (2500°F) under mechanical loads. After 13 test runs the vehicle forebody was found to be in excellent condition.

Table 49 lists various protected CCC components which have been fabricated along with the first year these articles were produced. The application prototypes include aerospaceplane (a) nosecaps, (b) leading edges, (c) seals, (d) tip fins, (e) rudders, (f) body flaps, (g) wingboxes, (h) structural panels, (i) optical system covers, and (j) impact protective shields.

Table 50 gives a chronology of protected CCC prototypes which were developed in support of various aerospaceplane components.

4.8.10.8 Chronology

4.8.10.8.1 *The 1960s*

CCC and protected CCC materials were in their infancy during the 1960s, and hence little consideration was given to their use in prototypes. The one

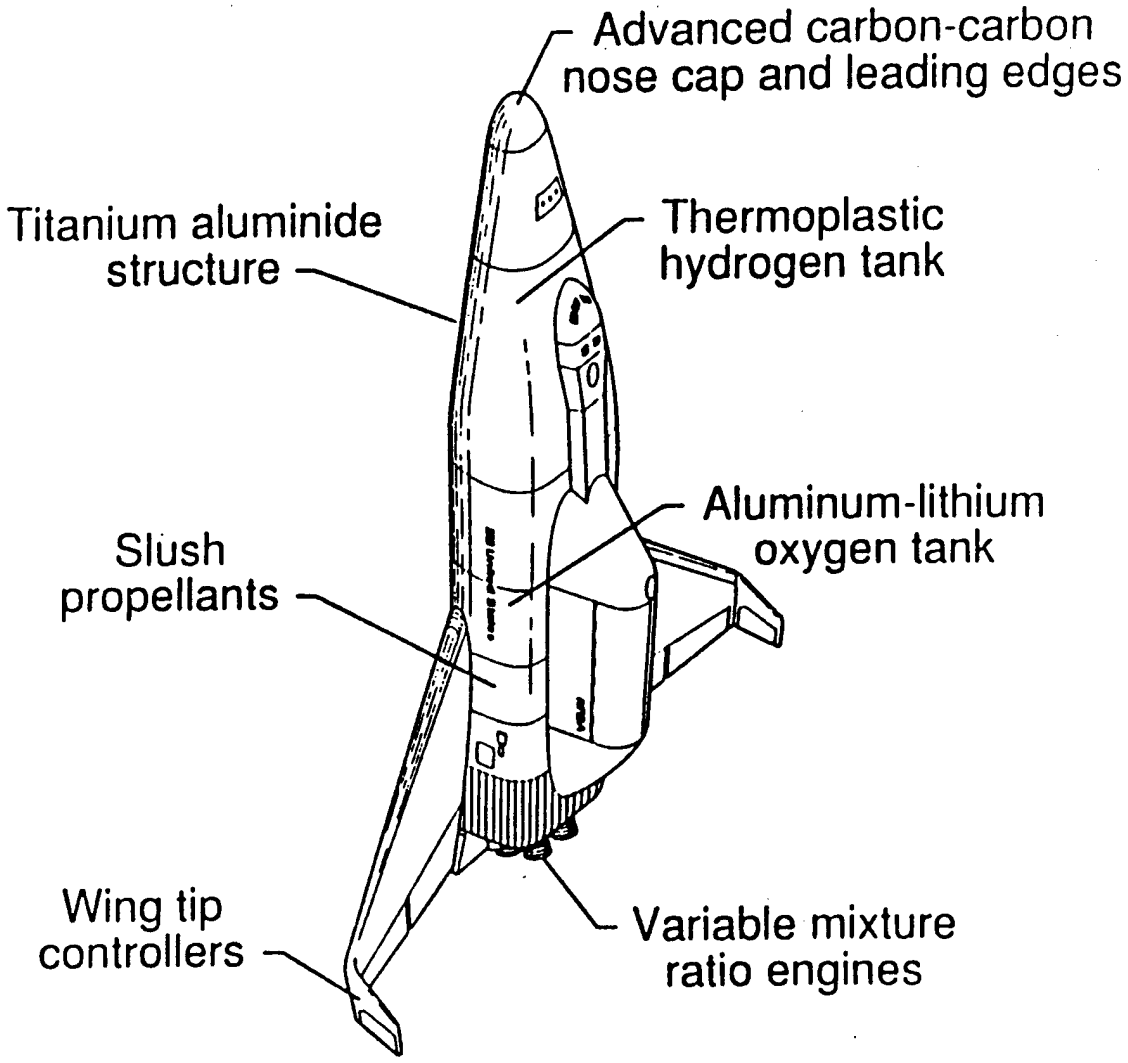


Figure 27. An Advanced Concept of a Single-Stage-to-Orbit Flight Vehicle.

TABLE 49

FIRST CCC PROTOTYPE COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLES

YEAR	PROTOTYPE	ORGANIZATION
1961	Dynasoar nosecap	Chance Vought Corporation/USA
1971	Orbiter nosecap, leading edges and seals	LTV Aerospace Corporation/USA
1985	Orbiter arrowhead structure	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1986	Boost glider forebody structure	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1987	Orbiter chin panel	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1990	Orbiter elevon	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1991	Tip fins, rudder, and body flaps	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1991	NASP wingbox and structural panels	LTV Aerospace & Defense Company/USA

TABLE 50

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1961/64	CCC nosecap fabricated for a hypersonic flight vehicle	First full-scale coated CCC prototype article fabricated for the Dynasoar vehicle	Chance Vought Corporation/USA
1971	Subscale, thick and complex configuration silicon-carbide coated 2-D CCC articles manufactured	First prototype leading edges and seals for the U.S. space shuttle orbiter flight vehicle	LTV Aerospace Corporation/USA
1971	Large (20 in. by 20 in. by 10 in.) silicon-carbide coated 2-D CCC leading edge delivered for U.S. shuttle orbiter	Second source identified for U.S. shuttle orbiter wing leading edges	McDonnell Douglas Astronautics Company-East/USA
1972	Full-scale silicon-carbide coated 2-D CCC components manufactured for aerospace flight vehicle	First full-scale nosecap and leading edges manufactured for U.S. space shuttle orbiter Over 400 sq. ft. of orbiter aerodynamic surface covered with silicon-carbide coated CCC Silicon-carbide coated 2-D CCC nosecap composed of one nosecap, three seal strips, and three expansion seals Silicon-carbide coated 2-D CCC leading edges composed of 44 panels and 44 seal strips	LTV Aerospace Corporation/USA
1976	NASA demonstrated two CCC leading edges and one seal during "drop test" of orbiter Enterprise	Coated CCC validated for flight application	NASA Johnson Space Center (Tests)/ USA Vought Corporation (Parts)/USA
1977	Delivered first full-scale nosecap and leading edges/seals for U.S. space shuttle orbiter	Production articles for first U.S. space shuttle orbiter Coated 2-D CCC material cost about $6000/lb in final component form	Vought Corporation/USA

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1980	Thermal/structural/acoustic certification ground testing successfully completed on full-scale shuttle 2-D CCC wing leading panels	Large 2-D reinforced coated CCC wing leading edge components qualified at high temperature, air loads and acoustics	NASA Johnson Space Center/USA
1981	Fabrication of a representative CCC airframe stiffened panel	First proposed use of CCC for hypersonic flight vehicle airframe structures	McDonnell Douglas Astronautics Company-East/USA
1981	First hypersonic manned flight of CCC space shuttle orbiter Columbia parts	Demostration that CCC can be successfully used as thermal protection system for hypersonic manned spacecraft at high temperatures and moderate stresses	NASA Johnson Space Center/USA
1981	Completed certification testing for space shuttle (RCC) material in simulated mission environments	Added confidence for the use of RCC for the space shuttle nosecap and wing leading edge	NASA Langley Research Center/USA
1981	Silicon-carbide coated CCC nosecap and leading edges/seals successfully flight tested on U.S. STS-1 OV-102 Columbia orbiter	First operational demonstration of performance and reliability of coated CCC for U.S. space transportation systems Protected CCC parts appeared suitable for additional flight tests Prospects for multi-mission use became very attractive	Vought Corporation (Coated Carbon-Carbon Parts)/USA Rockwell International (Orbiter Design)/ USA NASA (Flight Test)/USA
1982	Coated 2-D CCC design for U.S. shuttle orbiter body flap	Higher-performance, lighter-weight body flap compared to state-of-the-art insulated metallic parts Enlarged flight envelope and increased reliability of critical orbiter vehicle component	Vought Corporation/USA

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1986	Coated two 2-D CCC forebody fabricated for hypersonic boost glide flight vehicle	First coated CCC prototype boost glide forebody structure	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1986	Biaxially-stiffened structure designed and fabricated	Demonstration of inhibited CCC for airframe structures	McDonnell Douglas Astronautics Company-East/USA
1987	Large-scale flight vehicle CCC parts coated with oxidation-resistant (SiC) coating	CCC flight nosecap and reentry structure available for testing	Chromalloy American Corporation/ Chromalloy Research & Technology/USA
1987	Coated CCC chin panel fabricated for U.S. shuttle orbiter - replaced tile adjacent to nosecap seals lower aft position	Increased shuttle vehicle temperature reentry limits	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1987	Coated CCC arrowhead developed for shuttle orbiter	Eliminated damage from firing explosive bolts	LTV Aircraft Products and LTV Missiles & Electomics Groups/USA
1987	Concept design for control surface for NASP completed	CCCs are an attractive alternative to actively-cooled structures for temperatures to 1649°C (3000°F)	LTV Aircraft Products and LTV Missiles & Electronics Groups and NASA Langley Research Center/USA
1988	Full-scale coated CCC leading edge manufactured	First, large and structural CCC part for potential use on French Hermes SpacePlane	Aerospatiale/FRANCE
1988	Biaxially-stiffened CCC panels fabricated	First subscale structural components for hypervelocity aircraft	BFGoodrich Aerospace/Super-Temp/USA
1988-91	Actively-cooled ORCCC leading edges and nozzle components designed and fabricated	Pre-prototype thermal protection systems available for evaluation in the National AeroSpace plane (NASP) program	General Dynamics/Fort Worth Division/ USA Carbon-Carbon Advanced Technologies/ USA Refractory Technology Aerospace Components (RTAC)/USA BFGoodrich Aerospace/Super-Temp/USA BP Chemicals (HITCO) Inc./USA

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1988	Large, 2-D CCC structural I-beams and thick cruciforms and lugs fabricated	High-temperature coated CCC prototype structural parts for hypervelocity airframe evaluation	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1988	CCC blade stiffened compression panels and shear panels designed, fabricated, and tested	Potential of CCC for spacecraft thin structural panels demonstrated	NASA Langley Research Center/USA
1988	Soviet orbital reusable spaceplane "Buran" completed two earth orbits and successfully landed unmanned at the Baykonur Cosmodrome	Refractory silicon-carbide-moly disilicide-coated CCC nosecap survived peak temperature of about 1600°C (2912°F) Refractory silicon-carbide-moly disilicide-coated CCC hyperbolic-shaped wing leading edges survived a severe aerothermomechanical flight environment No fractures were found in the structural elements after flight About two tons of CCCs were used for the nosecap and leading edges	NIIGrafit (Nosecap & Leading Edge Parts)/RUSSIA
1989	Very large CCC biaxially-stiffened panel fabricated	First full-scale (4 ft. x 10 ft.) flight structural component demonstrated	BFGoodrich Aerospace/Super-Temp/USA
1989	Subscale coated 2-D ORCCC flight vehicle structure fabricated and ground tested	Hypersonic military flight vehicle primary structure fabricated and performance demonstrated	General Dynamics Corporation/Convair Division/USA Kaiser Aerotech (Fabrication)/USA Chromalloy American Company (Coating)/USA

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	Subscale (50 x 100 cm, 19.4 x 39.4 in.) CVD silicon-carbide coated sealed integral skin (three bladed-stringer panel) fabricated as a demonstration article of the H-II orbiting plane (HOPE) flight vehicle	Demonstrated fabricability of simulated primary airframe structural components for HOPE flight vehicle	Kawasaki Heavy Industries, Ltd./JAPAN Kawasaki Steel Corporation/JAPAN National Space Development Agency/ JAPAN
1989	Radiant heater test of 3-D CCC fixed yaw stabilizer	Design to incorporate 3-D CCC into cold structure successfully demonstrated	McDonnell Douglas Space Systems Company/USA
1989/91	Refractory composite/heat-pipe cooled wing leading edge designed for NASP	Advanced concept for cooling severely heated leading edges of very high-speed aerospacecraft Demonstrated potential for significant weight saving using CCC heat pipe concept over actively-cooled designs	NASA Langley Research Center/USA
1990	Large coated 2-D CCC rib-stiffened structure fabricated (4 ft. x 10 ft. structure joined with curved I-beam)	First prototype rib-stiffened coated CCC structure for potential use on hypersonic flight vehicles	BFGoodrich Aerospace/Super-Temp/USA
1990	Baseline CVD silicon-carbide coated 2-D carbon fabric/phenolic resin char CCC materials and processes established for HOPE nosecap, leading edges and joints	Highest temperature HOPE flight vehicle components to be manufactured with silicon-carbide coated 2-D CCC Baseline materials very similar to those used on the U.S. shuttle orbiter nosecap and leading edges	Kawasaki Steel Corporation/JAPAN Kawasaki Heavy Industries, Ltd./JAPAN National Space Development Agency/ JAPAN
1990	Large coated CCC fuselage subsection was fabricated from 12 panels	Demonstrated fabricability of 96 in. x 35 in. x 59 in. (LxDxW) assembly of coated CCC for NASP fuselage	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1990/91	Design, analysis, and fabrication of large coated CCC control surface for load testing	Largest coated CCC structure fabricated to date Higher temperature flap could enlarge the shuttle flight envelope (velocity-entry angle) Weight savings estimated at 1,360 kg (3000 lb)	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA NASA Langley Research Center/USA
1990/91	Full-scale (23 in. x 26 in. x 12 in.) subelement ORCCC structural components were manufactured	One-piece, integrally-stiffened leading edge skirt components available for NASP airframe testing	Rohr Industries, Inc./Refractory Technology Aerospace Components (Fabrication)/USA McDonnell Douglas Corporation/ McDonnell Aircraft Company (Design)/ USA
1990	Tested a leading edge made of a coated 4-D CCC with ceramic inhibitors in an arc jet at temperatures to 3500°F for 45 minutes with no recession	Viable passive leading edge material for hypersonic vehicles was demonstrated	Science Applications International Corporation (Substrate)/USA UltraMet (Coating)/USA
1991/92	Full-scale (0.9 m, 35 in. diameter) CVD silicon-carbide coated, 2-D CCC nosecap fabricated for the H-II orbiting plane (HOPE) flight vehicle	Full-size components became available for testing	Kawasaki Steel Corporation/JAPAN Kawasaki Heavy Industries, Ltd./JAPAN National Space Development Agency/ JAPAN
1991	Large (118 in. x 17 in. x 60 in.) wingbox was fabricated of coated CCC	Fabricability and assembly of a NASP-coated CCC wing section was demonstrated	LTV Aerospace & Defense Company/ USA
1991	2-D coated CCC components fabricated for evaluation on a hypersonic flight vehicle	Prototype leading edges for Japanese "HOPE" space flight vehicle	Mitsubishi Heavy Industries, Ltd./JAPAN

TABLE 50 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1991	Large (4 ft. x 4 ft.) CCC leading edge panel fabricated for hypervelocity flight vehicle thermal protection system	Airframe thermal protection component available for NASP tests	Rohr Industries, Inc./Refractory Technology Aerospace Components (Fabrication)/USA General Dynamics Corporation/Fort Worth Division/USA
1992	Large (1.35 m, 53.1 in.) lightweight and structural part was fabricated for potential use on French Hermes SpacePlane	Full-scale coated CCC nosecap manufactured	Aerospatiale/FRANCE
1992	2-D CCC flight structure designed and fabricated for a proprietary application	ORCCC components more attractive for future aerospace applications	General Dynamics/Fort Worth Division/ USA
1992	Primary structural component fabricated from I-beams bonded to thick CCC laminates	Demonstrated fabricability of highly-loaded CCC structure for hypervelocity vehicle applications	LTV Aerospace & Defense Company/ USA
1992	Full-scale (1.7 m diameter) silicon-carbide coated, PAN-based carbon fiber CCC nosecap fabricated for the H-II "HOPE" orbiting plane	Full-size orbiting plane components become available for testing	Mitsubishi Heavy Industries, Ltd./JAPAN
1992	Nosecap peripheral panels of coal tar pitch-based CCC fabricated for the H-II "HOPE" orbiting plane	First use of pitch-based carbon fibers in a spacecraft Full-size components available for evaluation	Mitsubishi Heavy Industries, Ltd. (Testing)/JAPAN Mitsubishi Kasei Corporation (Pitch Fibers & Composites)/JAPAN
1992	CCC torque-tube/attachment-ring joint analysis and tests completed	Potential for transmitting large torque loads in CCC spacecraft structures demonstrated	NASA Langley Research Center/USA
1992	Coated 2-D CCC nosecaps and leading edges successfully flown on 44 space shuttle orbiter flights	ORCCC components successfully used in multimission, reusable applications	NASA Johnson Space Center/USA

TABLE 50 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR AEROSPACEPLANE FLIGHT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1992	Large (20 in. x 20 in.) unidirectionally-stiffened panels and rib/T-stiffened panels were designed, fabricated and structurally tested	High-temperature ORCCC prototype airframe structure	Rohr Industries, Inc./USA
1994	Large reentry disc containing a coated CCC nosecap and 24 CCC surrounding thermal protection tiles available for HOPE mini-shuttle OREX earth reentry flight test	Largest (3.4 m, 11.2 ft.) coated CCC disc fabricated in the world Orbital reentry experiment (OREX) disc designed to withstand 1600°C (2912°F) peak reentry heating Coated thermal protection tiles will provide data for HOPE's leading edges	National Space Development Agency of Japan (NASDA)/JAPAN National Aerospace Laboratory of the Science and Technology Agency/JAPAN

notable exception was the development of a full-scale nosecap for the Dyna Soar X-20 hypersonic flight vehicle.

The United States' first aerospaceplane was the X-20 whose purpose was to research manned entry from space. It was designed as a glider vehicle capable of orbiting the Earth or gliding and skipping on the fringes of the atmosphere. The X-20 was constructed of metallic hot structures and ceramic materials in the areas of highest heating, thus making it fully reusable. During hypersonic flight in the atmosphere, aerodynamic heating would cause high vehicle surface temperatures. The nosecap was the most intensely heated and thus required the most efficient thermal protection system. It was estimated that nosecap heating would approach 40.7 cal/cm^2·s (150 Btu/ft^2·s) or a temperature rise of 27.7°C/s (50°F/s). Surface temperatures would peak at about 1650°C (3002°F), and the heating time would last from 15 minutes to one hour. These high heating rates and temperatures limited material choices to either ceramics or very heavy metals. The baseline nosecap consisted of a RVC grade (siliconized RT-0029) graphite structural shell. The entire surface was covered with zirconia tiles, each tile being held in place with a tapered zirconia pin passing through the graphite shell. Full-scale radiation-cooled nosecaps were fabricated and successfully tested, but the structure was (a) complicated, (b) difficult to fabricate, and (c) contained polycrystalline graphite that was prone to catastrophic mechanical or thermostructural failure. An alternate X-20 nosecap of higher reliability was constructed using a substitution design approach. A full-scale 38.7 cm (15.25 in) diameter nosecap with a substrate of 2-D CCC material was constructed, overlayed with zirconia tile, and successfully ground tested. The CCC substrate was shown to be rather insensitive to the presence of holes, quite unlike the behavior of bulk graphites. A flightweight design of this nosecap was never fabricated due to cancellation of the Dyna Soar program, but there is little doubt that it would have met all operational requirements. Within a few years thereafter, ceramic-coated CCC materials were developed, and the zirconia tile overlay was no longer needed.

4.8.10.8.2 *The 1970s*

The early 1970s were especially interesting and rewarding. Silicon carbide-coated 2-D CCC material was chosen as the baseline for the U.S. space shuttle orbiter nosecap and leading edges. Over 400 square feet of intensively-heated orbiter surface had to be covered with coated CCC material, because no other material could potentially satisfy all of the environmental and operational requirements. Over 95 different parts were fabricated for each orbiter, including the nosecap, seal strips, expansion seals, leading edges, and their adjacent seal strips.

All of the protected CCC parts on the U.S. space shuttle orbiter were fully evaluated in the mid-1970s. A high altitude drop-test of the flight vehicle Enterprise indicated that all parts were fully functional.

In the late 1970s production articles of the orbiter nosecap and leading edge were delivered for the first operational U.S. space shuttle. The material was quite expensive by any standard , i.e. about $13,200/kg ($6,000/lb).

4.8.10.8.3 *The 1980s*

During the early 1980s ground testing and certification of protected CCC parts were completed for the orbiter Columbia. The first orbiter flight into space and back again to Earth was a complete success. All of the protected CCC parts appeared undamaged and suitable for additional flights. The concept of multi-use protected CCC components was thus verified, and prospects were great for using these new materials on future hypersonic flight vehicles.

Other flight vehicle outlets for protected CCC materials began to become apparent during the mid-1980s. The NASP manned flight vehicle program was underway, and reusable structural materials were needed. Subscale structural panels were fabricated and tested. These panels were unidirectionally-reinforced rib/T-stiffened articles and biaxially-stiffened component subelements. The demonstration articles indicated that the necessary fabrication knowhow was available for NASP but not in the size needed for production aerospaceplanes. Another remarkable protected CCC fabrication effort yielded a full-scale forebody for the military hypersonic boost glide vehicle. All of the multiple parts were successfully fabricated and assembled.

Various aerospaceplane components and demonstration articles were fabricated in the late 1980s. Shuttle orbiter thermal protection system was upgraded with two new operational parts. A stronger and more impact-resistant chin panel was manufactured and fitted aft and below the nosecap. Previously-used ceramic tiles were routinely damaged by ground debris during vehicle landing. A second upgrading project involved the use of a two-piece arrowhead part for protecting the strut which fastens the orbiter to the adjacent propellant tank. The suitability of protected CCC materials for the nosecap and leading edges of aerospaceplanes was again demonstrated with the first flight of the Soviet Buran. During flight it was reported that the Buran nosecap experienced up to 1600°C (2912°F) temperature. Post-flight inspection indicated that there were no cracks in the structural elements. Meanwhile

both France and Japan were busy designing and fabricating protected CCC parts for their national aerospaceplanes. A full-scale leading edge was manufactured for Hermes, and subscale structural components were fabricated for Hope. NASP prototype parts became more numerous, and extensive ground testing took place. Perhaps the most impressive prototype fabricated during the late 1980s was the entire forebody of a military hypersonic glider. This article had a complex aerodynamic configuration. It was composed of silicon carbide-coated CCC substrate material. Other aerospaceplane demonstration articles included (a) larger biaxially-stiffened panels, (b) structural I-beam, (c) thick cruciforms and lugs, and (d) others.

4.8.10.8.4 *The 1990's*

Additional prototype articles were fabricated for NASP in the early 1990s. A very large protected CCC structural panel was fabricated. It was cut in half, coated with silicon carbide, and then reassembled with coated CCC mechanical fasteners. The finished panel was 1.0 m (40 in) wide and 3.5 m (137 in) long. A large wingbox was also assembled from smaller protected CCC subelements. The overall dimensions of the vehicle wing section were about 300 cm (118 in) long, 152 cm (60 in) wide, and 43 cm (17 in) in depth.

A large flight control surface component for NASP was designed, fabricated, and tested. This prototype was very large, provided considerable weight savings, and permitted higher temperature operation.

Continuing development of components for the French Hermes and the Japanese Hope aerospaceplane resulted in several impressive gains. A full-scale (1.3 m, 51.2 in dia.) protected CCC nosecap was manufactured for the Hermes flight vehicle. Full-scale nosecaps and leading edges were also fabricated for the Hope aerospaceplane. The 1.7 m (5.6 ft) diameter nosecap was later flight tested on the Orex reentry capsule.

4.8.11 Earth and Planetary Entry Vehicle Components

New knowledge concerning the planets and the atmospheres surrounding them is being obtained by (a) remote Earth sensing and (b) planetary entry vehicles. Both manned and unmanned entry vehicles are being used. The vehicles generally fly hypersonically in the planet's atmosphere to perform critical measurements, and in some cases they soft land on the planet.

4.8.11.1 Apollo Earth Entry Module

The U.S. Apollo spacecraft is the best known of the manned entry vehicles. The capsule protected three astronauts from the space environment during its long journey to the moon, and it provided the means for a safe return to Earth. During Earth reentry at orbital velocities of about 11 km/s (36 kft/s), the frontal area of the Apollo command module was subjected to considerable aerodynamic heating. Use of a blunt hemisphere-cone vehicle configuration, however, reduced the heating rate and permitted it to be protected with a low-density plastic composite. CCC materials were not needed for heat protection of the entry capsule, but backup heat shields were prototyped for the Apollo vehicles. One heatshield concept was based on a combination of radiative and ablative cooling schemes. The structure was composed of porous 2-D CCC face sheets attached to a core of ablative and insulative plastic. Both bonding and mechanical attachments were developed for this heatshield. The second Apollo heatshield concept utilized 2-D CCC face sheets attached to a stainless-steel sandwich substructure with CCC clips and closeout channels. Microquartz fibrous insulating materials were used in the honeycomb for temperatures less than 1650°C (3002°F). Fibrous carbon or graphite felts were employed for higher-temperature structures. Due to the success of the low-density ablator approach for capsule thermal protection, further heatshield development efforts were abandoned.

Although CCC materials were not well developed, they were actually used on operational Apollo vehicles. Thermal shields were needed to protect the optical telescope and sextant. 2-D CCC shields were fabricated and installed on the flight vehicles. They had a thin cone-shaped configuration similar to a large breakfast cereal bowl. The outer surfaces were coated with silicone rubber for weather and oxidation protection. These passive thermal protection shields flew successfully for the first time on August 25, 1966. They were likely the first use of CCC materials for shape retention during an Earth reentry flight.

4.8.11.2 Mars Planetary Probe

Manned trips to Mars and its possible colonization have been the subject of scientific fiction for many years. With the advent of huge chemical propulsion systems, Mars exploration is becoming more of a reality than a dream. Much information will be needed, however, in order to design an optimum vehicle configuration and thermal protection system. Vehicle designs in the 1960s suggested that an optimum shape would be parabolic with a base diameter of about 58 cm (23 in) and a length of about 46 cm (18 in). A tension shell structure was thus prototyped. It contained a small silica tip and a much larger trailing 2-D CCC

heatshield. As-fabricated CCC material was satisfactory because the planet's entry conditions did not require the use of an oxidation-resistant coating.

4.8.11.3 Jupiter Planetary Probe

The planet Jupiter is a member of the solar system, and due to its relative closeness to Earth, it has fascinated mankind for many centuries. Remote Earth sensors have revealed much about the planet and its surrounding atmosphere, but scientific probes flying through the Jovian atmosphere were needed to reveal comprehensive and quantitative information. Probes launched to Jupiter would be traveling at Earth escape velocities and, upon entry into the planetary atmosphere, experience severe gas-dynamic heating. Unlike Earth aerodynamic entry heating, the shock layer radiative flux will dominate and may be many times the convective heating rate. This condition poses a unique heatshielding problem. Few materials were available to accommodate these thermal conditions, and none of them had been ground qualified or flight tested for the Jovian entry. Only ablative resinous composites and CCC materials appeared to have potential for use. Due to the newness of CCC materials in the 1960s, a carbon-fabric/phenolic heatshield was chosen. There were uncertainties that this charring heatshield material would undergo excessive surface char layer spallation during entry with loss of the probe. The ablative plastic heatshield was already about two-thirds of the total probe weight, and additional protective material seemed to be out of the question. An alternate probe heatshield was therefore designed to assess any weight savings and systems benefits. Three types of CCC materials were used in this design study. It was shown that an optimum probe performance and weight could be achieved with the use of an insulated 4-D CCC integral nosecap-heatshield. About 4.2 cm (1.65 in) of multidirectionally-reinforced CCC material would be needed with about 1.0 cm (0.40 in) of fibrous carbon insulation for the most severe entry conditions. In this particular design advantages were taken of the excellent CCC reflective, emissive, structural, and insulative characteristics.

The 4-D CCC nosecap-heatshield was reduced from concept to reality with the fabrication of a subscale article. Before ground tests could be initiated, the alternate thermal protection materials project was cancelled due to the success of the ablative plastic composite material approach.

4.8.11.4 Solar Planetary Probe

The sun is the center of the universe, and accordingly man has always been interested in learning more about this planet and its atmosphere. NASA has studied various

missions to the sun and the information that could be obtained. It appeared that numerous scientific objectives could be achieved including (a) solar wind acceleration, (b) heating mechanisms and energy transport, (c) plasma turbulence near the sun, (d) dynamics of energetic particles, (e) coronal structure and variation, and (f) interplanetary dust sources and dynamics. Hence, the STARPROBE mission was created to study the near-sun environment. The spacecraft would first journey to Jupiter where it will experience a Jovian gravity assist and cause it to leave the plane of the ecliptic and fall toward the sun. It would then travel past the sun in a polar trajectory and come within four solar radii of the center of the sun at perihelion. While in the vicinity of the sun, the 300 kg (660 lb) probe would be exposed to a solar radiant energy flux of about 400 W/cm (352 Btu/ft^2·s) and an ultraviolet radiation flux of about 50 W/cm^2 (44 Btu/ft^2·s) during a flight time of about 13 hours. Solar radiation will impose severe thermal demands on the solar shield, which is designed to protect the payload at operating temperatures of about 55°C (131°F). CCC, tungsten alloy and silica materials have been assessed as the principal shield materials. The most critical thermal protection materials requirements relate to (a) mass and size constraints, (b) mass loss rate due to heatshield thermal vaporization, (c) allowable temperature of the payload, and (d) environmental survival in the space shuttle cargo bay. It appears at this time that only CCC thermal protection materials can offer the advantages of light weight, thermal protection, fabricability, and moderate costs for the solar probe. The present STARPROBE heatshield is envisioned to be about 5.2 m (17 ft) long with a base diameter of about 4.0 m (13.1 ft). The total heatshield weight will be less than 41 kg (90 lb). It will be assembled from smaller individual panels of 2-D CCC having a thickness of about 0.152 cm (0.060 in). The heatshield panels will be fastened together with CCC bolts. Underneath the CCC heatshield will be low-density, low thermal conductivity, fibrous graphite insulation. Primary heatshield issues yet to be resolved include (a) full heatshield prototyping to validate design, (b) confirmation of material optical properties and their variation with surface finish, (c) thermophysical and thermomechanical properties of the baseline materials, and (d) minimal acceptable thickness for the primary shield.

4.8.11.5 Titan Planetary Probe

The U.S. NASA/European ESA Cassini mission is designed to perform an orbital tour of the ringed planet Saturn and then deliver a secondary-descent probe Huygens into the dense atmosphere of moon Titan. The orbiter probe will be launched by a Titan 4 Centaur in 1997. After a Jupiter swingby in the year 2000, Huygens will arrive in the vicinity of and orbit Saturn in the year 2004. The orbiter will then perform a fly past Titan and descend into its atmosphere at about 5.75 km/s (3.57 mile/s). Atmospheric measurements will include (a) chemical composition, (b) temperatures, (c) pressure, and (d) wind profiles from 170 km (106

miles) to the planet's surface. These data are of particular interest because the organic processes taking place on Titan provide the only planetary-scale laboratory for studies of a pre-life terrestrial atmosphere.

The outer surfaces of the Huygens probe will be intensively heating during atmospheric flight at hypersonic speeds. A thermal protection system will thus be necessary for protection of onboard scientific instruments. CCC materials have been baselined for many parts of the probe because of their (a) high thermal accommodation, (b) high dimensional stability at very high temperatures, (c) no mass loss in the vacuum of space, (d) high specific strength and stiffness, and (e) suitability of the material in a nonoxidizing (nitrogen) atmosphere.

Figure 28 is a schematic of the presently envisioned Huygens probe. CCC materials are intended to be used for many different components including the (a) nosecap, (b) forward cone, (c) aft cone which seals the equipment case from the measurement case, and (d) aerobrake decelerator. The latter part performs the gas-dynamic braking during the entry phase and will be assembled from six CCC panels. The decelerator is expected to have an outer diameter of 3.1 m (10.2 ft), and an internal diameter of about 1.65 m (5.4 ft) and a CCC panel thickness of 0.5-1.5 mm (0.02-0.06 in). A spherical aft cover, which is needed to protect the parachute during the descent phase, will likely be composed of CCC material because it has to withstand intense radiative heating.

Table 51 lists the CCC components that have been prototyped for various planetary probe missions along with the year of their demonstration. These articles include (a) thermal shields for optical telescope and sextant systems, (b) heatshields for Mars, Jupiter, Solar and Titan probes, and (c) nosecap and deceleration panels for the Titan atmospheric entry vehicle.

4.8.11.6 Chronology

Table 52 lists a chronology of CCC prototype articles which were developed in support of various Earth and planetary capsule components.

4.8.11.6.1 *The 1960s*

The first applications envisioned for CCC materials were for thermal protection of missile reentry systems and solid propellant rocket motor nozzles. Due to the newness of the materials and the very demanding service environments, little progress was made in developing application prototypes. Attention was therefore redirected to their possible

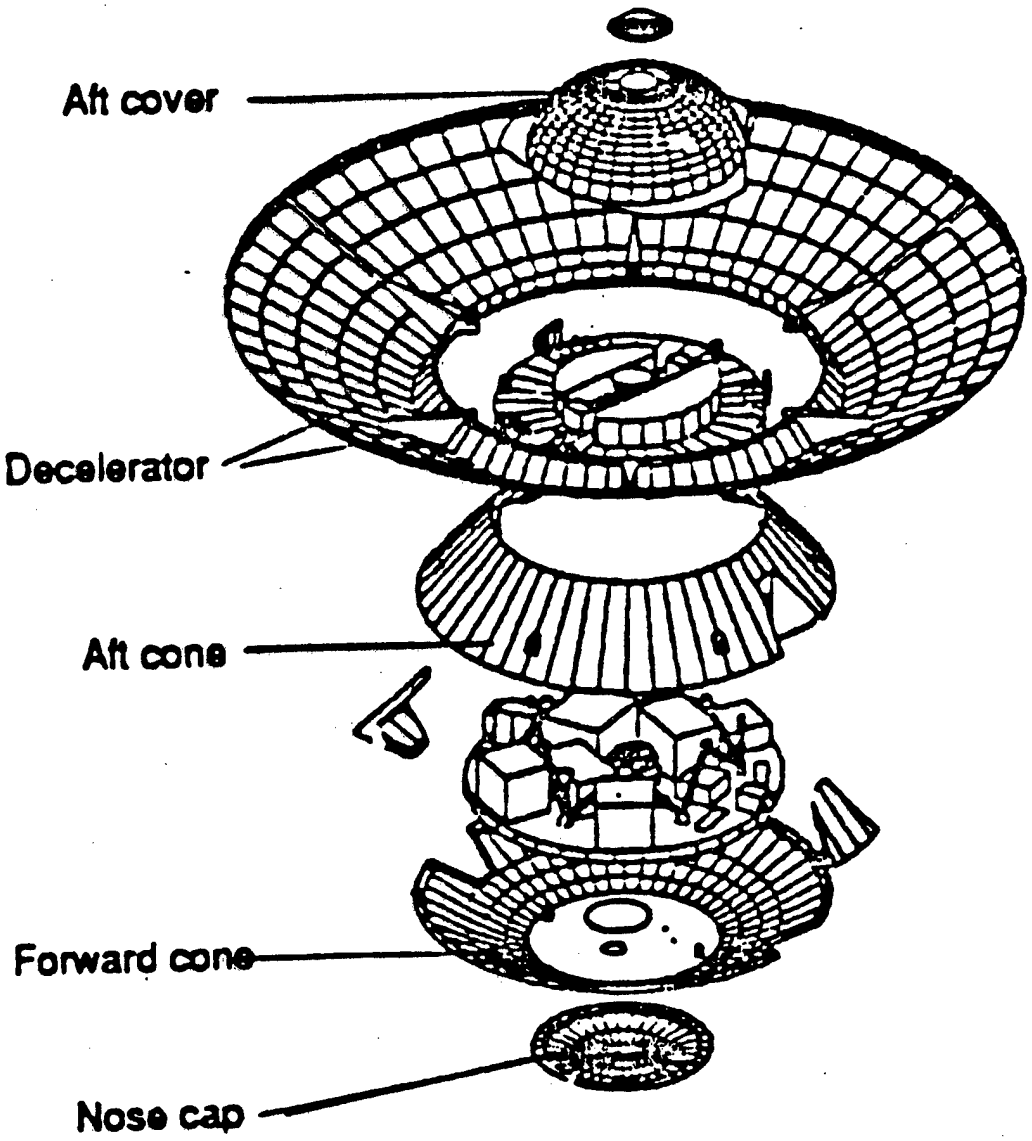


Figure 28. Schematic of the Planetary Titan Probe Huygens.

TABLE 51
FIRST CCC PROTOTYPES FOR EARTH AND PLANETARY ENTRY VEHICLES

YEAR	PROTOTYPE	ORGANIZATION
1965	Mars entry probe heatshield	LTV Aerospace Corporation/USA
1966	Apollo thermal shields for the optical telescope and sextant	LTV Aerospace Corporation/USA
1982	Jupiter entry probe heatshield	Science Applications, Inc. (SAI)/USA
1983	Solar entry probe heatshield	Science Applications, Inc. (SAI)/USA
1990	Titan entry probe nosecap, forward cone, aft cone, and deceleration panels	Societe Europeenne de Propulsion (SEP)/ FRANCE

TABLE 52
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR EARTH AND PLANETARY ENTRY VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1963	Full-scale, 2-D CCC afterbody protective structure fabricated for Apollo mission	First prototype CCC heatshield for Apollo lunar earth-reentry capsule backup heatshield demonstrated	Chance Vought Corporation/USA
1965	Full-scale, 2-D CCC tension shell structure fabricated for unmanned Mars flight	First free-standing CCC planetary structure for wind tunnel testing	LTV Aerospace Corporation/USA
1966	Full-scale, 2-D CCC shuttle protective covers fabricated	First prototype coated CCC sextant covers and telescope covers for U.S. Apollo moon mission vehicle	LTV Aerospace Corporation/USA
1982	CCC heatshield designed for the U.S. NASA solar probe	CCC was the material of choice for thermal protection of a planetary entry spacecraft	Science Applications, Inc./USA
1982	4-D CCC heatshield was designed and fabricated for the U.S. NASA Jupiter entry probe	Another potential application of CCC materials for thermal protection/structure of hypervelocity entry probes	Science Applications, Inc./USA
1983	Full-size heatshield elements were fabricated for the U.S. NASA solar probe	The large (5.2 m, 17 ft.), lightweight (41 kg, 90 lb) and thin (0.152, 0.60 in) STARPROBE heatshield became available for evaluation	Science Applications, Inc./USA
1990	CCC selected for the forward cone, nosecap and aft cap of the French hypersonic planetary (Titan) vehicle	CCC became the structural material of choice for ultrahigh heating environments associated with planetary spacecraft entry	Societe Europeenne de Propulsion (SEP)/ FRANCE
1990	Six large (1.7 m x 3.1 m x 1.5 mm) CCC demonstration panels fabricated for ground-based planetary heating tests	CCC baselined for aft cover of French spacecraft "Cassini" vehicle to the planet Saturn	Societe Europeenne de Propulsion (SEP)/ FRANCE
1991	Integration of 2-D and 3-D CCC materials into a single CCC aeroshell	Demonstration of ability to produce large complex CCC structures which integrate various multi-D material configurations	Fiber Materials, Inc./USA

uses for manned entry capsule and planetary probes. The optical sextant and telescope on the U.S. Apollo command module had special thermal protection requirements and, quite unexpectedly, CCC materials appeared to have the desired properties for the required optical covers. Prototypes were fabricated within two months after ordering, and they quickly became the baseline materials. The CCC shields were likely the first successful application of this material class for aerospace applications. Prototype CCC heatshields were also fabricated as a backup for the Apollo ablative thermal protection system. Lastly, a full-scale nosecap-heatshield for a Mars probe was assembled to demonstrate fabrication feasibility. The nosetip was composed of silica, and the heatshield was constructed of 2-D CCC material.

4.8.11.6.2 *The 1980s*

Planetary vehicle design, performance-materials trade studies, and material selection activities continued on into the 1980s. Very high radiative heating rates were expected during hypersonic flight in the planetary atmospheres. CCC materials appeared attractive, and backup heatshield designs were initiated for the U.S. Jupiter probe. Carbon fabric/phenolic resin ablator proved to be adequate for this mission, and due to its successful flight performance, further developmental efforts with CCC materials were abandoned. With time, the excellent optical radiative properties of CCC materials became documented, and they appeared attractive for most planetary heatshields. The U.S. NASA Solar Probe was the first planetary vehicle that CCC materials could be considered during concept definition. Full-scale articles were designed, fabricated, and shown to provide a lightweight solution for accommodation of the intense thermal problem.

In the early 1990s the space shuttle was still the primary focus of the U.S. space program. Interplanetary exploration was of great interest, but budgetary constraints kept the program low-keyed. Nevertheless the joint U.S./European Cassini project was underway to orbit planet Saturn and inject a secondary probe Huygens into the Titan atmosphere. The French designed probe will likely use CCC materials for various components including the nosecap, forward cone, aft cone, and decelerator brake assembly. All of these probe prototypes have been fabricated and are presently being evaluated.

4.8.12 Spacecraft and Satellite Components

Man's venture into space began on October 4, 1957 when the former Soviet Union launched its orbiting Sputnik I. This man-made satellite sent a soft beep-beep message to startled and incredulous listeners on Earth. The first U.S. successful Vanguard satellite was launched on

January 31, 1958 and carried two small Geiger counters. More Sputniks, Explorers, and Vanguards followed, and the small group of early Earth orbiters soon became a populous generation of bigger and higher-performance satellites. Manned spacecraft became a reality in April, 1961 when Yuri Gagarin of the former Soviet Union orbited the Earth. One month later Alan Shephard of the U.S. rode in the NASA Mercury capsule over a ballistic trajectory of 500 km (311 miles). In February, 1962 John Glenn became the first Earth-orbiting American astronaut. Hence the space age was underway with both unmanned and manned objects in space.

Spacecraft are designed to leave the Earth and its atmosphere, perform a useful mission in space or around the neighboring planets, sometimes returning to Earth and occassionally landing on other planets. Present space systems perform a variety of functions including (a) communications, (b) environmental monitoring (weather prediction), (c) navigation (global positioning), (d) surveillance (early warning), and (e) space exploration. The space system consists of the (a) space vehicle that collects and transmits data, (b) launch vehicle that places the space vehicle into orbit, and (c) ground system that receives and processes data. The basic spacecraft contains the payload that performs the mission. It also includes a bus that supports the payload, maintains orientation and environment, provides power, maintains attitude reference, and supports the communication link and processing. The spacecraft fly in (a) low-Earth orbits (LEO), (b) polar orbits, or (c) geosynchronous Earth orbits (GEO). The spacecraft are enormously expensive, with costs ranging from about U.S. $20-400 M. Launch vehicles are also very expensive and currently cost about U.S. $40-300M. Hence the costs of placing one pound into space are very high, i.e. about U.S. $44,000-88,000/kg ($20,000-40,000/lb).

Spacecraft materials and structures are exposed to harsh environmental conditions for a long period of time. Specific environmental conditions vary with spacecraft design, mission, and orbital altitudes, but in general they include (a) very low pressures or vacuum, (b) atomic species in low concentrations, (c) charged partlcles, (d) wide range of temperatures and thermal cycling, (e) electromagnetic radiation, (f) micrometeoroids, and (g) possibly orbital debris. Defense spacecraft may experience additional man-made threat environments including (a) intense heating from laser weapons, (b) x-ray radiation from nuclear weapons, and (c) debris or projectiles from non-nuclear weapons. These environmental parameters lead to certain hardware requirements which typically involve (a) dimensional stability, (b) high structural rigidity, (c) high load-carrying capability, (d) radiation hardened, (e) deployable or erectable, (f) rapid track and pointing, (g) repairable, (h) fabricable in complex shapes, and (i) low cost.

Spacecraft components advantageously utilize the unique properties of CCC materials. These attributes include (a) low density that yields high specific properties, (b) low

thermal expansion coefficient which yields high dimensional stability, (c) high thermal conductivity which is especially useful in thermal management components, (d) high stiffness and strength which is needed for structural rigidity to resist launch and mission loads, (e) high stiffness-to-density ratio which is required to raise the fundamental frequency of maneuverable structures and minimize active and passive controls, (f) high material dampening to control vibrations caused by maneuvering or onboard disturbances, (g) emissive surface for thermal control, (h) no vacuum outgassing to forgo spacecraft contamination problems, (i) high resistance to thermal cycling to accommodate diurnal solar heating and cooling, (j) high resistance to space radiation, micrometeoroid impact and deep space conditions, and (k) 10-20 years service life without significant property changes.

Spacecraft CCC materials have certain limitations which have restricted the number of applications to date and continue to challenge the materials and structural engineers. The major limitations are (a) a limited design database, (b) inadequate joining techniques, (c) long manufacturing times, (d) property variations with fabrication variation, (e) low resistance to atomic oxygen if deployed in LEO, and (f) high costs.

Many CCC material prototypes have been fabricated and ground tested for future space applications. These pioneering efforts have included (a) thermal management components like thermal planes for electronic circuit boards, (b) thermal radiator facesheets, fins, and heat pipes, (c) survivable structures (hollow tubes, trusses, and joints) for defense space platforms, (d) dimensionally-stable mirror substrates, (e) high precision parabolic antenna components, (f) high-temperature, corrosion-resistant battery containers and panels, (g) electric grids for ion engines, and (h) other specialty uses. Additional CCC demonstration efforts are underway for (a) deployable radiator panels, (b) storable solar array structures, (c) high-precision mirror (radio-frequency and optical) surfaces, and (d) other unique space application outlets.

4.8.12.1 Electronic Packaging

Electronic circuit board designs have been steadily moving toward more power per chip (power density), decrease in physical size, and increased complexity. These chips are placed as close as possible to minimize signal delay time and thus improve the signal processing speed. Waste heat is generated in these electronic packages during operation. As thermal energy accumulates and the device temperature increases, the shear strain at solder joints used to attach chip carriers to the printed circuit board (PCB) also increases proportionally to coefficient of thermal expansion differences between the chip carrier and the PCB and temperature differences across the junction. It is therefore apparent that any waste heat generated

by the electronic circuitry must be dissipated to maintain local temperature control and longevity of the components.

Defense and commercial spacecraft require hundreds of electronic boxes. Each box contains about 10-15 standard electronic modules (SEMs). Each SEM printed circuit board (also known as printed wiring board-PWB) card produces about 25-35 watts (1.4-2.0 Btu/min) of waste energy. This heat must be dissipated to maintain the PCBs below the maximum tolerable temperature of about 90°C (194°F). Much lower temperatures are desired. For every 10°C (18°F) drop from maximum operating temperatures, the reliability of the electronic component and circuit will be doubled.

The configuration of an SEM is illustrated in Figure 29. The SEM is composed of PCBs which are mounted on a central thermal plane (TP) (also known as a heat sink). As noted in Figure 29 the thermal plane is mounted in a perpendicularly-oriented SEM frame with the aid of a wedgelock. During operation, heat is generated by the electronics, and it is conducted from the chips through the PCB into the thermal plane. It is then further spread and conducted through the chassis/TP interface to an externally-cooled heat exchanger.

PCB thermal planes have many functions. They (a) regulate the overall temperature of the SEM, (b) provide structural support and stiffness, thereby insuring the integrity of the solder joints and the printed circuitry, (c) permit assembly and disassembly of the PCB, and (d) dampen vibration loads carried into the PCB.

SEMs are either actively or passively cooled. The latter thermal management approach is preferred because it (a) is less complex, (b) is lighter in weight, (c) involves less costs, (d) increases reliability in the system, and (e) offers other attributes. Passive cooling in space is quite challenging because the total lack of an atmosphere precludes cooling by convection. Thus only conductive and radiative modes of heat transfer are available to the space radiator designer.

Conventional aluminum thermal planes having a thickness of about 0.25 cm (0.10 in) have been adequate to dissipate up to about 25-35 watts. Future electronic packaging in an ever-shrinking volume to increase computer speed will result in higher thermal fluxes. Up to an order of magnitude higher waste heat loads may be experienced. Without more efficient thermal control, local temperatures will increase and the lifetime of the electronic component will decrease. Hence novel SEM designs and materials must be developed to rapidly relocate thermal energy from the point-of-origin to the point-of-dissipation. In addition local hot

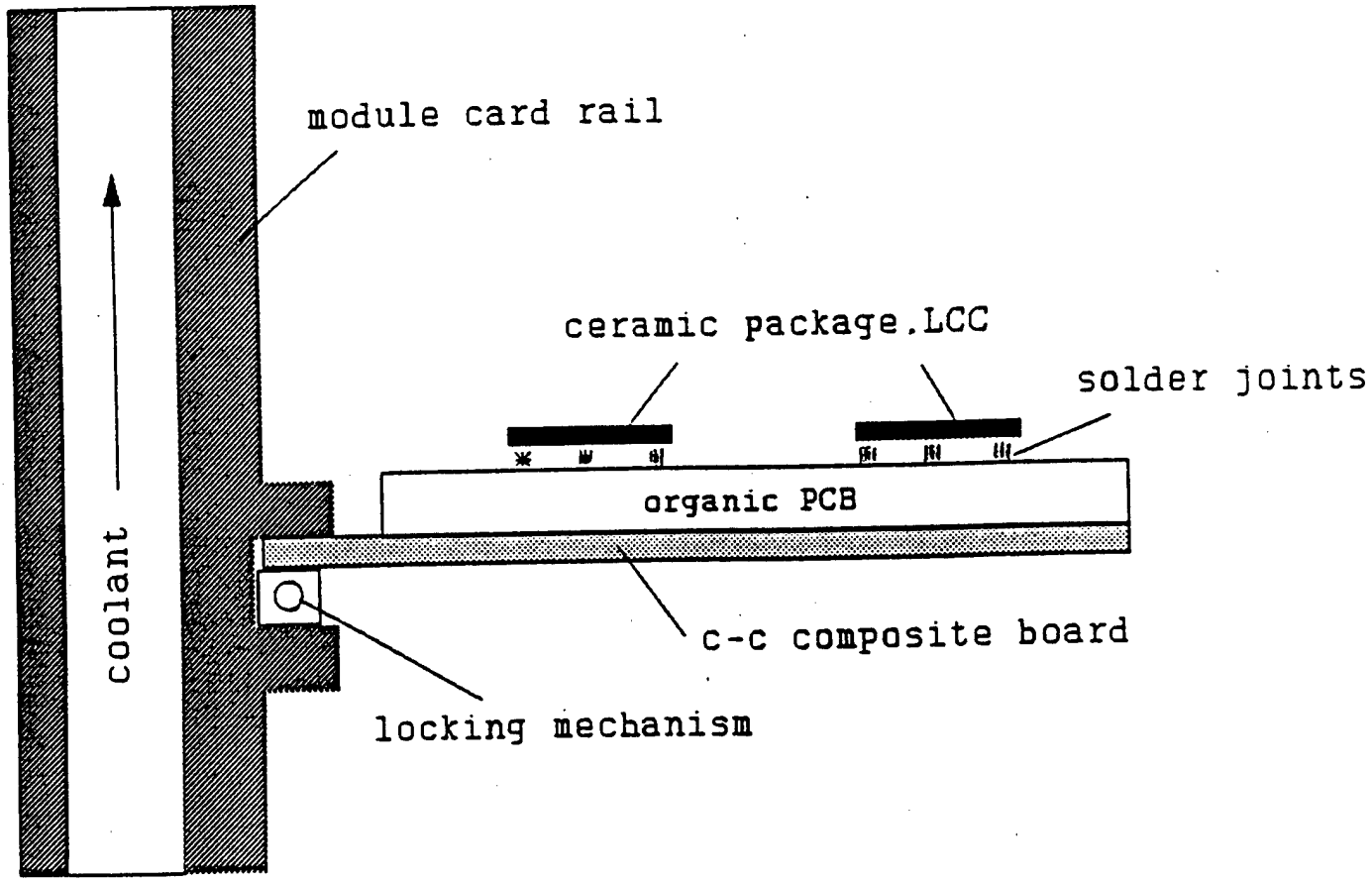


Figure 29. Schematic of a Standard Electronic Module (SEM).

spots on the PWB must also be reduced. Secondly, the mismatch of thermal expansion between the chip and the board must be reduced to achieve greater component reliability with little-to-no weight penalty.

CCC materials offer many thermal management-related properties that could be used advantageously in SEMs. They have (a) highly directional thermal conductivity, (b) low density, (c) high stiffness, (d) high strength, (e) high emissivity, (f) low thermal expansion, (g) resistance to thermal cycling effects, and (h) other properties of importance. In-plane thermal conductivity and low density are the key properties of CCC materials. The in-plane thermal conductivities of a unidirectionally-reinforced or unbalanced woven fabric-reinforced CCC material exceed those of all known materials. Low composite density also contributes to low component weight.

SEM-E thermal planes have been designed, fabricated, and tested with 2-D CCC materials. The composite panels were 20.3 by 25.4 cm (8 by 10 in) and composed of mesophase, pitch-based graphite fibers in a woven-fabric construction and a matrix of either CVI pyrolytic graphite, pitch coke, or a combination of CVI PG and pitch-based coke. The best results were obtained with unbalanced woven fabrics having an 8-harness satin construction and warp/fill ratios of 3/2 and 4/1 and a mixed matrix of pitch-based coke and CVI pyrolytic graphite. These composites had an in-plane thermal conductivity in the range of 150-350 W/m·K (87-202 Btu/ft·h·°F), a tensile strength of about 20-50 ksi (138-345 MPa), a tensile modulus of about 15-40 Msi (103-276 GPa) and a density of about 1.8 g/cm^3 (0.065 lb/in^3). With newly-available mesophase pitch-based graphite fibers, in-plane composite thermal conductance values were increased up to about 400-483 W/m·K (231-279 Btu/ft·h·°F) and with about the same density value. Thermal conduction in the transverse plane of the advanced CCC composite was about 46-50 W/m·K (27-29 Btu/ft·h·°F). Successful use of the new high thermal conductivity CCC thermal planes could provide weight savings up to about 60 percent compared to conventional aluminum. The major obstacle in the development of high-performance CCC thermal planes is the very high cost of available, mesophase pitch-based graphite fibers. The most thermally-conductive fiber available in the U.S. costs about U.S. $5280/kg ($2400/lb). Few applications can justify this high-cost product, but with expanding fiber usage, CCC thermal planes will become more attractive for future applications. Developmental issues now being addressed include (a) durability and handling, (b) adequacy of a database, (c) shorter manufacturing times, (d) degree of cleanliness, and (e) lower-priced constituents.

Systems benefits to be derived by the use of CCC thermal planes are enormous. It is anticipated that local temperatures could be reduced by at least 50 percent

compared to conventional aluminum, minimum weight savings of 30 percent could be achieved and componentry life extended by 150-200 percent. These technical benefits can translate to many hundreds of millions of U.S. dollars for a single weapon or commercial space system.

While space applications are the most promising applications for SEM-E CCC thermal planes, it is anticipated that advanced aircraft and helicopters will also use this new technology. Advanced aircraft, for example, may need as many as 1500 SEM-E thermal planes. With a weight savings of about 50 g (0.11 lb) per SEM-E versus aluminum planes, the aircraft avionics package could weigh about 75 kg (165 lb) less. Even greater potential weight savings has been calculated versus other candidate thermal plane materials.

4.8.12.2 Space Radiators

Spacecraft electronics and power sources generate surplus heat. This energy must be discarded from the spacecraft in order to maintain proper thermal control and on-board temperature. Spacecraft electrical demands are presently at the 5 kilowatt electrical (kWe) which can be dissipated by body-mounted radiators. Such heat-generating components are mounted on the inboard side of a honeycomb sandwich panel with heat pipes embedded between two face sheets. The outboard face sheet surface acts as the primary heat rejection surface. It is usually covered with a thermal control coating.

Aluminum is the state-of-the-art material for radiator face sheets and heat pipes, because it exhibits high specific thermal conductivity at relatively low initial costs. Several other classes of advanced composites offer higher performance at lower weight, including (a) CCC materials, (b) metal matrix composites, and (c) possibly graphite fiber-organic resinous composites.

Future spacecraft will generate a larger amount of waste heat, possibly up to an order of magnitude greater than in conventional systems. In addition to the higher amounts of surplus heat, the spacecraft will function for longer operational times and be of higher performance. These demanding requirements can probably be met with the development of (a) improved heat pipe concepts, (b) two-side fixed or deployable space radiator designs to maximize radiant energy losses from the emitting surfaces, and (c) satisfactory materials to build these components. The deployable radiator is perhaps the answer to future space thermal management needs. This type of space component consists of an integrally-finned heat pipe array with appropriate coatings. The heat pipe is a closed pressure vessel consisting of a shell and an enclosed wick. The working fluid is typically composed of (a) ammonia, (b) methanol, or

(c) water. However, the working fluid potassium will likely be necessary to obtain the highest thermal efficiency. The radiator fin, which is the primary heat rejection surface, is composed of a thermally-conductive, structural, and environmentally-resistant material. To maximize heat transfer the space radiator may be steerable and contain a joint between the heat pipe array and the fin. The joint serves to (a) rotate the fin, (b) connect the necessary parts, and (c) resist heat transfer between the parts. A multifunctional coating on the radiator fin provides the necessary thermal control and environmental protection for the underlying substrate.

A key element in advanced space radiators is the heat pipe. The four major heat pipe elements include (a) the primary structural heat pipe tube, (b) metallic liner, (c) end caps and fill tubes, and (d) wicks. CCC tubes are candidate materials if not the prime material for heat pipes. The materials must have (a) excellent corrosion resistance, (b) good thermal conductivity, (c) high strength and stiffness at elevated temperatures, (d) low density, (e) high surface emissivity, and (f) high survivability in both natural and man-made threat environments.

Candidate CCC tubes have been fabricated with a diameter of 2.5 cm (1.0 in). Two CVD carbon layers were then deposited to (a) improve the thermal contact between the CCC and liner materials and (b) increase the shear bond strength and reduce carbon diffusion into the liner material. The CCC liner was coated with a thin metallic liner to keep the hot working fluid (potassium) from intercalating the carbon with an attendant loss of strength and material swelling. Brazing was selected as the primary joining technique for bonding the metallic liner to the CCC tube, based on (a) wettability, (b) adherence of CCC to metallic surfaces, (c) chemical reactivity, and (d) thermal stability.

Special CCC materials have also been designed to meet the needs of future space radiator fins. These composites typically contain mesophase pitch-based graphite fibers and CVI pyrolytic graphite matrices. The pitch-based graphite fibers have exceptionally high axial thermal conductivity values, but the transverse thermal conductivity is only a small fraction of the axial value. Thus the thermal conductivity of a CCC composite is controlled by (a) axial thermal conduction of the fiber, (b) orientation of the fibers, and (c) volume fraction of the fiber employed. To obtain maximum axial thermal conductivity, mesophase pitch-based graphite fibers are heat treated at very high temperatures. Maximum composite directional thermal conductivity is obtained by orienting the major fiber axis parallel to the heat path. Unidirectionally-reinforced composites offer the highest directional heat flow, but due to their poor off-axis properties, woven fabrics and sometimes 3-D composites are used. Unbalanced

fabric constructions offer the opportunity to maximize heat conduction in a single plane while maintaining adequate structural properties in a second (90°) direction.

Several material and design issues remain to be solved before CCCs are widely used in space radiators. They include (a) a decrease in thermal conduction rate as the temperature is increased, (b) very high cost of the mesophase-pitch-based filamentous materials, (c) composite fiber fraction volume and handling characteristics of less-expensive, vapor-grown, short graphite fibers, (d) low fiber elongation that restricts handling and weaving, and (e) low fiber transverse thermal conductivity that may force the use of multidirectional fibrous preforms with associated higher costs.

The in-plane thermal conductivities of CCC materials are temperature dependent. Conductance values decrease slightly with increasing temperature. Since space thermal radiators operate over a rather narrow temperature range, this reduction in thermal efficiency tends to be minor. For example a 1.8 g/cm^3 (0.065 lb/in^3) unidirectional mesophase pitch-based graphite fiber-reinforced petroleum pitch-based graphite-matrix composite had an in-plane thermal conductivity of 700 W/m·K (4854 Btu·in/h·ft^2·°F) at 20°C (68°F). At 200°C (392°F) the in-plane composite thermal conductivity decreased only 17 percent. Other thermal composite materials exhibited about the same property-temperature trend. The exceptionally high cost of high axial thermal conductivity carbon fibers remains as a major impediment for space component uses. Some progress has been made, however, in reducing fiber costs via alternate processing routes. Low-modulus and low thermal conductivity pitch-based fibers were woven into the desired fibrous construction and then heat treated to a substantially higher modulus fiber. This approach avoided the problem of weaving high-modulus, low strain-to-failure, pitch-based graphite fibers into the desired fabric construction.

Attention must also be paid to the design of efficient interfaces and joints which are critical to thermal management and component structural integrity. With continued component design and development, it is expected that CCC space radiators will potentially eliminate the need for heat pipes in systems having nominal component heat fluxes and loads. For higher load systems the number of heat pipes could be reduced depending upon the criteria such as spacing and redundancy.

Subscale space radiators have been designed, fabricated, and ground-based tested. These early prototypes utilized a thermally and structurally efficient CCC fin with internally-contained metallic heat pipes. The new CCC radiator components were about one-third the weight of conventional all-metallic radiators. Efforts are continuing to (a) further

upgrade the CCC materials, (b) fabricate metal-lined CCC heat pipes, and (c) evolve new designs which incorporate the unique thermal properties of CCC materials into advanced space radiator systems.

4.8.12.3 Solar Power Heat Storage Panels

Advanced solar dynamic power systems require compact, lightweight heat storage elements. One approach being developed involves lightweight panels containing phase-change materials. Exposure to the sun's rays (insolation), causes heat to be stored in the panels via the latent heat of fusion of a phase-change substance. During low insolation heat is withdrawn from the panels. The panels thus act to level the thermal load between alternating periods of sunlight and full or partial solar eclipse. Practical applications for these heat storage elements are (a) on an orbiting space station, (b) Earth solar-power systems, and (c) others.

Prototype panels have been fabricated and tested. The material consisted initially of a 4-D fibrous carbon preform impregnated once with a pitch matrix and carbonized. Germanium was then infiltrated into the porous CCC substrate. Germanium melts at a temperature of 938°C (1720°F), has a high latent heat of fusion, and is chemically compatible with carbon. The composite was hot isostatically pressed, coated with a thin layer of pyrocarbon, and then overcoated with a thin layer of CVD silicon nitride. The pyrocarbon layer prevented chemical attack of germanium by chlorine which is present in the CVD coating process. Hybrid CCC materials were obtained with 30 volume percent of germanium, and even higher metallic contents are expected with more open woven 3-D and n-D fibrous preforms. The metal-CCC composite had a thermal conductivity of about 10 W/m·K (5.8 Btu/ft·h·°F) which is quite satisfactory for heat-storage systems.

4.8.12.4 High-Temperature Battery Containers

Satellites and spacecraft operating in near-Earth orbits derive their main source of energy from solar arrays. These orbiting vehicles require a secondary source of energy, which is typically furnished by batteries of low mass, small size, and large electrical energy storage. Batteries currently in use include (a) nickel-cadmium and (b) nickel-hydrogen. They are required to run over 20,000 cycles.

High-temperature batteries composed of sodium-sulfur (Na-S) electrochemical cells are particularly attractive for satellites operating in geosynchronous Earth orbits and for future space needs. Typical battery lifetimes involve less than 2000 cycles and charge/discharge rates less than batteries used in LEO satellites. The specific energy (160 Wh/kg, 73 Wh/lb) of sodium-sulfur batteries is approximately four times higher, and their specific peak

power levels are about twice that of lead acid batteries. This type of advanced, high-energy battery also has (a) low operating costs of about $200/kWh (U.S. $0.059/Btu), (b) up to 1000-6000 charge/discharge cycle life, (c) low-cost active materials, and (d) very safe operation. Other characteristics of the batteries include (a) an onboard heating system, (b) well insulated, (c) sealed for life, and (d) maintenance free. The sodium-sulfur battery cells operate at high temperatures which are considerably above the normal spacecraft environmental temperatures. Thus thermal control of the battery and thermal integration of the batteries into a spacecraft are challenging design problems. For example a primary battery would be needed to heat the sodium-sulfur battery in space, and for that reason a hot launch is preferable to a cold launch.

Sodium-sulfur battery technology is being pursued for at least three major application outlets. Potential space uses have been mentioned, but in addition they are very promising for (a) electric-powered automobiles and (b) stationary energy-storage devices for electric utility systems. Successful application to electric-powered vehicles would reduce the dependence on petroleum fuels and reduce air pollution. The successful use of sodium-sulfur batteries for utility load-leveling would permit the storage of cheap base-load energy during the off-peak period and energy discharge during the period of high demand. The charging of electric vehicles during the off-peak period (at night) would also serve to beneficially level the load demand on utilities.

The sodium-sulfur battery operates at a temperature of about 300-350°C (572-662°F). The essential parts of the battery are (a) a liquid anode of metallic sodium, (b) a cathode of molten sulfur/polysulfides, and (c) a solid sodium ion-conducting electrolyte of sodium aluminate (sodium beta-alumina). The anode is separated from the cathode by a tubular polycrystalline ceramic electrolyte of beta-alumina. In this type of cell sodium ions diffuse during discharge from the anode to the cathode by ionic conduction through the ceramic electrolyte. Two different battery designs have been evaluated, but sodium core cells have been found to be more promising than sulfur core cells. In the sodium core cell battery, sodium is placed inside a sodium beta-alumina tube. The tube is then sealed to an alpha-alumina header. The tube is placed inside a chromium-plated mild steel container which houses the sulfur electrode. The steel container is chromized, since both sulfur and polysulfides are highly corrosive. The liquid electrode is composed of electrically-insulative sulfur impregnated in an electrically-conductive carbon felt which carries the current. Heat generated during the charging and discharging operations is rapidly removed by thermal conduction of the carbonaceous felt. See Figure 30.

Material requirements for sodium-sulfur battery cell cases (sleeves) include (a) chemical stability in molten sulfur and sodium polysulfides, (b) high electrical

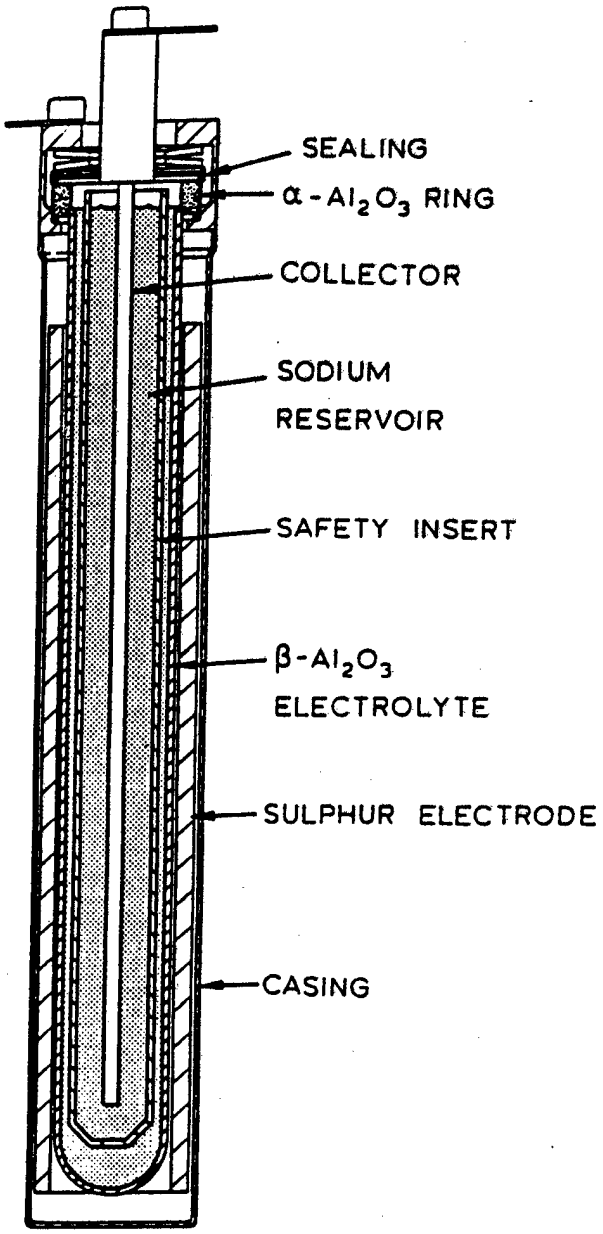


Figure 30. Diagram of a High-Temperature Sodium-Sulfur Battery.

conductivity, (c) high thermal conductivity, (d) low density, (e) impermeability, and (f) adequate mechanical properties. The materials should also be (a) low cost, (b) fabricable with state-of-the-art methods, and (c) be sufficiently available from multiple sources.

Container corrosion represents one of the major materials challenges of the sodium-sulfur battery. Chromized steel containers exhibit (a) corrosion leading to a shorter cell life, (b) low thermal conductivity that causes limited heat dissipation during the charge/discharge process, and (c) high material density that results in low energy density (energy/weight) values.

CCC materials have many intrinsic properties that lend themselves to containers for sodium-sulfur batteries. The materials are (a) highly resistant to chemical attack by molten sulfur and sodium polysulfides, (b) electrically conductive, (c) thermally conductive, (d) low in density, (e) high in strength, (f) high in stiffness, and (g) resistant to vibrations. Needed functional properties coupled with low mass density lead to high specific material properties which are very important in space applications. For example the specific thermal conductivity of 2-D filament-wound CCC composites in the plane of the reinforcement is about 25 times higher than that of steel. Thermal management design thus becomes lesser of a problem with CCC materials.

CCC cylindrical containers (sleeves) have been successfully prototyped for high-temperature sodium-sulfur batteries. The CCC tubes were fabricated with a length of 25 cm (10 in), an outer diameter of 5.1 cm (2 in), and a very thin wall thickness (1.5-2.0 mm, 0.059-0.079 in). The tubes were composed of filament-wound carbon fibers with a char matrix derived from phenolic resin. The CCC container costs were about 10 percent of the total fuel cell costs. The CCC sleeves were mounted to a thermally-conductive CCC baseplate, using collar or brazing techniques, in order to maximize rapid heat transfer from the battery cells to the mounting structure. Results to date have been quite impressive, but additional design and materials fabrication efforts will be needed to optimize the high-temperature, sodium-sulfur battery.

The exceptional high-temperature corrosion resistance of CCC materials makes them prime candidate materials for use in other space batteries, like the nickel-hydrogen ($Ni-H_2$) battery thermal control components. Nickel-hydrogen batteries provide electrical power to a satellite when it is in the Earth's shadow and the solar panels are not operating. Thermal management of the battery is important because the charge/discharge operation is strongly affected by cell temperature. Heat generated in the cell during charge/discharge is typically dissipated by a circumferential band located on the midplane of the battery cell. CCC materials

have been prototyped for battery sleeves and structural baseplates to assist in thermal management and accommodate any chemically-corrosive environment.

4.8.12.5 Survivable Space Structures

Present spacecraft structures constitute about 15-30 percent of the vehicle weight. They accommodate all of the unique and diverse mechanical and thermomechanical loads experienced during pre-launch, launch, and on-orbit station while satisfying the design volume and weight constraints. There are basically three types of spacecraft structures. The primary structures (a) transfer launch accelerations to all vehicle components, (b) maintain alignment of components, and (c) provide environmental protection. They are typically composed of honeycomb or hollow tubes. The secondary structures (a) connect subsystem components to the primary structure, (b) deploy appendages, (c) enable controlled motion, and (d) provide environmental protection. Typical secondary structures are composed of lightweight, stiff, hollow tubes. The third class of space structures are those that support subsystems. They include (a) thermal subsystems like flat panel radiators, heat pipes, etc., (b) propulsion subsystems including tankage, pipes, etc., and (c) electrical power subsystems like solar array substrates, printed wiring board substrates, and others. Structures contained on the exterior of the spacecraft experience the most damaging effects of the space environment, i.e. greater temperature excursions, particulate erosion, thermal cycling effects, etc. Structures within the spacecraft are protected from some of the elements of the space environment, and hence materials requirements are less severe.

Material needs vary with design, but in general they are based on (a) mission objectives, (b) specific environmental parameters, (c) configuration, and (d) whether the spacecraft has a crew or is unmanned. These design criteria require detailed consideration of a host of factors including (a) static loads, (b) rigidity, (c) dynamic loads, (d) atmospheric pressure loads, (e) acoustical loads, (f) thermal loads, (g) vacuum, (h) planetary atmospheres, (i) meteoric particles, (j) solar radiation pressure, (k) energetic particles, (l) magnetic forces, and (m) sterilization requirements. The most significant loads are associated with (a) propulsion, (b) control systems, (c) pressure vessel loads, and (d) reentry or entry loads. Launch loads typically dominate spacecraft structural design, and thus high material stiffness (modulus) is needed to minimize deflections and elongations.

Typical spacecraft structural materials include (a) alloys of aluminum, (b) beryllium, (c) magnesium, (d) organic matrix composites, (e) steel, (f) stainless steel, and (g) superalloys. Preference is typically given to lightweight and stiff (high modulus) materials like

aluminum and graphite fiber-reinforced organic-matrix composites. Aluminum is the most widely used material because of its low density, acceptable strength and stiffness, low cost, and ease of fabrication. For higher stiffness structures, beryllium may be used, but high costs and toxicity restrict its application. Ultrahigh stiffness metal-matrix and organic-matrix composites are rapidly becoming the materials of choice for benign space environments.

Future defense spacecraft will require structures for extended operation in space and reduced vulnerability to potential hostile countermeasures (laser energy, nuclear radiation, particles and projectiles). Conventional space structural materials like aluminum and organic-matrix composites will likely not survive high transient temperatures or thermal distortion, thus reducing or destroying their functional capabilities. Specialty structural materials are thus required with outstanding mechanical, thermal, and nuclear-related properties.

CCC materials have been prototyped in several space systems structures. These structures were composed of various building-block elements like (a) thin-walled round or square tubes, (b) joints for extending the tubular components, (c) rib-stiffened panels, (d) T-section stiffened panels, (e) U-channel sandwich construction, and (f) honeycomb facesheets. The most common structural subelements are hollow tubes which are characterized by (a) high elastic and shear moduli, (b) high compressive and tensile strengths, (c) high torsional strength and stiffness, (d) low thermal expansion, (e) vibration dampening, (f) uniform and minimal wall thickness, (g) dimensional straightness and cylindricity, and (h) possibly other considerations. Several types of 2-D CCC materials have been developed with (a) temperature capabilities over 1927°C (3500°F), (b) axial Young's modulus over 345 GPa (50 Msi), (c) axial tensile strength of about 587 MPa (85 ksi), and (d) near-zero coefficient of thermal expansion in the longitudinal and circumferential directions. These materials were also highly survivable in man-made threat environments. The CCC materials absorbed about 30 kJ/g (12.9 kBtu/lb) during thermally-induced sublimation which is the highest heat of ablation of all known structural materials. This feature coupled with excellent thermal shock characteristics make them ideal for accommodating laser energy threats regardless of the incident irradiance level. High-purity CCC materials also have low x-ray (spectrum dependent) and neutron cross sections, thus enabling survivability in a nuclear radiation environment. Surface degradation by atomic oxygen is an important concern for LEO missions, but multifunctional coatings have been developed to enable their use. At higher satellite orbital altitudes, atomic oxygen is not an issue due to its lower concentration.

Hollow structural CCC tubes have been fabricated with high tolerances and a uniform wall thickness of about 0.1 cm (0.04 in). Both concentric and square tubular

components were made available. Each of the individual tubes were joined together with various techniques like (a) clevis end-fittings, (b) mechanical fittings and pins, (c) fasteners, (d) brazing and (e) other attachment methods. Static loads well over 73 kg (1606 lb) were demonstrated in lateral, torsion, and vertical directions. All of the joining techniques were workable, but additional developmental efforts are needed to optimize weight and performance considerations.

One of the most impressive articles fabricated was a very large deployable/retractable pantograph CCC structure that supports the spacecraft solar array. Tubular struts, fittings and hinges for the pantograph were designed, fabricated, and evaluated to quantify systems benefits and identify any material limitations. The results of these thermal, laser, mechanical, and tribological tests provided the necessary database for optimization of component design.

Full-scale modular truss structures have also been fabricated and assembled on the ground. Their overall dimensions have exceeded 102 cm (40 in) which is adequate to illustrate that CCC materials are feasible structures for future space applications.

4.8.12.6 Space Shields

Defense assets in space may cost many hundreds of millions of U.S. dollars. During time of international conflict, protection of these defense spacecraft is of paramount importance. Protective space shields have been developed in support of the Strategic Defense Initiative (SDI). While details have not been reported in the open literature, it is known that the space shields have been prototyped and composed of coated, multilayered CCC materials. Such lightweight shields have been designed to withstand intense laser energy irradiation and hypervelocity particulate impact.

4.8.12.7 Parabolic Antennas

CCC spacecraft antenna reflectors that are freestanding and dimensionally stable have been designed, fabricated, and successfully ground tested. The unique space articles were shown to be (a) lightweight, (b) ultrastiff, (c) electrically conductive, (d) dimensionally stable over a wide temperature range, and (e) thermally stable.

A 2-D CCC antenna reflector prototype was fabricated with a 61 cm (24 in) diameter, a center depth of 11.4 cm (4.5 in), and a density of 1.8 g/cm^3 (0.065 lb/in^3). The CCC material was composed of a woven fabric of pitch-based graphite fibers and a carbon powder-filled resin coke matrix. The CCC antenna represented a true parabolic surface of

revolution with a focal length of 23.3 cm (9.22 in). This antenna dish was representative of antenna reflectors used in satellite communications. Laboratory testing was accomplished at radio frequencies of 20 to 60 GHz which is typical of U.S. spacecraft usage.

4.8.12.8 Laser Mirror Structures

During the Strategic Defense Initiative, space-based lasers were expected to be deployed for target identification and destruction. Fortunately that scenario never developed, but the technology for deployment remains. CCC space-based laser mirror systems were developed based on the versatile properties of CCC materials. A 5-D CCC material was selected because it possessed the best balance of anisotropic properties including (a) low thermal conductivity, (b) low thermal expansion coefficient, (c) good mechanical properties, (d) moderate costs, and (e) compatibility with laser-reflective coatings. Mirror substrates up to 70 cm (27.6 in) diameter were fabricated and coated with high-performance, laser-reflective coatings. Laboratory tests verified adequate performance of the CCC substrate.

4.8.12.9 Ion Engine Components

Interplanetary and earth-orbital space missions require ion propulsion systems that operate at high power levels and for long periods of time. The ion thruster is the center of the propulsion system, and its performance depends mainly on ion extraction grids. The maximum beam current that the grids can extract for a fixed specific impulse is limited by a number of factors which, in turn, are related to the hole alignment between the screen, accelerator grid, decelerator grid, and to the grid-to-grid separation distances. At present there are two major problems inherent in increasing total thrust and thrust density of an ion engine. They are (a) grid erosion and (b) thermal distortion which changes the grid separation distance. Grid erosion is caused by ion sputtering of the grid surfaces. Thermal distortion results from nonuniform heating of the grid electrodes in the form of radial and grid-to-grid temperature gradients. Sputter erosion of the accelerator grid must be held to a minumum because it shortens the lifetime of the thruster engine. State-of-the-art grids are fabricated from thin molybdenum sheets. To minimize grid distortion the ion grid is hydroformed about 2.0 cm (0.79 in) over a 30-cm (11.8-in) diameter. Uniform hydroforming across the diameter of the grid is difficult, and this situation may lead to a nonuniform grid gap. Hydroforming may also cause grid-to-grid hole misalignment. In addition thermal distortion of the grid becomes more severe as the grid diameter is increased. CCC materials offer promise for minimizing these ion optics problems, because they have (a) high thermal stability, (b) near-zero coefficient of thermal expansion, (c) superior strength and stiffness, (d) high resistance to ion sputtering, (e) no vacuum outgassing, and (f) fabricable to high

tolerances. The key property appears to be the near-zero coefficient of expansion which will prevent thermal distortion of the grids. Hence, grids may be made from easier-to-fabricate flat sheets rather than dished grids. Flat sheets enable superior hole alignment between the screen, accelerator grid, and decelerator grids. Reduced thermal distortion permits the use of thicker grids but with the same small hole diameters [about 1.2-2.0 mm (0.047-0.079 in)].

Flat grids have been fabricated with resin char/pitch coke matrix reinforced with square woven, mesophase-pitch based carbon fabric. The panels were up to 30 cm (11.8 in) square with a thickness of 1.0 mm (0.039 in). The three-ply thick CCC panel had a density of about 1.69 g/cm^3 (0.061 lb/in^3). Ion extraction aperatures (hundreds of holes) were drilled in the CCC plates with electric discharge machining (EDM). The ion extraction holes had a uniform diameter and possessed straight sidewalls (no taper). The new CCC grids were evaluated in laboratory sputter erosion tests and found to be superior to state-of-the-art molybdenum. The CCC erosion rate was only a fraction of the conventional grid material. Fabrication and machining efforts are continuing to (a) increase the grid diameter, (b) improve material strengths, and (c) maintain grid flatness.

4.8.12.10 Chronology

A number of CCC components have been prototyped for evaluation in future spacecraft. These prototypes are primarily of a thermal management type, but others like survivable structures, dimensionally-stable reflectors, etc. have also been fabricated. Table 53 lists the various types of CCC parts for space applications along with the first year of availability in the United States. Table 54 is a chronology of space CCC materials and components.

4.8.12.10.1 *The 1980s*

As CCC prototypes for Earth reentry and solid rocket motor nozzles advanced during the early 1980s, attention was directed to other possible defense and commercial applications in space. The CCC materials had four attractive properties that lent themselves to uses in space, i.e. (a) low-to-zero coefficient of thermal expansion, (b) very high in-plane Young's modulus, (c) high thermal stability, and (d) low density. These properties were utilized in obtaining the first space prototype, namely a large 5-D CCC substrate for a space-based laser mirror. No further information has been published in the open literature concerning its suitability for this application. By the late 1980s it was clear that CCC materials were candidates for survivable space structures and various thermal management components. A host of different

TABLE 53
FIRST CCC PROTOTYPES FOR SPACECRAFT AND SATELLITES

YEAR	PROTOTYPE	ORGANIZATION
1981	Laser mirror structure	Fiber Materials, Inc. (FMI)/USA
1988	Parabolic antenna reflector, subreflector, struts and structure	Ford Aerospace/USA HITCO/USA Aerospace Corporation/USA
1988	Tubular structures (tubes & joints)	Fiber Materials, Inc. (FMI)/USA Lockheed Missiles & Space Co., Inc./USA
1989	Radiator honeycomb skin panels	Lockheed Missiles & Space Co., Inc./USA
1990	Radiator heat pipe structure	Rockwell International Corp./Rocketdyne Division/ USA
1990	Battery container (holder) and panels	Kaiser Aerotech/USA
1990	Integral fin-heat pipe radiator	Rockwell International Corp./Rocketdyne Division/ USA
1991	Electrode grids for ion engines	BFGoodrich/Super-Temp/USA Jet Propulsion Laboratory/USA
1991	Deployable solar array structure	Kaiser Aerotech/USA
1991	Deployable truss structure	TRW, Inc./Applied Technology Division/USA
1992	Electronic printed circuit board heat sinks	BFGoodrich/Super-Temp/USA BFGoodrich Aerospace/USA

TABLE 54

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SPACECRAFT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1981/82	Large coated 5-D CCC prototype mirror was designed, fabricated, and tested for space survivable optical systems	First mirror application of CCC materials Coated 5-D CCC potential demonstrated for space-based laser mirrors	Fiber Materials, Inc. (Mirror)/USA General Dynamics/Convair Division (Design)/USA
1988	Development of braided tubes and joints	CCC provided thin-walled structural components for space structure applications	Fiber Materials, Inc. (Materials)/USA Lockheed Missiles & Space Co., Inc. (Design)/USA
1988/91	Design, development, fabrication and testing of three 24-in. cassegrainian antenna reflectors (subreflectors, struts, and attachment fittings) using 2-D CCC	Advanced, lightweight, hardened, dimensionally-stable, high-temperature antenna components for space applications Hardware fabricated to net shape to demonstrate low-cost potential System tested relative to existing standard metallic reflectors with no loss in performance	Ford Aerospace (Design and Test)/USA Aerospace Corporation/USA HITCO (Part Fabrication)/USA
1988	2-D CCC hinge fabricated for a space load-bearing structure	First prototype hinge for a precision space structure	Harris Corporation/Government Aerospace Systems Division/USA
1989	3-D CCC joints were designed and fabricated for survivable space-based radar, communication, and defense satellites	Unique 3-D CCC joints available, thus eliminating need for secondary bonding or joining procedures	General Dynamics Corporation/Convair Division/USA
1989	2-D CCC tubular structural parts were fabricated for potential space applications	First prototype ultrahigh stiffness structural parts for high-temperature space uses	Kaiser Aerotech/USA
1989	CCC radiator panels fabricated	First prototype radiator panels for space thermal management High thermal conductivity and space environmental resistance of CCCs advantageously used for spacecraft design	Lockheed Missiles & Space Co., Inc./ USA
1990	Coated 2-D CCC space structures fabricated with high resistance to space thermal environments	Survivable CCC materials for future space survivable systems	Lockheed Missiles & Space Co., Inc./Space Systems Division/USA

TABLE 54 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SPACECRAFT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1990/91	Angled interlocked CCC tube containing integrally-woven fins and an internal CVD metallic coating was fabricated for a space radiator prototype	High-temperature potassium space radiator prototype became available for nuclear space power evaluation	Rockwell International Corp./Rocketdyne Division/USA
1991	2-D CCC ion extraction grids fabricated and tested for space ion engine	CCC grids were more dimensionally-stable and ion sputter-resistant than conventional materials Increased prospects for higher power level and longer-life ion engines	BFGoodrich/Super-Temp (CCC Grids)/ USA Jet Propulsion Laboratory (Testing)/USA
1991	CCC truss structure was fabricated and assembled	Deployable structure was made available for space part evaluation	Kaiser Aerotech/USA
1991	Tubular integral Clevis attaching device (TICAD) was designed and fabricated	Integral clevises were fabricated on both ends of a CCC tube, thus eliminating joining of tubes to clevises	Kaiser Aerotech/USA
1991	A CCC mast plate was fabricated	A deployable and stiffened mast plate prototype became available for a space solar array	Kaiser Aerotech/USA
1991	A CCC space structural deployable boom was designed	Thin and lightweight CCC materials were chosen for the space structural design	Kaiser Aerotech/USA
1992	2-D CCC thermal planes (heat sinks) fabricated and evaluated for standard electronic modules (SEMs)	Highest in-plane thermal conductivity demonstrated for all known materials Significant weight savings, reliability and life of SEMs demonstrated Large potential market for space, aircraft and helicopter uses	BFGoodrich/Super-Temp/USA BFGoodrich Aerospace/USA
1992	Space antenna-reflector panels fabricated with polished and coated graphite foil bonded to substrate CCC	Very smooth surface CCC created for space antenna-reflector applications	Jet Propulsion Laboratory/California Institute of Technology/USA

TABLE 54 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR SPACECRAFT VEHICLE APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1992	Coated CCC insulative/impact-resistant shield developed for protection of space defense assets	Low-density CCC shield ground-validated for protection against hypervelocity particles, x-ray radiation, and laser energy	Martin Marietta Space Systems/USA
1992	Lightweight CCC bonded, brazed, and bolted tube-to-node, tube-to-tube, and tube-to-clevis joints designed	Lightweight attachment and joining approaches devised for spacecraft composites	Materials Sciences Corporation/USA
1993	Germanium-imbued CCC materials developed for lightweight, phase-change solar power structures	New materials approach for heat-storage elements of a solar dynamic power system Materials appear promising for use aboard an earth-orbiting space station	Foster-Miller, Inc./USA
1993	Very large (32 ft. x 10 ft.) 2-D CCC space structure fabricated and assembled	First prototype radiation-hardened solar array structure for space applications	Martin Marietta Space Systems/USA

space parts were fabricated in support of (a) structural, (b) antenna, and (c) radiator prototypes. All of the basic space structural configurations were fabricated and component properties measured. A lot of attention was paid to joining and attachment of these CCC parts to adjacent metallic parts. Flat panels for spacecraft radiators were also fabricated during the late 1980s. CCC facesheets were shown to be more thermally efficient than conventional aluminum sheets. Fewer heat pipes were needed to dissipate the electronic waste heat, design was simplified, costs were reduced, and lifetime expectancies were increased. CCC materials seemed to come of age for both defense and commercial space radiator applications.

4.8.12.10.2 *The 1990s*

CCC materials continued to be attractive for Star War components because of their intrinsically survivable features. Space structural components and radiators of increased complexity and sizes were also fabricated. Large fixed and deployable truss structures were designed, fabricated, and laboratory tested. Several mechanical and chemical attachment methods were developed to obtain lightweight joints with other CCC or metallic units. The largest space-survivable structure fabricated to date was for a solar array. This lightweight CCC structure had external dimensions of 10.5 m by 3.3 m (32 ft by 10 ft). In spite of the many impressive structural elements fabricated and tested for potential space applications, it is expected that few if any will be used in the near future. CCC structures are not competitive with other metallic or organic-matrix composites for conventional space structures. Their militarily-survivable features will be become of lesser importance as Star Wars possibilities fade in the future.

CCC prototypes for space thermal management appear to have greater importance and a more lasting feature. Double-sided CCC radiators were designed, fabricated, and demonstrated to be quite superior to conventional space radiators. Large performance and weight savings have been demonstrated. It appears that this technology will be further refined for future defense and commercial applications. Another thermal management application of great importance is thermal planes (heat sinks) in standard electronic modules. With further reduction in the cost of high-thermal conductivity CCC materials, it is expected that usage will greatly increase for both space and aeronautical electronic packaging.

Lastly, CCC materials have been successfully prototyped for very low thrust, space ion engines. Thin and flat CCC grids with many EDM drilled holes were fabricated and shown to be greatly superior to conventional molybdenum grids. While this

application is not high volume, it nevertheless illustrates another way of solving a critical component problem with one of the many available CCC materials.

4.8.13 Nuclear Components

Space power reactors and defense componentry are or may be exposed to nuclear radiation. CCC materials are highly resistant to these environmental conditions, and hence they are viable engineering materials for such applications.

CCC materials have many inherent properties that lend themselves to uses in nuclear radiation environments. These desirable attributes include: (a) low atomic number (Z) for high transmission of high-energy x-rays, (b) high thermal stability to withstand very high radiation-induced temperatures, (c) excellent thermal shock resistance to accommodate steep temperature gradients due to energy deposition, (d) efficient crush-up and attenuation of blow-off impulse stresses, (e) high resistance to neutron radiation, (f) erosion resistance to plasma sputtering, (g) high thermal dissipation especially in the plane of the reinforcing fibers, (h) high dimensional stability based on low thermal expansion coefficients in all three principal directions, (i) high strength and stiffness at room-to-elevated temperatures, (j) low outgassing in vacuum and at high temperatures, (k) reduced sputtering erosion with the addition of ingredients such as boron to carbon materials, and (l) possibly other systems-related properties and characteristics.

The uses of CCC materials in nuclear applications are restricted by three considerations. Neutron irradiation in fission reactors has revealed that carbon/graphite fibers decrease in length and expand in diameter. 2-D CCC materials exhibit similar effects depending upon the specific material and processing history. Multidirectional-reinforced CCC materials exhibit better isotropy. Dimensional changes during irradiation are undesirable, since they produce additional stresses on any brazed interfaces between a carbon material and a metallic heat sink. Other effects of neutron irradiation on CCC thermal properties are presently being assessed. The second material limitation involves creep at high temperatures. This property can be somewhat controlled, however, by proper composite design and choice of constituents. The third limitation pertains to high material costs. Ultrahigh-purity CCC materials are much more expensive than nuclear-grade graphites, but they seem to be competitive with compression annealed pyrolytic graphite. One should note, however, that essentially all CCC materials tested have been developed for other purposes. With devoted materials development it is expected that the proper balance of composite properties will be obtained, and nuclear-grade CCC materials will become the material of choice in various components of fusion reactors.

4.8.13.1 Radioisotope Thermoelectric Generators

Satellites and spacecraft require a reliable source of electrical power to run various subsystems. With few exceptions, the power systems for U.S. satellites have used photovoltaic generation for power, batteries for energy storage, and a host of electrical equipment for appropriate regulation, conversion, and distribution. Present spacecraft fly power systems from tens of watts to several kilowatts. The weight of current spacecraft power systems ranges from 15-25 percent of the total spacecraft mass. These mass fractions may even increase further as future space systems require significantly greater power. Dramatic improvements in design, materials, and energy conversion are required to meet future space power needs.

Nuclear power sources have been used to generate electricity for spacecraft. Nuclear reactors convert the heat from fissioning of uranium-238 into electricity through static (thermoelectric elements) or dynamic (rotary shaft) subsystems. Nuclear reactors offer the possibility of electrical power in the hundreds of kilowatts-to-megawatts. Space nuclear power reactors have only been used once by the U.S. (500 W SNAP-10A system). The reactor was placed in a near-circular polar orbit in 1965, performed successfully for 43 days, and then was shut down by a spacecraft voltage regulator failure. On the other hand the former USSR routinely used space nuclear reactors for power generation. After a USSR space power reactor impacted and contaminated Canadian soil, world pressure emphasized the need for a safer space power system.

Radioisotope thermoelectric generators (RTGs) are space power sources that have (a) powered, or augmented solar power on, a few planetary missions and probes, (b) powered lunar instruments left on the moon by U.S. Apollo missions, and (c) augmented the solar array battery power system on at least one Earth-orbiting spacecraft. RTGs are best known for providing power to spacecraft on their epic journeys to the outer solar systems where sunlight is too feeble for solar cells to be effective. Missions requiring RTGs include (a) the European Ulysses probe which will circle the sun in polar orbit, (b) Galileo which has orbited Jupiter, (c) Cassini which will orbit Saturn, and (d) possibly others like the Pluto Fast Fly-By.

The development of RTG power systems began in 1956, and the first use in space was in 1961 at a power level of 2.7 W. By 1969 the RTG power level had been boosted to 56 W with a one-year design lifetime. Two 15 W radioisotope heater units (RHUs) provided heat for the U.S. Apollo scientific experiment package left on the moon in 1969. Subsequent Apollo missions carried a SNAP-27 RTG which provided at least 63 W of electrical

power and kept the man-made lunar instruments operational for many years. Between 1961 and 1981, 22 space systems were powered by RTGs. Each mission used from one to three RTGs to satisfy their electrical power requirements. By the early 1990's the RTG's performance and lifetime had been greatly increased by the use of new designs and materials. Power levels were increased over 100 times and approached 300 W. In general, the advantages of RTGs are (a) simplicity, (b) high reliability with no moving parts, (c) high resistance to space and planetary atmospheres, (d) self-sufficient, and (e) extremely high reliability.

An RTG is a thermal-to-electric converter device that consists of (a) an outer case, (b) thermoelectric elements, and (c) a gas management system. Electrical power is generated by decay of radioactive plutonium-238 with the emission of alpha particles (helium nuclei), and these particles are self-absorbed in the heat source to produce thermal energy. Present designs use many hundreds of thermocouples to convert decay heat from the fuel directly into electrical energy. Since the 1960s RTGs have used thermoelectric materials of the telluride and silicon germanium alloys classes. These generators yielded efficiencies in the 5-7 percent range and a specific power of about 2.2-4.4 W/kg (1-2 W/lb). Subsequently selenide elements were developed with thermoelectric efficiencies over 13 percent and specific power levels of about 8.8 W/kg (4 W/lb). The cost of space power generation also decreased to U.S. $11,000/kg ($5,000/lb) per W.

Figure 31 is a diagram of an RTG used to power the U.S. Apollo lunar geophysical station in 1969. The RTG outer protective heatshield shell and end caps were originally composed of polycrystalline graphite to accommodate high service temperatures during operation or possible aborted mission. The graphite shells were brittle, subject to thermostructural failure during reentry heating, and had poor impact characteristics. With the advent of CCC materials in the 1960s, a new heatshield material became available and was substituted for the previously-used graphite. The 2-D CCC material was manufactured by the following method. Low-modulus (rayon-based) carbon fabric was impregnated with phenolic resin, and the prepreg cloth laid in an involute pattern about 6-9° to the tangent of the barrel-shaped cylinder. After molding and carbonizing the composite, it was heat treated to about 2327°C (4221°F) and then CVI infiltrated with pyrolytic carbon to densify the outer layers to about 1.5 g/cm^3 (0.054 lb/in^3). The center of the 2-D CCC material remained at a density of about 1.3 g/cm^3 (0.047 lb/in^3). The lower elastic modulus of the lower density material contributed to a reduction in thermal stresses. Mechanical properties of the CCC container material were low by today's standards. The tensile strength was approximately 90 MPa (13.1 ksi) in the axial direction, 30 MPa (4.35 ksi) in the circumferential direction, and 6 MPa (0.87 ksi)

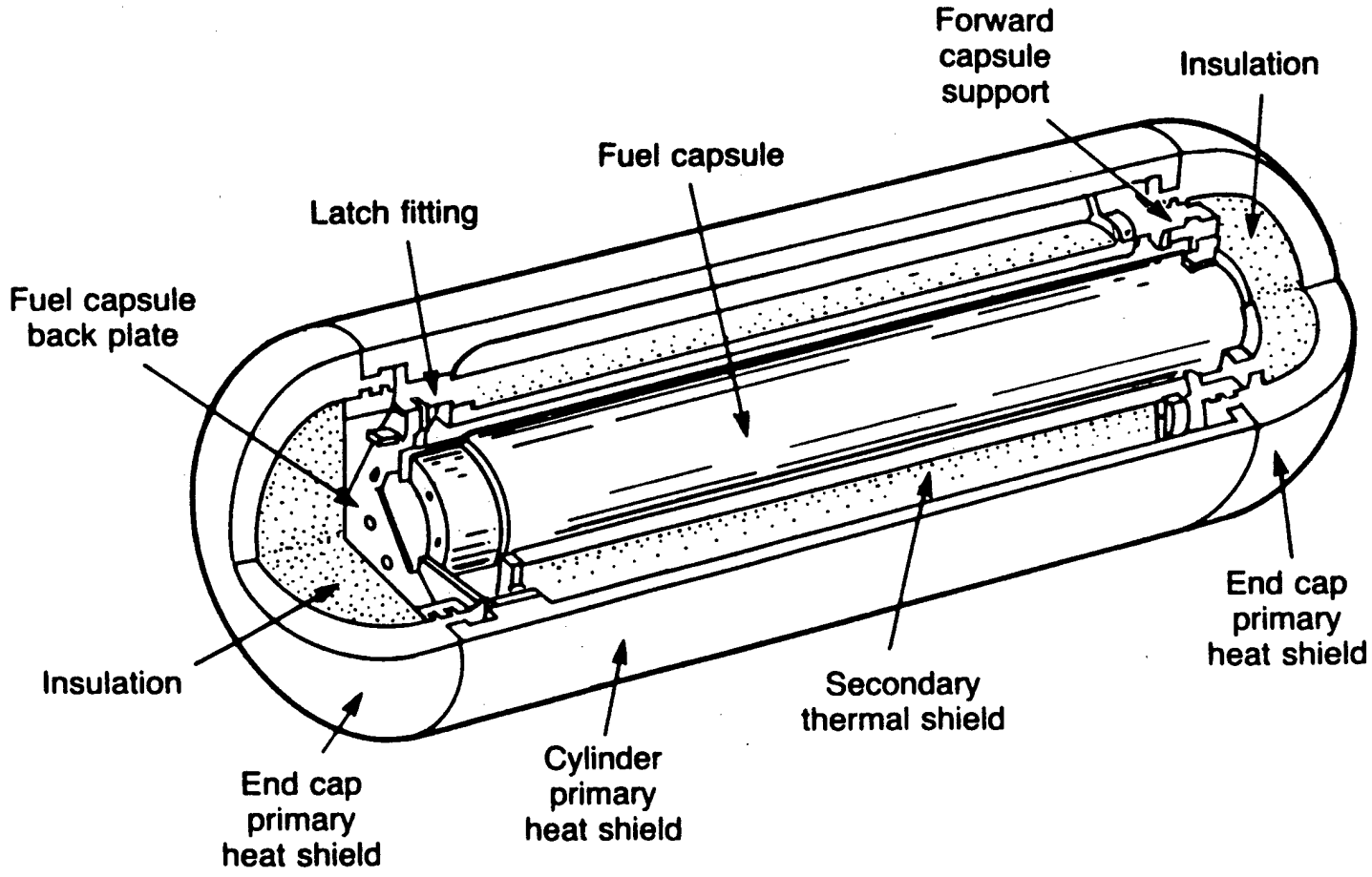


Figure 31. Diagram of a Radioactive Power Source Used on the Lunar Surface.

in the through-the-thickness direction. Nevertheless, the radioactive fuel container had adequate structural properties and much better resistance to crack propagation. During the aborted Apollo 13 mission, the CCC-protected power generator successfully survived the ablation and thermal stress during reentry to the south Pacific Ocean. The CCC-protective shell thus worked as intended.

The latest generation of RTGs is known as General Purpose Heat Source Radioisotope Thermoelectric Generators (GPHS RTGs). These generators consisted of a GPHS and a thermoelectric converter.

Figure 32 is a diagram of an RTG. The generator was fueled with radioactive plutonium-238 dioxide, weighed about 55.5 kg (122 lb), had a temperature of about 160°C (320°F), was pressurized with argon to keep oxidizing species away from the components, provided a minimum of 290 W of electrical (e) power, had a specific power of about 5.14 We/kg (2.34 We/lb), and a thermal-to-electrical efficiency of about 6.8 percent. One RTG contains 18 individual GPHS module. Each GPHS module contains one aeroshell of 3-D FW CCC material and two graphite impact shells (GISs). Each GIS contains two fueled clads. Each fueled clad contains one iridium shell and one plutonium fuel pellet. Hence the total components in each RTG involve (a) 18 GPHSs, (b) 36 GISs, (c) 72 fueled clads, and (d) 72 fuel pellets. At initial assembly the RTG had a thermal power of about 4.2 kW.

The radioactive plutonium-238 fuel must be immobilized to the maximum extent possible on all mission phases including (a) ground handling, (b) transportation, (c) launch, (d) ascent, and (e) orbit or planetary station. The fuel is contained in a ductile refractory metal cladding which can stretch appreciably without rupturing in the event of impact with a rigid target. Within the RTG low-density carbon-bonded carbon fiber is used as both an insulator and an energy impact absorber. Externally, each GIS is a container of 3-D FW pierced fabric CCC for both thermal and impact purposes. For added safety each GIS is designed to separate into individual modules should an accidental reentry occur.

4.8.13.2 Radioisotope Heater Units

Interplanetary probes, such as Galileo, experience exceptionally low environmental temperatures. These temperatures can adversely affect various systems on the spacecraft and probe. Auxiliary heat is thus needed in increments of 1 watt (thermal) to areas needing thermal input. The heater unit thus reduces the spacecraft electrical energy drain.

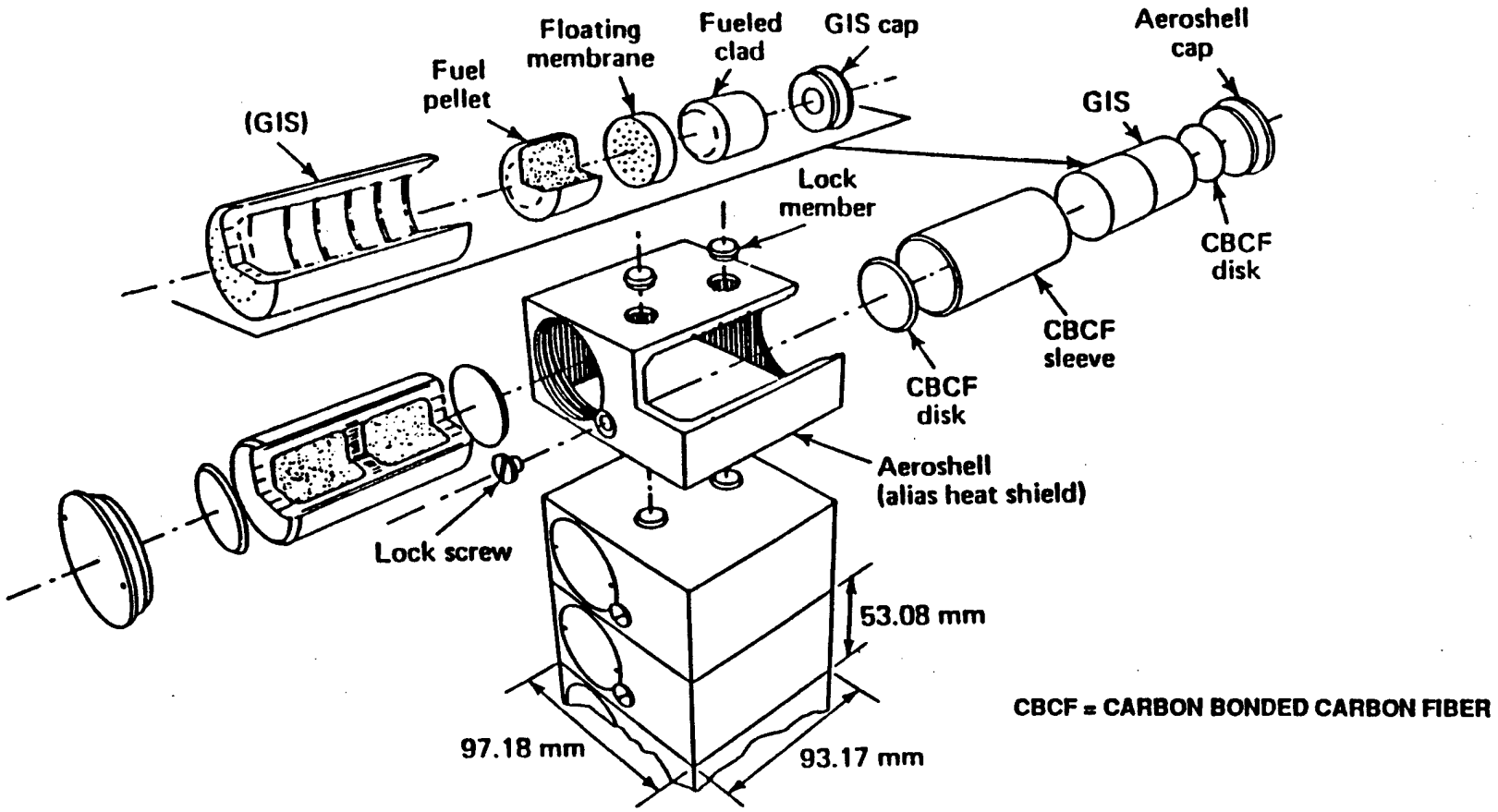


Figure 32. Schematic of a Radioisotope Thermoelectric Generator (RTG).

Lightweight radioisotope heater units (LWRHUs) have been developed for low-level, secondary energy sources. The LWRHU is a radioisotope-fueled system consisting of (a) plutonium-238 dioxide fuel, (b) a clad of platinum-30 percent rhodium, (c) a pyrolytic graphite insulation system, and (d) an aeroshell/impact structure of 3-D FW CCC material. Each LWRHU weighs about 40 gm (1.4 oz) and has exterior dimensions of about 26 mm (1.0 in). Figure 33 is a diagram of a low thermally-powered heater unit.

4.8.13.3 Thermonuclear Fusion Power Reactor Components

Thermonuclear fusion is an energy-releasing rearrangement collision which can occur between various isotopes of low atomic number but at very high temperatures. The fusion reactants exist in the form of very hot ionized gas of stripped nuclei and free electrons (plasma). The agitation energy of the nuclei can overcome their mutual repulsion under these conditions and cause reactions to occur. This is the mechanism of (a) fusion power reactors, (b) fusion bombs, and (c) energy generation in stars. Current interest in this technology arises from the expectation that it may someday be used to produce vast quantities of power for the ever-increasing industrialized nations. The self-sustaining fusion reaction of primary interest involves the union of the hydrogen isotopes deuterium (D) and tritium (T) to form helium and the release of energy and neutrons. Since the primary fusion fuel occurs naturally and is obtainable in an unlimited supply, fusion power could permanently solve the international energy problem or rapid depletion of fossil fuels.

Current fusion reactors are of the Tokamak designs. The promise of Tokamak fusion reactor was first demonstrated about 1968, and since that time great progress has been achieved. In the current generation of practical fusion reactors, the natural ohmic heating mechanism of Tokamaks has been supplemented by various high-powered auxiliary heating techniques like injection of beams of energetic neutral atoms and the excitation of certain plasma waves that are strongly absorbed at characteristic frequencies. Large Tokamaks have driven plasma-current pulses lasting tens of seconds, and future reactors are expected to have hour-long burn pulses. The ultimate objective, of course, is to have steady-state reactor operation.

The potential uses of CCC materials in fusion power reactors is rather exciting from both a humanitarian and engineering viewpoint. CCC materials were originally exploited for their military uses in nuclear weapon delivery systems (missile nosetips and nozzles). Now, the materials offer new possibilities for assisting in the creation of low-cost power to be used for the benefit of all mankind.

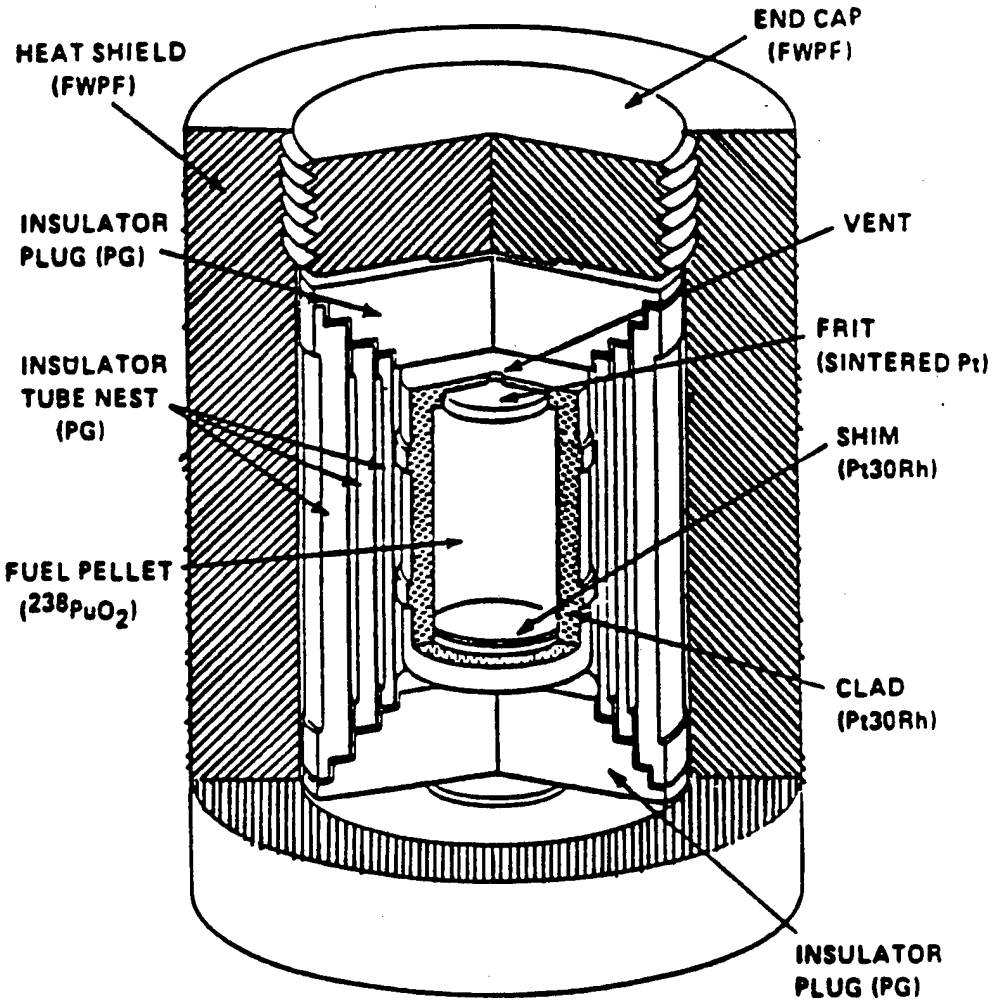


Figure 33. Diagram of a Lightweight Radioisotope Heater Unit (LWRHU).

Advanced Tokomak fusion reactors burning plasma will create ultrahigh temperatures which may approach 200 million °C (360 million °F). Magnetic confinement of the hot plasma keeps it away from the vacuum vessel surfaces. Plasma disruptions or plasma instabilities during off-controlled conditions permit the plasma-facing components to be exposed to intense nominal heat and energetic particle fluxes (charged and neutral particles, neutrons, etc.). For magnetically-confined plasma, these heat fluxes are concentrated on the container diverter and limiter plates. Typical heat flux levels for next-generation international thermonuclear experimental reactor (ITER), for example, will be about 0.1-0.6 MW/m^2 (8.8-53 $Btu/ft^2 \cdot s$) at the limiter and approximately 0.6-30 MW/m^2 (53-2640 $Btu/ft^2 \cdot s$) at the diverter. Because the ITER is an ignition machine, it will produce substantial neutron fluences from the D,T fusion reaction. Peak particle fluxes may be up to $3x10^{23}$ D,T $ions/m^2$ ($3.2x10^{24}$ D,T $ions/ft^2$). The vessel walls have to withstand these fluxes during the plasma operating time without losing their integrity or excessively contaminating or destroying the fusion plasma. Current fusion reactor designs and materials indicate that the net erosion rates of plasma facing components may be on the order of 10 cm (3.9 in) per burn year which may be acceptable.

The requirements for vacuum-vessel wall materials are many and complex. The wall material should have a low atomic number (Z) to prevent contamination of the plasma with wall atoms and excessive thinning of the wall plates. The maximum tolerable impurity concentration depends upon the atomic number of the impurities, because energy losses from the plasma by radiation increase proportionally to the contaminant atomic number. High-Z impurities are particularly damaging. The wall materials should be very erosion resistant (low plasma sputtering) to minimize impurities introduced into the plasma by sputtering the vessel walls. The materials must have a very high thermal conductivity in order to quickly remove deposited energy. A very high melting or sublimation point is also desired to maintain material integrity at high temperatures.

Fusion reactors are complex high-temperature energy machines which vary greatly in design, performance, and operation. For illustrative purposes a few details of the Japanese Atomic Energy Research Institute J-60 Tokamak will be given. The machine has a doughnut shape and a rather small internal volume of 60 m^3 (2119 ft^3). The fusion reactor is intended to produce superheated plasmas by burning deuterium and tritium. Plasma temperatures are expected to be in the range of 10 keV (100 million °C, 180 million °F). Hydrogen within the interior is heated by a microwave system and 14 neutral beam injectors to form helium with an attendant release of thermal energy. Circular webs of coils produce huge magnetic fields to confine the hot plasma with the Tokamak ring and keep the plasma away from the inside surface

of the ring. Figure 34 is a schematic of the major plasma facing components in a Tokamak fusion device.

First-generation fusion reactors effectively utilized metallic materials (stainless steel, nickel-based alloys, or refractory metals) in the first stage. However, higher-performance fusion machines dictated the need for higher plasma temperatures in the range of 100 million °C (180 million °F). The approach taken was to use low atomic number (Z) materials for plasma-facing walls and thereby permit a cleaner, less metal-contaminated plasma. The plasma-facing materials should have a high resistance to thermally-induced stresses which may be caused by arcing. A large thermal shock resistance is also a necessity to accommodate pulsed plasma operations. Mechanical properties of the reactor materials should be adequate to withstand electromagnetic forces in plasma disruptions. Only small and tolerable changes in material thermophysical properties are permitted during exposure to large fluxes of 14 MeV fusion neutrons as well as lower energy neutrons. The vessel wall material should have a minimum of adsorbed water and oxide layers to lower the major impurity (oxygen) in today's plasma. The vessel wall material should also have good hydrogen recycling behavior. In other words it should not permanently trap the incident hydrogen ions which will enable better control of the plasma density. The wall tiles should be fabricable into large components of complex design. They should also be replaceable using remote maintenance equipment.

Current prospects are very attractive for using CCC materials in the wall lining, diverter, and limiter of fusion reactors. The materials offer (a) special physical properties like toughness and high strength, (b) unique thermophysical properties like high thermal conductivity along the fiber axis, (c) highly tailorable properties through composite design, and (d) fabricable in complex and thick configurations. Mesophase pitch carbon fibers and mesophase pitch-based carbon matrix, both containing highly-graphitic structures, enabled the fabrication of CCC composites having a thermal conductivity value of about 400 W/m·K (231 Btu/h·ft·°F) at room temperature and in the through-the-thickness (Z) direction. This composite thermal conductivity exceeded that of all other composite materials, and it was about four times better than fine-grained graphites. Even at 1400°C (2552°F), the CCC Z-direction thermal conductivity was about 140 W/m·K (80.9 Btu/h·ft·°F). Most applications have focused on 3-D and 4-D CCC materials because of their balance of properties. Such CCCs contain up to 50 volume percent of fibers, but only a fraction of the fibers can be oriented perpendicular to the heat flux for maximum internal heat transfer. An orthogonal 3-D CCC, for example, contained about 33 volume percent of mesophase, pitch-based carbon fibers in the Z-direction, and about five volume percent of structural PAN-based carbon fibers in each of the X- and Y-directions. Hence the proper choice

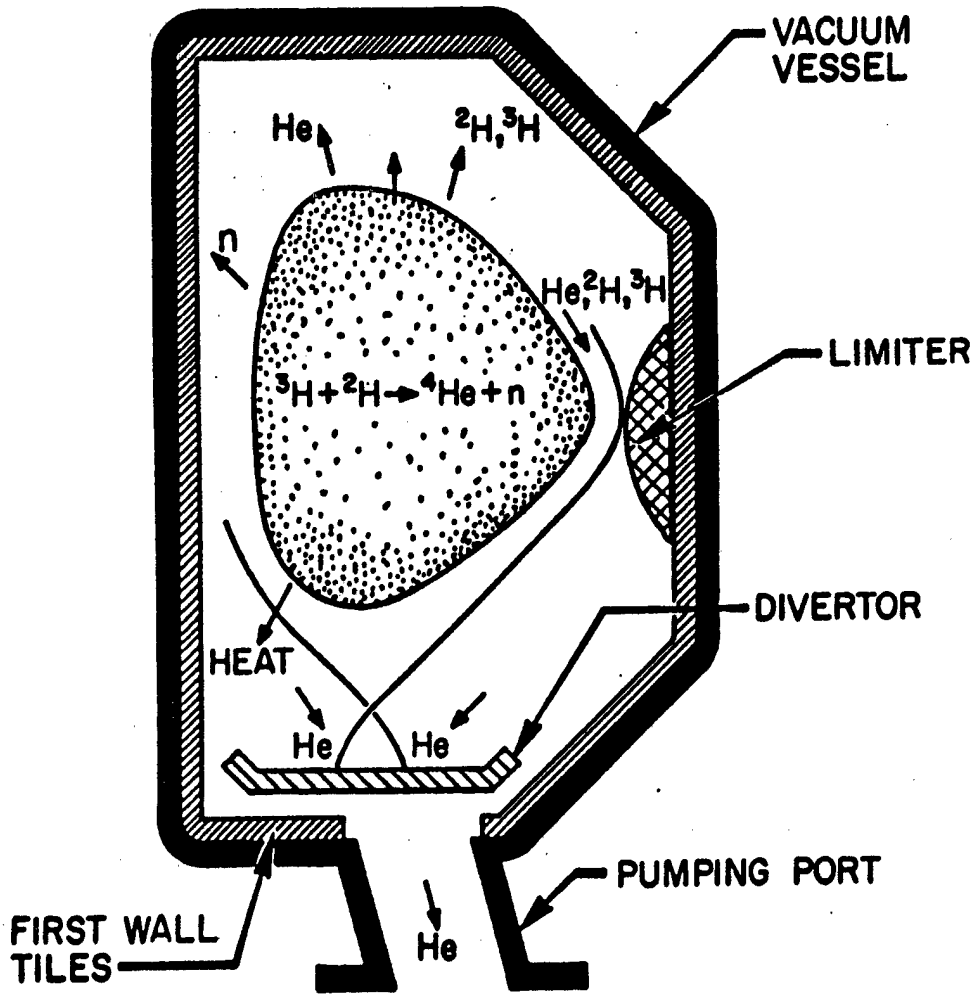


Figure 34. Schematic of Major Plasma-Facing Components in a Tokamak Fusion Machine.

of fiber type, orientation, and volume in any given composite direction will provide a wide range of thermal, thermophysical, and mechanical properties. Like polycrystalline graphites, the n-D CCCs also have equivalent densities and high purities.

While CCC materials have gained much interest for the design of fusion reactors, they have certain limitations. At high temperatures CCC materials (like graphite) exhibit enhanced erosion yield due to particle impact. Around 527°C (981°F), incident hydrogen ions react chemically with carbon atoms and a volatile hydrocarbon is formed. Above 927°C (1700°F), radiation-enhanced sublimation occurs in which incident ions cause the release of thermal carbon atoms in an erosion process. Another problem with CCC wall materials is that composite design limits the volume of fibers which can be placed perpendicular to the wall surface to enable maximum through-the-thickness heat transfer. At least five volume percent of fibers must be placed in both the X- and Y-directions in order to maintain adequate composite properties and insure fabricability of the part. Another concern involves material damage by radiation. Radiation damage causes the graphite crystal to expand in the c-direction and contract in the a- and b-directions with essentially no change in volume. Composite thermal conductivity is decreased at low neutron doses below one displacement per atom (dpa). Structural properties like strength and Young's modulus are also degraded by energetic fission neutron fluences (below 1 dpa). CCC materials also experience transmutational neutron effects, but the magnitude is relatively unknown because fission-reactor experiments are unsuitable to study these effects. To minimize radiation damage both the carbon fibers and matrix should be highly graphitic and ultra-pure in composition. To summarize, the major materials selection criterion for plasma-facing components will likely be neutron radiation damage, composite thermal conductivity and dimensional change.

First-generation fusion machines used fine-grained or reactor-grade graphites for the plasma-facing components. For example early experimental Tokamaks utilized graphite in their first-wall armor and plasma limiters. Later graphitic materials were replaced with CCC materials and pyrocarbons. The latter materials had only been used sparingly for such components as the leading edges or deflection plates of pump limiters. More extensive applications of CCC materials are being made in current Tokamak fusion machines like the (a) Tokamak fusion test reactor (TFTR) and DIIID in the USA, (b) joint European Torus (JET), Tore Supra and TEXTOR in Europe, and (c) JT-60U in Japan. For example the U.S. TFTR using ion cyclotron radio frequency heating contained CCC materials in the RF limiters. CCC materials were chosen because they permitted the design of a self-supporting tile with no backing plate. The use of CCC is also ideal for pumped limiter designs. Lower limiter costs are

anticipated provided larger self-supporting tiles can be fabricated. Without the conventional metallic backing plate, there are very small disruption-induced eddy current forces.

Next-generation plasma fusion reactors, like the ITER and the burning plasma experiment (BPX), will require a new generation of advanced CCC materials having extremely high thermal conductivity to manage severe heat loads. However at present the ITER considers compression-annealed pyrolytic graphite as the reference material for the diverter, and CCC as the alternative. CCC materials, however, are the baseline for the first-wall, plasma-facing armor.

4.8.13.4 X-ray Shields

Carbon has a low atomic number and thus is relatively transparent to high-energy x-rays. CCC materials have similar characteristics depending upon their purity level. CCC materials are also highly resistant to low-energy x-rays. Energy deposited on the surface and in the surface region of the material is converted to thermal energy. If the energy density is of sufficient magnitude, carbon will be explosively vaporized. This situation induces a tensile stress in the residual CCC material, and due to its porosity (voids and cracks), the material crushes to a smaller volume and attenuates the induced stress. CCC materials containing high atomic number compounds are capable of absorbing x-rays over a very wide spectrum. X-ray energy deposited in high atomic number compounds is instantaneously converted to thermal energy, and the local temperature of CCC is increased as energy leaks from the absorber to the adjacent carbonaceous material. A large amount of heat can be absorbed by the CCC material due to its high heat capacity and high thermal stability, thus enabling subsequent energy dissipation by conduction, radiation, and possibly convection.

X-ray absorbing CCC shields have been developed, evaluated, and are being used in service. Few material compositions and performance features have been disclosed in the open technical literature.

4.8.13.5 Fission Power Reactor Heat Exchanger Tubes

Gas-cooled, high-temperature reactors (HTRs) offer many advantages compared to other power reactor types, such as high thermal efficiency due to the high coolant (helium) temperature. A smaller proportion of waste heat is generated which in turn means less thermal pollution, reduced cooling water requirements, and larger inherent safety margins. CCC materials have been fabricated and evaluated for the liner of high-temperature nuclear reactors gas ducting. Small-to-very-large size hollow tubes were successfully filament wound and fabricated.

Standard tube sizes had a maximum wall thickness of about 20 mm (0.79 in), a maximum outer diameter of 950 mm (3.1 ft), and a maximum length of about 1000-2000 mm (3.3-6.6 ft). Even larger sizes were also produced with a maximum wall thickness of 50 mm (1.97 in), a maximum outer diameter of 2000 mm (6.6 ft), and a maximum length of 3500 mm (11.5 ft). Multiple-part CCC support rings with a diameter of 700 mm (2.3 ft) were successfully tested for carrying and connecting hot gas pipes. CCC rings were subjected to a working pressure of 43 bar (624 psi) and to a sudden pressure drop to 20 bars (290 psi) at 1000°C (1832°F). Additional evaluations are continuing on the effects of high acoustical noise levels (170 db), contaminants like water vapor, and strength reduction with service life.

4.8.13.6 Nuclear Rocket Fuel Elements

During the early 1970s the NERVA nuclear rocket engine was of great technical importance. This nuclear rocket engine was intended to be powered by a high-power-density reactor that operated at an impressive temperature level of about 2087°C (3790°F). The propellant was hot hydrogen which, at the operating temperature, could form hydrocarbons like methane and other products. A 285 cm (112 in) diameter exit cone for this nuclear rocket motor was baselined with 2-D CCC materials, coated if necessary for oxidation protection. Unfortunately the nuclear-powered rocket engine program was cancelled prior to building the first demonstration article. Work conducted up to this point in time indicated that structural CCC exit cones would be suitable in large diameter exit cones for such nuclear reactors.

4.8.13.7 Space Nuclear Thermal Propulsion Components

Maximum specific impulse (ISP) and thrust-to-weight ratio are keys to the development of practical, high-performance nuclear rockets. The turbopump, which is a necessary component of the engine, is designed to pump pressurized liquid hydrogen propellant to the reactor inlet. The propellant is rapidly heated to thousands of degrees Fahrenheit in a particle-bed reactor and then exhausted and expanded through a high-temperature nozzle to provide propulsive thrust. The goal is to establish an ISP of 1000 s and a thrust-to-weight ratio of up to 35:1 unshielded. A design concept for a high-performance engine has been developed which is based on the use of an uncooled CCC nozzle and duct turbine inlet. Figure 35 is a schematic of CCC materials for different locations of the nozzle. It is noted that extensive use has been made of CCC materials in the hot sections including (a) structural parts, (b) turbine nozzles and stators, and (c) turbine rotors.

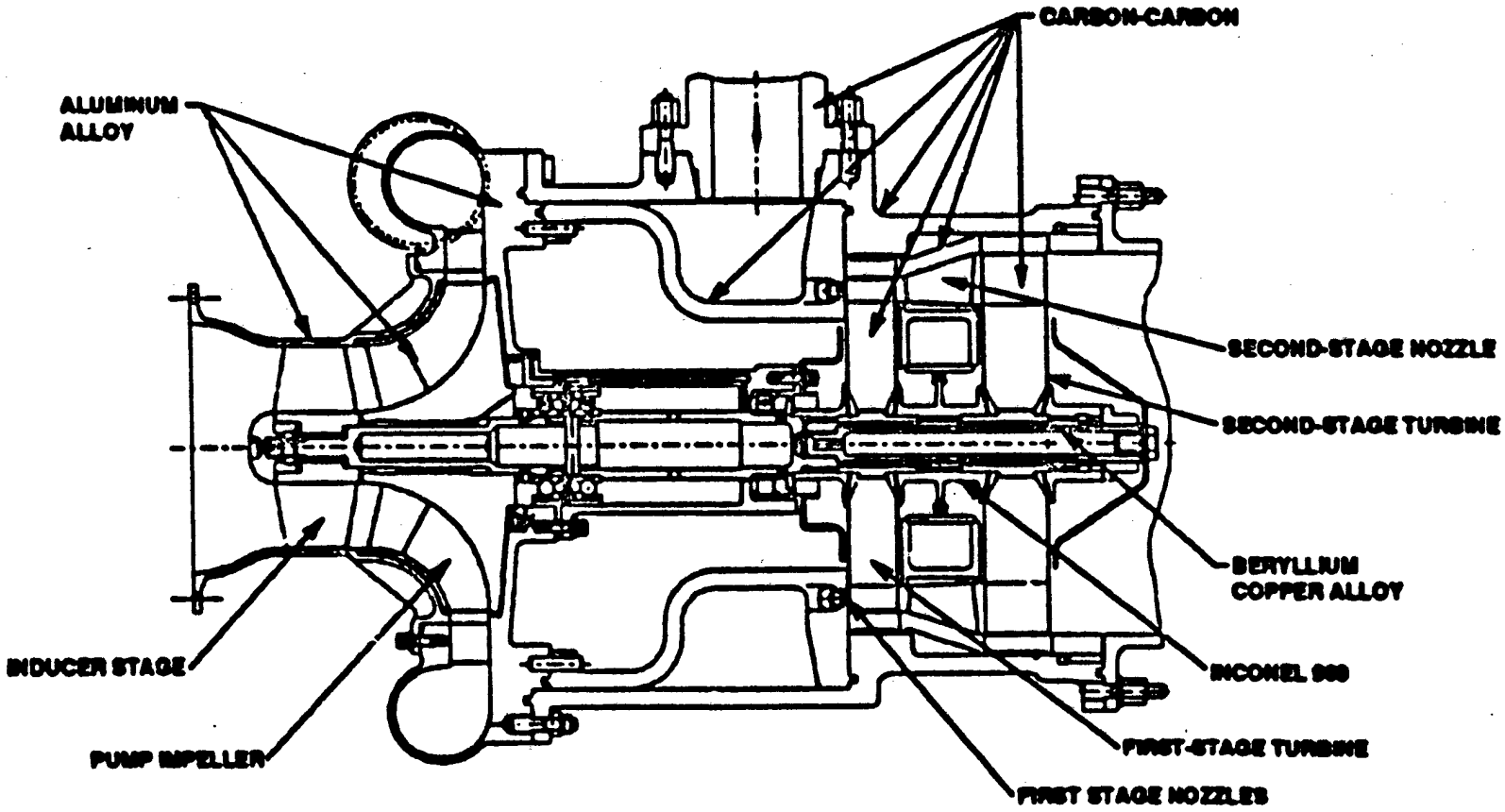


Figure 35. Schematic of an Advanced Turbopump Concept for a Space Nuclear Thermal Propulsion System.

4.8.13.8 Chronology

CCC materials have replaced nuclear-grade graphites in a number of specific applications, but the uses to date have been limited. Eight different prototypes have been fabricated and tested. Some of these articles have reached operational status while others remain promising for future uses. Table 55 lists the various CCC prototypes fabricated by various government or industrial agencies. Table 56 contains a more detailed chronology of CCC materials for nuclear applications.

4.8.13.8.1 *The 1960s*

Accommodating the destructive effects of nuclear weapons became a major technological problem in the 1960s due to a great proliferation of these weapons by certain highly-industrialized nations. Materials approaches were thus sought to withstand intense x-rays and blast effects. The element carbon in its many forms offered potential solutions. Nuclear-grade and aerospace-grade polycrystalline graphites, in combination with other refractory compounds, often provided interim solutions, but lighter-weight and stronger materials were needed for aerospace systems. CCC materials appeared to offer great potential. Specially-formulated CCC materials were formulated, fabricated into useful shielding configurations, and successfully evaluated in both ground-based and underground nuclear events. Nuclear-grade CCC materials were demonstrated to be effective x-ray energy absorbers, convert the incident energy to thermal energy, and then dissipate the energy through conductive and radiative modes. Additional material and performance details have not been published in the open technical literature.

4.8.13.8.2 *The 1970s*

By the early 1970s CCC materials properties and quality had reached a state where additional uses could be contemplated in the nuclear application area. Nuclear power sources were designed for use in deep space exploration, but due to the concern of an accidental aborted mission and Earth reentry, efforts were focused on safer power systems. Radioisotope thermoelectric generators were developed and encased in an outer heatshield of nuclear-grade graphite. While this material worked satisfactorily, CCC materials were found to provide greater strength and acceptable ablation-insulative characteristics. To enable even greater isolation of the plutonium-238, the fuel elements were enclosed in a thin shell of porous CCC material. During high-speed impact these protective shells absorbed a great amount of impact energy and assisted in limiting fuel fracture and dispersion.

TABLE 55
FIRST CCC PROTOTYPES FOR NUCLEAR APPLICATIONS

YEAR	PROTOTYPE	ORGANIZATION
1968	Shipping cask for space power generator	HITCO Inc./USA
1970	Impact shells for radioisotope fuel capsules	HITCO Inc./USA
1977	Thermal protection canister for radioisotope thermoelectric power source	Teledyne Corporation/USA
1985	Heat exchanger tubes	Sigri Electrographit GmbH/GERMANY
1987/88	Plasma-facing limiter, diverter, and wall components for fusion power reactor	BFGoodrich Aerospace/Super-Temp/USA Japan Atomic Energy Research Institute/JAPAN Fiber Materials, Inc. (FMI)/USA Princeton TFTR/USA Showa Denko KK & Others/JAPAN
1991	Turbopump components for space nuclear propulsion	Oak Ridge National Laboratory/USA
1993	Control rods for nuclear fusion power reactor	GA Technologies, Inc./USA
1993	Anti-extrusion ring for valves of nuclear power plants	Allied-Signal Fluid Systems/USA

TABLE 56

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR NUCLEAR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1967	X-ray-absorbing particles uniformly dispersed in 2-D CCC materials	Lightweight x-ray shields demonstrated for aerospace systems Efficient shielding approach to accommodate destructive effects of nuclear weapons x-rays	LTV Aerospace Corporation/USA
1968	2-D CCC container developed for radioisotope thermoelectric power generator	First prototype CCC flight shipping cask for SNAP-27 space power source Reliable energy source for Apollo lunar surface equipment package	HITCO/USA
1970	CCC exit cone designed and fabrication facility built for the U.S. NERVA space propulsion system	CCC identified as the baseline exit cone for hot hydrogen nuclear propulsion system Nuclear propulsion system program was cancelled prior to fabricating exit cone	Aerojet-General Corporation/USA
1977	CCC aeroshell designed and fabricated for a high-power satellite thermoelectric generator	Prototype CCC container for high-temperature radioactive materials	Teledyne Corporation/USA
1979	Prospects of using CCC materials in nuclear power engineering discussed in published article	Pure CCC could possibly replace nuclear-grade graphites in structural nuclear applications	State Research Institute of Graphite/ RUSSIA
1985	CCC heat exchanger tubes fabricated for nuclear power systems	First prototype, high-temperature CCC heat exchanger tubes for helium-cooled nuclear reactor	Sigri Elektrographit GmbH/GERMANY
1987	CCC plasma limiters (first wall) fabricated for Princeton Tokamac fusion power reactor	First full-scale prototype CCC parts for an advanced nuclear fusion power plant Ultrahigh thermal stability and high thermal conductivity of CCC advantageously utilized	BFGoodrich Aerospace/Super-Temp/USA

TABLE 56 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR NUCLEAR APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1988	Design of RF limiter CCC material	Significant application of CCC to nondefense usage	Materials Sciences Corporation/USA BFGoodrich Aerospace/Super-Temp/USA Princeton University/USA
1988/89	CCC plasma-facing components fabricated and tested in Japan, USA, and European fusion reactors	Various CCC materials survived intense heating and neutron irradiation in a fusion reactor Fine-grained graphites exhibited cracking and damage during similar exposures in a fusion reactor CCC materials are excellent candidates for plasma-facing components of high-power nuclear fusion reactors	Showa Denko KK & Others (CCC Materials)/JAPAN BFGoodrich Aerospace (CCC Materials)/USA Japan Atomic Energy Research Institute (Reactor Tests)/JAPAN Princeton TFTR (Reactor Tests)/USA
1988	3-D FW CCC used for the aeroshell/impact structure of U.S. NASA deep space radioisotope power generators	3-D FW CCC enhanced the reliability and safety associated with the use of radioisotope power sources	Textron Specialty Materials (Aeroshell Material)/USA
1990	High-density, HIP processed 3-D CCC materials fabricated for testing in a fusion power reactor	3-D orthogonally-reinforced PAN-based or pitch-based carbon fiber/coal tar pitch-based CCC appeared promising for reactor use	Shikibo, Ltd. (3-D Fibrous Preforms)/JAPAN Government Industrial Research Institute of Osaka (Densification)/JAPAN Japan Atomic Energy Research Institute (Testing)/JAPAN
1991	Advanced CCC with high neutron stability fabricated for nuclear fusion power reactors	Tile structures for first wall plasma containment in Tokamak fusion reactors	Nuclear & Aerospace Materials Corp. (NAMCO)/USA

4.8.13.8.3 *The 1980s*

Advanced designs of radioisotope power generators during the 1980s create new opportunities for CCC materials. The aeroshell/impact structure for multi-hundred watt space power systems was constructed of 3-D FW CCCs, replacing earlier baselined 2-D CCC container materials. 3-D FW CCC material was also used for the protective aeroshell of lightweight, low-power radioisotope auxiliary heater units.

CCC materials uses in both fission and fusion power reactors continued on into the 1980s. Gas-cooled, high-temperature fission reactors required a substantial number of gas-ducting and support rings. Filament-wound CCC tubes of greatly varying diameters and lengths were fabricated and tested. The hot gas tubing was found to have many useful characteristics, but much additional material upgrading and evaluations were necessary to satisfy all of the requirements.

The prospects of using CCCs for fusion power reactors began in the mid-1980s. Advanced Tokomak fusion reactors burning hot plasma required improved plasma-facing components. High thermal-conductivity CCC materials were developed, installed in various fusion reactors, and performed successfully. The CCC materials were used for the wall lining, diverter, and limiter components.

4.8.13.8.4 *The 1990s*

Additional 3-D and n-D CCC materials were prototyped in the early 1990s for uses in upgraded fusion reactors. Materials development efforts were devoted to improving (a) resistance to neutron damage, (b) increase through-the-thickness thermal conductivity, and (c) part fabricability.

4.8.14 Industrial Components

Industrial applications for CCC materials have been limited and highly specialized. Typical application outlets have been (a) furnace elements, (b) mechanical fasteners, (c) tooling parts, and (d) others.

The development of industrial CCC parts has been slow for a variety of reasons. Very low-cost carbonaceous constituents have not been developed and commercialized. Secondly, most low-cost processes are either relatively new or in their developmental stage. Thirdly, the substitution design approach has been used instead of the design-to-use concept.

CCC articles have been routinely machined from larger billets and then evaluated as a replacement material for the presently-used carbonaceous, ceramic, or metallic parts. Fourthly, most of the past design efforts have focused on high-performance defense applications, and little attention has been paid to commercial outlets. Fifthly, little design data have been generated on low-cost materials. Lastly, key material:performance:cost tradeoff studies have not been available to quantitatively demonstrate the superiority of CCC materials for certain applications.

Low-density, fibrous carbon insulation is the largest volume CCC material used in the industrial field. This material was originally developed in 1968 for use as a high-temperature insulation in vacuum or inert gas furnaces. The composite material is composed of a fibrous carbon network lightly bonded together with a carbonized organic matrix. The material is presently available from sources in the United States, Scotland, Germany, and other locations.

4.8.14.1 High-Temperature Insulators

Insulation materials for high-temperature applications are required for a variety of industrial, aerospace, and defense uses. Lightweight carbonaceous materials have been developed for inert or vacuum conditions, and they exist in the form of (a) powders, (b) fibers, (c) felts, (d) woven fabrics, (e) multidirectional woven fibrous preforms, (f) foams, (g) honeycombs, (h) exfoliated materials, and (i) carbon composites spanning a great range in densities. Carbon-bonded carbon fiber (CBCF) materials have attracted considerable attention because of their balanced properties compared to other lightweight carbonaceous materials.

CBCF materials belong to the family of carbonaceous composites because they are composed of discontinuous carbon fibers lightly bonded together with a carbonized matrix to form a rigidized shape. The materials were first developed in the United States to meet critical nuclear and aerospace insulation needs. Similar products were later developed and commercialized in other countries. The manufacturing process employed was a vacuum casting operation. The first step was to prepare short, discontinuous-length carbon fibers by either (a) chopping continuous tow in a mill or (b) cutting organic fiber with a flock cutter, blending the fibers and then carbonizing them. The carbon fibers were then mechanically slurried in water, phenolic resin powder added to the water-fiber mix, and then blended to make a homogeneous mixture. The dilute slurry was then vacuum molded into flat, cylindrical, or other shaped configurations. Resin particles were uniformly dispersed throughout the fibers. The slurry contained in a mixing tank was transferred to a molding tank containing perforated mandrels. The solids were deposited onto the mandrel while the water flowed through the mandrel holes. Fibers were deposited essentially perpendicular to the thickness direction of the part. Excess water in

the preform was removed by vacuum, and then the fibrous deposit was air dried. Heated air completed the drying process and cured the resin. At this point the resin-rigidized part was removed from the mandrel and placed in a carbonization furnace. Furnace temperatures from 1600-2300°C (2912-4172°F) were used to pyrolyze the resin binder. Insulation materials intended for graphitizing furnaces and other very high-temperature uses were processed at a higher heat treatment temperature to minimize outgassing during operation. The carbonized material was then machined to the desired dimensions. Products formed in this manner are commercially available in a variety of thicknesses, sizes, and configurations. Typical shapes include flat boards and hollow cylinders, but just about any configuration is feasible. Standard commercial sizes for flat stock are a maximum of about 152 cm (60 in) long, 152 cm (60 in) wide, and 15 cm (6.0 in) thick. Hollow cylinders were fabricated with multipiece flat stock or fabricated to shape. Maximum dimensions have been about 178 cm (70 in) outside diameter, 75 cm (30 in) high, and up to 7.5 cm (3.0 in) thick. Increased wall thickness has been obtained by concentric placement of cylinders within cylinders. Increased lengths have been obtained by step-joint additions. Maximum service temperatures are reportedly a maximum of (a) 3000°C (5432°F) in vacuum depending upon system pressure, (b) 3000°C (5432°F) in argon, (c) 1800°C (3272°F) in nitrogen, (d) 1100°C (2012°F) in hydrogen, (e) 800°C (1472°F) in carbon dioxide, (f) 700°C (1292°F) in steam, and (g) 425°C (797°F) in air.

Properties of low-density, carbonaceous insulation material varied with materials constituents, processing parameters, and density. Typical near-room temperature properties of a 0.19 g/cm^3 (0.0069 lb/in^3) material were (a) thermal conductivity of 0.17 W/m·K (0.10 Btu/h·ft·°F), (b) thermal expansion coefficient of 1.3 ppm/°C (0.70 ppm/°F), (c) specific heat of 712 J/kg·K (0.17 Btu/lb·°F), (d) compressive strength of 0.21 MPa (30 psi), (e) flexural strength of 1.52 MPa (220 psi), and (f) porosity of about 89 percent. Other material attributes include (a) low outgassing at high temperatures, (b) resistance to thermal cycling, (c) low mass for rapid furnace heating and cooling, (d) high purity, (e) high resistance to most chemicals, (f) low wettability by most molten metals, and (g) other specific features.

Low-density carbonaceous materials have found a number of important applications in the industrial world. Most of the uses have been in vacuum or inert gas furnaces. These furnaces have typically been employed for (a) heat treatment of metals, (b) manufacture of powder metallic components, and (c) high-purity crystal growing for the semiconductor industry. CBCF materials are widely used in vacuum or inert gas furnaces where they replace molybdenum and other metallic heatshields. CBCF materials are about the same cost as metallic shields, but they have cost advantages due to their reduced installation time, faster heating cycles, and

simplified maintenance. CBCF materials are also employed in furnaces that grow silicon, germanium, and gallium crystals. The low-density fibrous material has been typically used around the furnace melt area for both thermal insulation and spill trays. Figure 36 is a schematic of a typical crystal-growing furnace and the areas where CBCF "Calcarb-TM" material is used.

4.8.14.2 Hot Pressing Dies

A hot pressing process is typically used to obtain high-density ceramic and refractory metal components. The basic process equipment includes either a reusable piston-cylinder die press or a gas bonding facility. In the hot pressing process, high-quality metallic or ceramic powder is compressed under high pressure and temperature to form a useful article. When hot pressing temperatures exceed about 816°C (1500°F), the number of available die materials is very limited. Polycrystalline graphitic materials are most often selected because of their (a) strength retention at high temperatures, (b) machinability, (c) availability, and (d) low costs. The low mechanical properties of these graphitic materials, however, necessitate high wall thicknesses and limit the hot die press diameter to about 51 cm (20 in).

Pioneering work by the industrial world during the late 1960s demonstrated the utility of CCC materials for this new and important applications area. Prototype hot pressing die bodies were fabricated with CCC flat laminates for the plunger and the base plate and CCC filament-wound materials for the hollow cylindrical body. Although the CCC materials had considerable porosity and a density of only 1.40 g/cm^3 (0.051 lb/in^3), they provided rather high strengths. The inside and outside diameter of these CCC dies were protected with conventional graphite sleeves. These sleeves were needed to (a) minimize surface crush-up, (b) protect the die inside surfaces from reaction with hot pressed powders and from being scored during loading and unloading operations, and (c) protect the outside of the die from oxidation during heat-up and cool-down. Limited laboratory evaluations of CCC and conventional graphite hot pressing dies indicated that the CCC dies had (a) plunger pressing strengths up to five times higher, (b) barrel hoop strengths about 13 times higher, (c) lower die weight, (d) a 33 percent shorter pressing cycle, (e) a die life 40 times higher, and (f) a cost 40 times higher. The actual die cost per run was the same for both graphite and CCC dies.

CCC properties were greatly improved during the 1970s and 1980s, thus making them more attractive for hot pressing dies. New CCC molds were evaluated along with electrographite for hot pressing cobalt alloys and tungsten carbide powders. The evaluation criteria included (a) quality of the sintered parts, (b) lifetime of the mold, (c) temperature distribution within the mold, (d) failure probability, and (e) cost parameters. The significantly

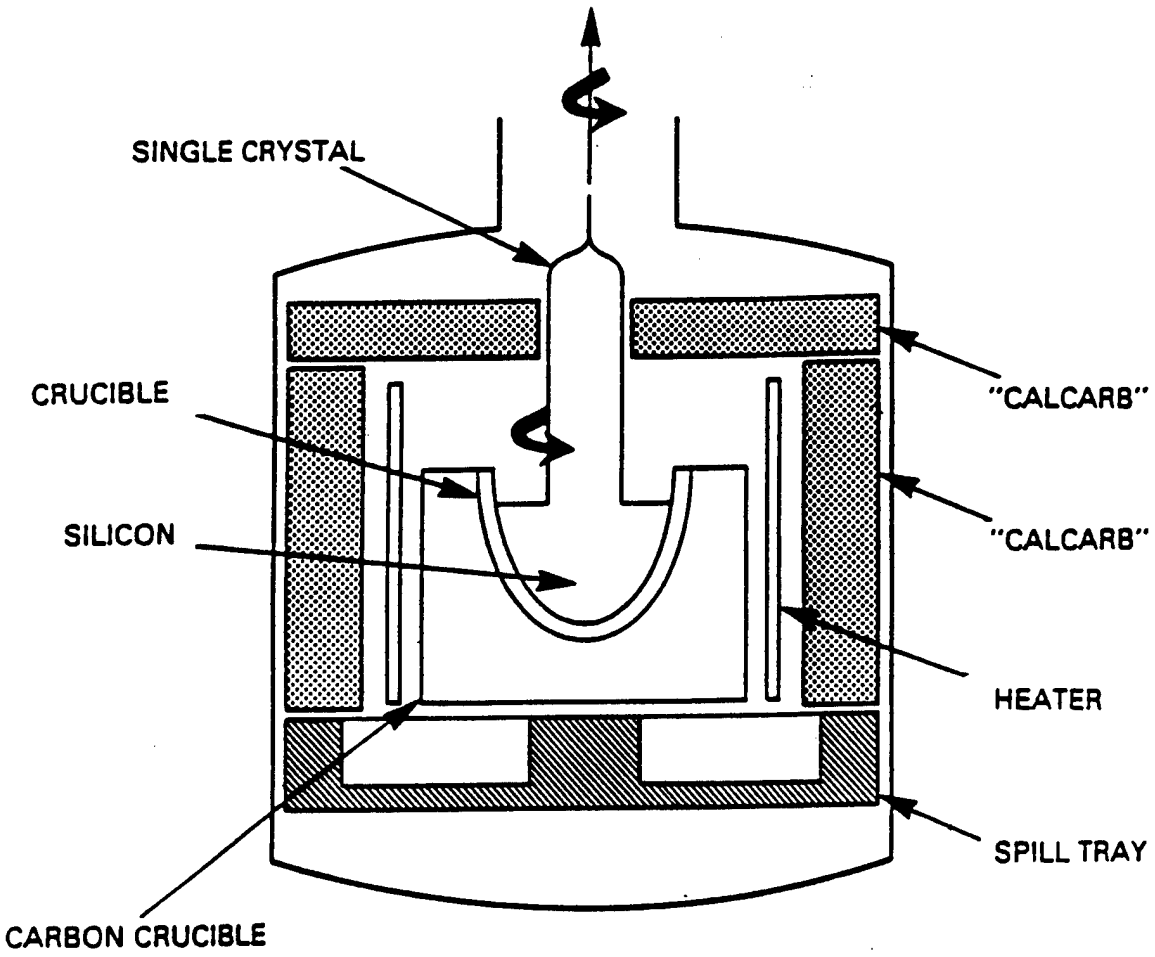


Figure 36. Diagram of a Typical Crystal-Growing Furnace.

higher CCC strengths, compared to electrographite, permitted molds with thinner separator-, side-, or end-plates. More homogeneous cobalt alloys were hot pressed with CCC molds, but conventional graphite molds were superior for hot pressing tungsten carbide. The prototype CCC parts were shown to have long lives, i.e. the wear rate was low and the probability of failure was negligible. Except for one separator plate, all of the CCC parts withstood the handling parameters, oxidation, mechanical forces, and chemical attack. Weight loss of the CCC molds during service life was also significantly less than state-of-the-art materials. From an economic point of view, the CCC molds were also more advantageous. The rate of segment sintering per hour was up to 120 times higher, and the energy consumption per segment was lower.

Today CCC hot pressing dies are used throughout the industrialized nations of the world. Both die design and materials have been significantly improved. They exhibit (a) proper distribution of strength and stiffness by mold designing-to-use, (b) more uniform heating and shorter heating cycles due to thinner wall materials, (c) better surface quality, (d) higher resistance to chemical attack by oxidizing constituents in liquid sinter powder, (e) greater surface impermeability to restrict infiltration of the molten material, (f) improved resistance to handling damage, (g) up to 80 percent increase in free sintering volume, and (h) less scatter in material properties.

4.8.14.3 Superplastic Forming Tools

Titanium alloys are widely used for very high-temperature aerospace applications. Compared to aluminum they have (a) higher strength retention at elevated temperatures, (b) higher specific strength, (c) better fatigue life, (d) improved corrosion resistance under normal aircraft usage, and (e) higher resistance to crack growth. Titanium alloys are difficult to form and machine, and hence simpler and less-costly metallurgical hot forming techniques are needed to work with these expensive materials.

Certain titanium alloys possess the unusual ability to elongate uniformly at elevated temperatures. This material characteristic enabled the development (mid-1970s) of superplastic forming (SPF) and superplastic forming with concurrent diffusion bonding (SPF/DB) techniques. Such techniques permitted the fabrication of strong, lightweight structural components from sheet material with (a) close tolerances, (b) minimal costly and time-consuming machining, and (c) avoidance of costly assembly operations (normally 50 percent of the final part cost).

Superplastic forming methods require the use of high-temperature, strong and heavy tooling. In most cases graphite dies are used. Pioneering efforts by German industrial firms demonstrated that lighter-weight, 2-D CCC molds could be used to superplastic hot form titanium parts. By using CCC liners the wall thickness of the graphite die was reduced. A CCC die having a wall thickness of only 15 mm (0.59 in) was successfully designed, fabricated, and used. The hot forming process was carried out at 1000°C (1832°F) and involved a simple blowing up procedure which started with tubes that were closed on one end. Longer (5 m, 16.4 ft) and similar CCC molding fixtures were later developed and used. Shorter heating cycles and more homogenous temperature distributions in the hot pressed products were also noted. The fabricated parts were for the European JF-90 military aircraft. Little additional progress has been reported on the use of CCC molds for metallurgical forming processes. The major limiting factors appear to be (a) high initial costs of CCC structures and (b) lengthy time required to obtain the necessary parts.

4.8.14.4 High-Performance Tooling

CCC materials are high-priced material candidates for tooling. They have (a) high strength, (b) high modulus, (c) low thermal expansion, (d) high thermal stability, and (e) possess other properties which lend themselves to high-performance tooling. While the technology is still being refined, CCC material has been successfully used to process PEEK/carbon fiber-reinforced composite panels at 399°C (750°F) and 1.4 MPa (200 psi) pressure. CCC tooling was noted to offer many benefits compared to monolithic graphites or ceramics including (a) higher thermal conductivity, (b) thinner tools, (c) higher heat transfer rates, and (d) reduced life-cycle times. Longer lead times (3-4 months) are needed to make custom CCC tools, but needed parts can often be bonded together with existing materials. In summary the principal CCC limitation is the high initial cost of the material. Any dedicated effort in this area will surely lower the cost of CCC tooling and make them more competitive for this purpose.

4.8.14.5 Mechanical Fasteners

High-temperature components are frequently fabricated and assembled from dissimilar materials like refractory metals and ceramics. With the advent of CCC materials, attachment methods were needed to join these materials to each other or to adjacent metallic and ceramic structures. High-temperature metallic or ceramic pins and bolts have historically been used for mechanical fastening, but at temperatures above about 750°C (1382°F) their strength properties decrease rapidly.

First-generation CCC fasteners were prepared with diamond wheel and lathe tool-post grinding of medium density materials. Filament-wound, chopped-fiber and woven-fabric composite constructions served as the precursory material, but 2-D woven-fabric laminates were the most commonly used. Typical parts included (a) studs, (b) bolts, and (c) nuts. Studs and bolts were machined in diameters from 0.63-3.8 cm (0.25-1.5 in) and lengths up to 30 cm (12 in). Bolts were available with square or hexagonal heads. Nuts had a square, round, or hexagonal configuration. Belleville and Plain washers were also commercially available. Fasteners intended for prolonged use in high-temperature oxidizing environments were coated with 0.025 mm (0.001 in) thickness of silicon carbide or silicon nitride. While these mechanical fasteners exhibited surprisingly high strength properties, certain properties needed upgrading. Second-generation CCC mechanical fasteners were tailored to meet thread shear, pin shear, tensile, or head shear load requirements. Unique fibrous weaving approaches and special matrix processing methods were employed to obtain thread shear strengths greater than 55 MPa (8 ksi) and pin shear strengths greater than 140 MPa (20 ksi). Various 3-D fibrous architectures have been employed to obtain balanced properties. A through-the-thickness braid generally yielded the best balance of pin shear and thread shear strengths. Best results were also obtained by densifying the fibrous preform with CVI pyrolytic carbon followed by liquid pitch infiltration and graphitization.

4.8.14.6 Furnace Heating Elements

Graphites are commonly used as the resistance heating elements in vacuum and inert gas furnaces. These refractory materials have well served the furnace industry, but they are limited by (a) low mechanical properties, (b) sensitivity to notches, (c) low impact resistance, and (d) difficulty in fabricating intricate shapes. CCC materials do not suffer from any of these deficiencies, and for that reason a number of heating element units have been fabricated and evaluated. Most of the prototyping involved 2-D fabric-reinforced CCC materials machined to the desired configuration. Costs of the machined CCC parts were naturally quite high which will greatly limit uses in commercial furnaces.

4.8.14.7 Furnace Charging Stages

The working volume in vacuum and inert gas heat-treating furnaces is of paramount importance. To effectively use the furnace heat volume, charging stages are employed. They are usually composed of high-temperature alloys, ceramics, or graphites. CCC materials offer the potential for (a) reducing the size of a charging unit, (b) increasing life cycle, and (c) greatly reducing heating and cooling periods. Various 2-D CCC demonstration articles

have been fabricated and successfully evaluated. The material's low mass, high impact resistance, high mechanical properties, and high resistance to thermal cycling all contributed to significantly improved article performance. Heating and cooling cycles were reduced up to five times compared to other conventional materials.

4.8.14.8 Molten Glass Container and Transfer Units

High-temperature, corrosive-resistant materials are used in the manufacture of various-shaped glass articles. Essential properties vary with the specific application, but in general they entail: (a) reasonable strength, (b) adequate lubricity and nondamaging to hot glass, (c) chemical inertness, (d) good wear resistance, (e) low thermal conductivity, (f) nonflammability, (g) environmentally safe, and (f) reasonable cost. In addition impermeability is sometimes required to cope with the problem of oil contamination. Various materials have been used including (a) asbestos or glass fiber-reinforced composites, (b) carbon, (c) ceramic materials, and (d) various plastics based on polytetrafluoroethylene and silicones.

CCC materials were used as replacements in many glass manufacturing parts. CCC shear blades were used to remove a small amount of molten glass from the main stream. See Figure 37. The molten gob was then transferred to a mold with the aid of a CCC distributor, trough, and deflector. After formation of the desired glass article (like a bottle), the hot object was moved to an annealing furnace with the aid of CCC pushout pads, stacker bars, wear transfer pads, and machine conveyor wear guides. Pushout pads were assembled by mechanically fastening the CCC pads to a steel backup plate. Their useful lives ranged from 8-12 months, after which the worn pad was removed and replaced with another CCC pad. Total annual operating costs with the new CCC pushout pads were about one-fourth that of the previously-used asbestos material. Straight and saw tooth stacker bars were also fabricated with CCC and installed on production machinery. Life of the CCC part was approximately nine months. The annual operating costs of the part were about one-fifth that of the asbestos part. CCC spacer pads were also installed on the wear transfer mechanism. Parts have run an excess of one year without problems. Cost savings were not calculated, but the CCC spacer pads resulted in fewer replacement labor hours and minimum wear during the changing of other adjacent pads. CCC wear guides for the machine conveyor were also fabricated and operated successfully for over three years. The inherent lubricity of the CCC material minimized part drag which can result in bottle-to-bottle contact and damage. To summarize, many CCC parts for transfer and handling of hot glass articles have been fabricated and successfully evaluated in the manufacturing environment. The CCC parts had wear rates between 100-300 percent better than typical

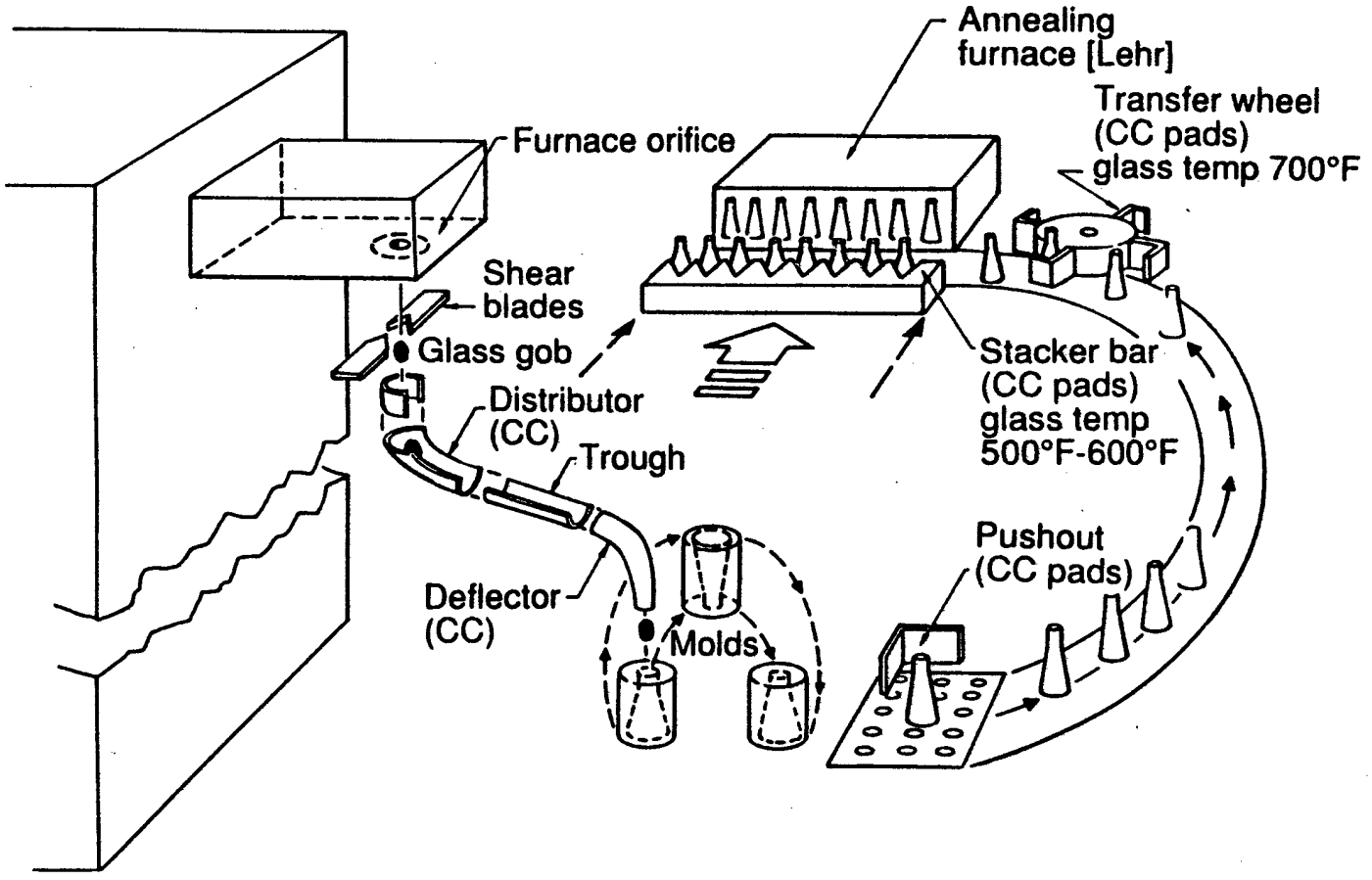


Figure 37. Schematic of CCC Component Locations in a Glass-Forming Machine.

asbestos articles. The CCC materials were demonstrated to be cost effective, and their use in lieu of asbestos aided in providing a more environmentally-safe working environment.

4.8.14.9 Corrosion-Resistant Containers

Polycrystalline graphite has been widely used in the chemical and metallurgical community for containing, transfer, and processing of hot corrosive materials. Graphite is relatively inert, i.e. it has good corrosion resistance at ambient and elevated temperatures. Morever, the material is not wet by many molten materials. In certain applications the design of unique and complex tubes and crucibles did not lend itself to the use of bulk graphite. Unique CCC crucibles were therefore fabricated and successfully used. Significant additional uses are not expected due to the high cost of the CCC materials, but with the recent development of low-cost materials and processes, the prospects for additional applications appear to be brighter.

4.8.14.10 Internal Combustion Engine Components

Internal combustion reciprocating engines, like gasoline and diesel machines, require more thermally-stable materials with good wear resistance. Engine operation at higher temperatures could provide (a) increased engine efficiency, (b) reduced emissions, and (c) reduced weight. CCC materials have superior thermal and structural properties compared to typical engine materials, and hence they offer interesting possibilities for future uses.

Cast and forged aluminum alloy pistons are used in various applications including (a) buses, (b) trucks, (c) automobiles, (d) motorcycles, (e) lawn mowers, (f) go-carts, (g) chain saws, and (h) recreational remote-controlled model airplane engines. Aluminum pistons have proven to be quite durable, inexpensive, and capable of mass production. Typical piston designs and materials, however, have certain limitations particularly at high revolutions-per-minute (rpm). These limitations include (a) complex asymmetrical shapes, (b) high thermal conductivity with heat removal from the combustion chamber, (c) high thermal expansion coefficient which necessitates undersizing of the piston and using one or more sealing rings with attendant frictional losses, and (d) operating temperature limited to about 149°C (300°F). Expansion of the piston with increasing temperature may cause it to contact the cylinder wall, induce frictional heating, and embed cast iron in the piston wall. This undesirable process plastically deforms the piston, increases the loads, and may cause failure of the connecting rod and associated bearings.

A hybrid CCC-metallic automobile piston was designed, fabricated, and tested in the late 1980s. The piston head was fabricated with n-D carbon fibrous reinforcement and a carbon matrix derived from both resin and CVI pyrolytic graphite. The connecting structure was composed of lightweight aluminum. This hybrid CCC piston exhibited impressive performance improvements over aluminum pistons including: (a) thermal efficiency, (b) structural efficiency, (c) absence of normal failure modes, and (d) lower frictional losses. The pistons operated at a higher temperature, thus permitting more complete combustion of hydrocarbon gases and with lower noxious emissions. Improved structural efficiency enabled higher engine speeds. Typical aluminum piston failure modes like galling, seizing, and melting were not exhibited by the CCC parts. The extremely low coefficient of friction material allowed the CCC piston to be lapped into the bore, thus eliminating the need for conventional sealing rings. Piston design was greatly simplified, and frictional losses associated with the sealing rings were eliminated.

Diesel engines also represent a promising and potentially high-volume outlet for CCC materials. Turbocharger and piston parts have been fabricated and evaluated. They have been run at substantially higher temperatures than state-of-the-art materials. With further design and material improvements, they would permit reduced airflow and a smaller engine volume. Other diesel engine components that could benefit from the use of CCC materials are: (a) valves, (b) piston crowns, (c) cylinder liners, and (d) the foredeck. Much additional design and materials evaluation remains to be accomplished.

Valves of internal combustion engines play a major role in determining performance and time between their overhaul. Considerable research and development is underway to (a) reduce the valve mass for better response and (b) reduce wear and erosion. Lower valve mass is being sought to decrease inertial forces and reduce noise and vibration associated with the valve train. In addition the mass of other peripheral components (valve springs, rocker arms, and push rods) should be reduced. The overall result could be a reduction in fuel consumption and increased engine power density. For long-term uses, wear and erosion of valve surfaces become of paramount importance.

State-of-the-art valves for internal combustion engines are made from metals and alloys. High-temperature ceramics like silicon nitride are being evaluated, but they presently suffer from reliability and cost constraints. Other ceramic-like materials such as CCC materials may offer a better balance of properties, and for that reason CCC valves have been evaluated for internal combustion engines. The CCC valve provided the lightness, hardness, and heat resistance of monolithic ceramics while imparting the desirable impact toughness and design

flexibility inherent in composite materials. A prototype CCC valve body was fabricated for an internal combustion engine application. The valve body was composed of a carbon char matrix with unidirectional carbon fibers in the stem and multidirectional carbon fibers in the valve head. Laboratory testing of the CCC valves provided interesting but not totally unexpected results. The uniaxial CCC composite showed excellent in-plane strength properties but low interlaminar shear strength. The head-stem transition region was also a problem area. As with many of these applications, materials design, and in particular the reinforcement scheme employed, played a major role in the success or failure of the prototype. Ultimately acceptable reinforcing preforms will become available to satisfy the many and demanding structural requirements of CCC valves.

CCC materials have been successfully prototyped for various piston engine components. First uses have been on experimental motorcycle engines. Many issues remain to be resolved prior to component certification, like (a) wear rates, (b) oxidative effects, (c) oil and fuel contamination effects, and (d) other specialized concerns.

4.8.14.11 Electrochemical Grinding Wheels

Conventional grinding wheels are based on an abrasion wiping action to remove material. In the process a brittle refractory material impacts a softer or more ductile material causing a plastic deformation, shear, tensile, or brittle fracture.

With the advent of CVD/CVI processing technology, grinding wheels containing silicon-carbide or aluminum-oxide particulates bonded tother with CVD/CVI pyrolytic carbon/graphite matrix became a reality for use in electrochemical grinding. In electrochemical machining a work piece is made from the anode, and it is brought into contact with a rotating conductive bonded abrasive wheel (cathode). See Figure 38. A conventional coolant is not used, but rather a conductive solution (electrolyte) is applied to the workwheel contact surfaces. As electrolysis occurs an oxide film is formed on the surface of the anode. If allowed to remain on the surface, the electrically-insulating oxide film would slow or stop the process. Therefore an abrasive in the cathode wheel removes the oxide and exposes more metal for continued oxidation. This electrically-assisted grinding process provides for high removal rates on difficult to machine materials like nickel-cobalt alloys, steels, and carbides. The machining process is also used on complex shapes, such as turbine buckets. The method provides cool surface grinding and burr-free grinding of tubing.

Hybrid carbon-matrix composite grinding wheels were fabricated and evaluated. Carbon-matrix composites heat treated to the graphitic state by high temperatures

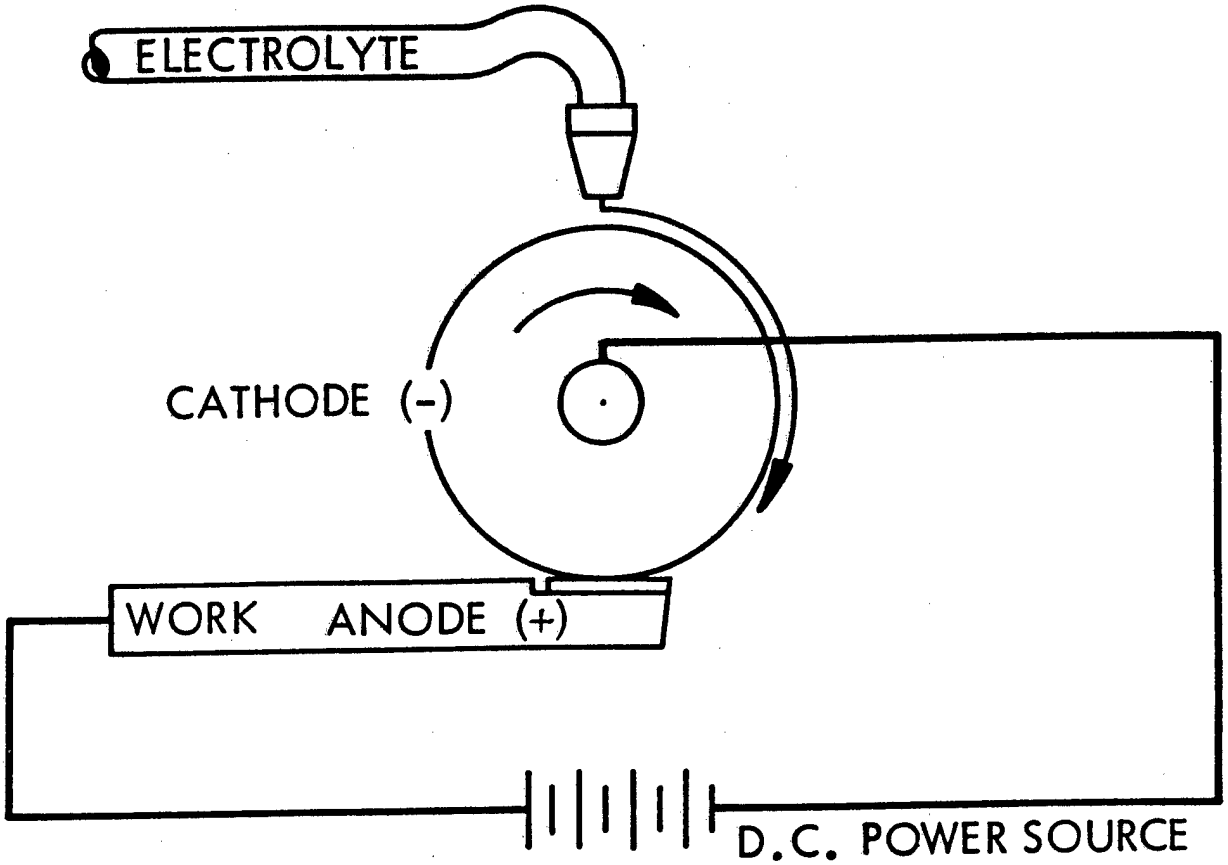


Figure 38. Schematic of an Electrochemical Grinding Machine.

were found to have the necessary thermal stability, electrical resistivity, strength, and wear resistance for electrochemical grinding operations. Carbon-bonded grinding wheels exhibited superior performance to copper-bonded wheels, often requiring less than 10 percent of the time needed compared to state-of-the-art materials. In addition they were (a) stronger, (b) more crush resistant, and (c) exhibited lower wear rates. These promising materials evaluations were carried out in the early 1970s, but follow-on publications could not be located concerning their everyday uses or developmental progress.

4.8.14.12 Gas Turbine Components

High-speed turbines are used to transport gases over considerable distances. High-temperature turbines require the use of refractory and strong materials. Monolithic ceramics appear to be suitable for turbine blades, but high centrifugal stresses may induce premature tensile failure.

A unique gas turbine prototype has been demonstrated in Germany. It was composed of: (a) metallic drive shaft, (b) ceramic wheel and blades, and (c) an overwrap of filament-wound CCC material. The CCC outer ring brought the ceramic blades under additional compressive prestress. The CCC ring had to be cooled below 400°C (752°F) or coated if used in an oxidizing gaseous environment.

Gas turbines built entirely of CCC materials have also been fabricated and tested in the United States. They appear particularly promising for uses in high-temperature, chemically-inert environments.

4.8.14.13 Chronology of Industrial CCC Components

With the discovery of CCC materials, initial thoughts were given to their possible military uses. Within three years, however, it became apparent that this new family of materials may also have industrial and commercial applications. If CCC structures were to become a reality, then joining methods would be necessary. First-generation CCC fasteners were fabricated in 1963. Thereafter, many more industrial prototypes were built and evaluated. Most of the parts were highly specialized. Low-density CFCB insulation materials became a significant business entity. High material costs in virtually every case kept CCC materials from being more widely used.

The first reported CCC prototypes for industrial applications are listed in Table 57. Also listed in the table is the organization responsible for the accomplishment and the year of availability.

The chronology of CCC materials for industrial uses is given in Table 58. Although many prototypes are cited, few uses have been commercialized to date.

4.8.14.13.1 *The 1960s*

As a sideline to the development of CCC materials for defense applications, a number of small efforts were devoted to commercialization. Furnace elements appeared attractive, and parts were fabricated and tested in the form of various furnace components like (a) heater elements, (b) heatshields, (c) furnace walls, shelves, and trays, and (d) hot pressing dies. It was noted that the CCC dies, which replaced previously used ceramic parts, were very long lived.

4.8.14.13.2 *The 1970s*

Only two commercial applications for CCC materials were cursorily investigated during this time frame. They were (a) a substrate for electrochemical grinding wheels and (b) armor protection. The advantages afforded by CCC materials were insufficient to warrant further investigation and use.

4.8.14.13.3 *The 1980s*

Rather interesting potential uses for CCC materials were studied during the 1980s. Crucibles or other configurations for ceramic crystal growing and pulling were demonstrated with very low replacement rates. High-temperature tooling parts for thermoplastic forming of metallic parts (like titanium) also offered new opportunities to use CCC materials. Fastening elements like screws, nuts, bolts, and washers were redesigned to accommodate existing fibrous constructions, and rather interesting uses were demonstrated. Threaded rocket propulsion parts were examined in great detail. Significant guidance was furnished on upgraded parts. Pistons for internal combustion engines were also evaluated. The basic concept was to substitute metallic wall materials with higher-temperature CCC materials, thereby improving the combustion efficiency and lowering the unwanted emissions. While each of the part demonstrations was impressive, much additional development will be required to use CCC materials in engine piston and wall applications.

TABLE 57

FIRST CCC PROTOTYPES FOR INDUSTRIAL COMPONENTS

YEAR	PROTOTYPE	ORGANIZATION
1963	Mechanical fasteners (nuts and bolts)	Chance Vought Corporation/USA
1963	Induction heater assemblies (susceptor and cover)	Union Carbide Corporation/Carbon Products Division/ USA
1967	Hot pressing dies (tool segments, pressure plates, and resistance elements)	Carborundum Company/USA
1968	Furnace components (heater elements, heatshields, structural walls, shelves and trays)	Carborundum Company/USA
1969	High-temperature furnace vacuum/inert gas insulation	Union Carbide Corporation/Nuclear Division Y-12 Plant/USA
1970	Electrochemical grinding wheels	Super-Temp Company/USA
1970	Projectile armor protection	Naval Surface Warfare Center/USA
1983	Truck internal combustion engine pistons	Proprietary Source
1985	Hot tooling parts (dies, pistons, liners, and plates)	Sigri Elektrographit (GmbH)/GERMANY
1987	Pistons for gasoline engines	Fiber Materials, Inc. (FMI)/USA NASA Lewis Research Center/USA
1988	Semiconductor manufacturing components (boats, crucibles, trays, and tubes)	Several Organizations/USA
1988	Electrical discharge machining (EDM) electrodes	NIIGrafit/USA
1994	Coil springs	Across Company, Ltd./JAPAN
1994	Link belts	Across Company, Ltd./JAPAN

TABLE 58
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR INDUSTRIAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1963	CCC mechanical fasteners fabricated	First-generation attachment and joining concepts demonstrated for CCC structures	Chance Vought Corporation/USA
1963	Mascerated graphite cloth and cloth-reinforced CCC laminates fabricated for potential industrial applications	Prototype susceptor and cover assemblies for induction heater applications	Union Carbide Corporation/Carbon Products Division/USA
1967	2-D CCC hot pressing dies fabricated for use at 10,000 psi pressure and temperatures up to 2000°C	One of the first industrial applications for CCC materials	Carborundum Company/USA
1968	2-D CCC high-temperature/high-pressure heating element fabricated	One of the first industrial uses for 2-D CCC	Carborundum Company/USA
1968	Low-friction, 2-D CCC fabricated	First prototype CCC for impact-resistant bearings	Carborundum Company/USA
1968	Full-scale, 2-D CCC turbine wheel fabricated	First prototype CCC turbine wheel for high-temperature, inert gas, high-speed fluid pumping applications	Philco-Ford Corporation/Aeronutronic Division/USA
1969	Low-density carbon fiber insulation produced	First prototype high-temperature carbon insulator Later commercialized by Fiber Materials, Inc. and Calcarb for missile insulation, furnaces and other applications	Union Carbide Corporation/Nuclear Division Y-12 Plant/USA
1973	Large (29 in. O.D., 24 in. I.D., 24 in. long) CCC hot pressing die fabricated and produced a ceramic material with 97% theoretical density	Cost of hot pressing reduced by longer-life CCC materials Larger hot-pressed parts obtained at higher pressures and temperatures	Union Carbide Corporation/Nuclear Division Y-12 Plant/USA
1977	2-D CCC nuts and bolts manufactured	Mechanical attachment and joining approaches for CCC structures	Societe Europeenne de Propulsion (SEP)/ FRANCE
1979	CCC advanced bonding materials and methods developed	Low volatile, higher-temperature adhesives available for joining CCC	Aerojet Solid Propulsion Company/USA

TABLE 58 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR INDUSTRIAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1985	Thermal stress-free metal fasteners demonstrated with CCC joints at elevated temperatures	Innovative approach for attachment of CCC using metallic fasteners	NASA Langley Research Center/USA
1985	Heating elements, heatshields, and insulation parts developed for high-temperature furnaces	Improved components for commercial vacuum, sintering, HIP, and melting furnaces	Schunk Kohlenstofftechnik GmbH/ GERMANY
1985	CCC takeout tongs and Lehr stacker were successfully evaluated for handling hot glass bottles	New and important cost-effective application of CCC materials in the glass manufacturing industry	United Glass Limited (CCC Part Evaluation)/ENGLAND
1985	2-D CCC hot tooling parts used to superplastic form titanium parts for European JE-90 aircraft air inlet channels	First prototype CCC tooling parts for commercial aircraft titanium inlet channel applications	Sigri Elektrographit GmbH)/ GERMANY
1986	Demonstration and evaluation of 3-D CCC fasteners	Enhanced the structural integrity of high-temperature joints	Fiber Materials, Inc./USA
1987/88	4-D CCC piston fabricated and successfully tested in small combustion engine	First prototype CCC and test in an internal combustion reciprocating engine Potential applications of coated CCCs extended to large-to-small combustion engines	Fiber Materials, Inc. (Piston)/USA NASA Langley Research Center (Test)/ USA
1988	2-D CCC nuts and bolts fabricated and evaluated	CCC mechanical fastening and joining approaches demonstrated	LTV Aircraft Products and LTV Missiles & Electronics Groups/USA
1988	Electrical discharge machining (EDM) CCC electrodes fabricated and tested	CCC electrodes had a longer life than previously-used metallic electrodes	NIIGrafit/RUSSIA
1988	CCC nuts, bolts, screws, and washers fabricated for high-temperature fastening applications	Improved mechanical fasteners became available for joining CCC components	Schunk Kohlenstofftechnik GmbH/ GERMANY
1989	CCC fasteners molded using braided preforms	Innovative approach for low-cost fabrication of CCC fasteners	NASA Langley Research Center/USA

TABLE 58 (Continued)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR INDUSTRIAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1989	Solid-state diffusion bonding and brazing processes developed for CCC materials	Molybdenum disilicide interlayer joint shear strengths were in excess of 2-D CCC interlaminar shear strengths	Wright State University/USA
1990	CCC heating elements were fabricated for a high isostatic pressure (HIP) facility	Another commercial source for HIP heating elements	Kaiser Aerotech/USA
1990	CCC containment cylinders were fabricated for a vacuum furnace	Another commercial source for vacuum furnace parts	Kaiser Aerotech/USA
1990	CCC tubes were fabricated for heat exchangers	Another commercial source for heat exchanger tubes	Kaiser Aerotech/USA
1990	CCC rods were fabricated for high-temperature push-pull applications	Another commercial and specialty use for CCC materials	Kaiser Aerotech/USA
1990	Inert 2-D CCC parts developed for hot transfer of molten glass	Long-life parts developed for important new commercial applications	Schunk Kohlenstofftechnik GmbH/ GERMANY
1991/92	Developed high-temperature brazing process for attachment of CCC to CCC	Combined through-the-thickness reinforcement with refractory metal brazing to produce joints with increased strength and thermal conductivity	Foster-Miller, Inc./USA Wright State University/USA
1991	High-strength, porous CCC papers developed for catalyst substrates and electrodes for fuel cells	Replaced previously-used brittle and heavy carbon materials New electrical application area for CCC materials	Spectracorp/USA
1993	Lightweight CCC platforms developed for annealing steel powder	23% savings in heating energy and 80% improvement in heating speed compared to previously-used graphite racks	Across Company/JAPAN
1993	Antiextrusion CCC ring developed for maintaining placement of braided packing in high-temperature/pressure valves for nuclear power plants	CCC replaced brittle, low shear strength extruded graphitic material	Spectracorp/USA

TABLE 58 (Concluded)

CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR INDUSTRIAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1994	CCC helical-shaped coil springs became commercially available	In a nonoxidizing atmosphere, the springs were lighter than metals, had a longer operating life, greater resistance to corrosion, and other desirable thermophysical properties	Across Company, Ltd./JAPAN
1994	CCC link belts became commercially available	In a nonoxidizing atmosphere, the continuous link belts were used from 1-3 years without problems Better high-temperature, continuous conveying method was demonstrated	Across Company, Ltd./JAPAN

4.8.14.13.4 *The 1990s*

The early 1990s witnessed two new CCC applications, including (a) a structural casing material for high-temperature batteries and (b) transfer of molten glass from one location to another.

While the remainder of the 1990s is uncertain, it is apparent that several new applications of CCC materials will be investigated. Specialty industrial CCC materials are expected to grow slow in the 1990's and then grow dramatically during the next century. Potential uses will take advantage of new low-cost materials and processes. Part designers will be more cognizant of CCC materials, and design-to-use methodologies will evolve to enlarge the industrial base.

4.8.15 Biomedical Components

Bone replacement is often required in humans suffering from (a) bone degeneration, (b) disease like cancer, or (c) catastrophic destruction caused by accidents or war. The most common bone replacements are hip joints and knee segments. Many elderly patients are afforded enhanced mobility which would not be possible without prosthetic devices.

All forms of carbon are excellent biomaterials. They have been used in fibrous bundles for the repair of tendons and ligaments or as open-woven carbon fibrous patches in the regeneration of articular surfaces of osteoarthritic joints. Carbonaceous materials in all forms and their wear products are chemically stable in body fluids. They do not corrode even after many years of use. The materials are compatible with blood, soft tissues, and bones, and their use avoids such issues as hypersensitivity, toxicity, and carcinogenicity. Currently-used metallic implants are susceptible to (a) slow corrosion in an aqueous chloride environment and (b) enzymatic release of metallic ions in the body. Such metallic ions may induce allergic reactions.

The major application outlets for CCC materials in the biomedical field have been for (a) stems of artificial hip joints, (b) reinforcing plates for bone mending, (c) rods or pins for fixation of artificial limb extension, (d) cancerous bone replacement, and (e) other novel uses. Material requirements for most of these applications include (a) corrosion resistance in the presence of body fluids, (b) biocompatibility of the bulk material and its wear particles, (c) mechanical compatibility with bone (high fatigue strength, low modulus, and high elongation-at-break), (d) low wear, (e) low coefficient of dry friction, (f) long-term dimensional stability, and (g) bone ingrowth into a porous surface if desired. CCC materials possess all of

these properties and characteristics to varying degrees. While CCCs appear to be the ideal material, only slow progress has been made in developing and applying them to the biomedical field.

CCC materials have several limitations that restrict their biomedical uses. The materials have (a) low shear properties, (b) low torsional properties, and (c) marginal abrasion resistance. Once the structure is formed, it cannot be post-formed. Many spin plates and bone plates are bent interoperatively to fit the shape of the bone. The exposed ends of fractured CCCs are very rough and sharp, and may lead to substantial wear debris being formed. To obtain long-term wear behavior, the sliding surfaces of CCC parts are typically coated with a ceramic coating such as silicon carbide. These hard surfaces cause a slightly stronger early tissue reaction compared to pure carbon materials, but their wear products are biocompatible. The silicon carbide-CCC materials are stronger than CCC equivalents, and the surfaces can be machined to higher tolerances. The hybrid surface materials have lower porosity and inhibit bone ingrowth.

A typical CCC artificial hip joint is composed of a specially-designed CCC stem and ball. The ball wearing surface is coated with silicon carbide and mated to a plastic acetabulum socket. The CCC stem is inserted into a drilled-out bone and bonded to the internal surface of the bone. Methacrylate adhesive bonding of metallic, ceramic, and CCC stems to bone structures is an undesirable operation because the adhesive has a useful life of only 7-10 years. Ultimately bond failure occurs and a second replacement is needed. Bone resorption resulting from the presence of a prostheses now limits the number of transplants to two for each patient. The use of slightly porous CCC stems, however, permits the prosthetic device to be mated directly to the bone. Body calcium is deposited into the porous CCC surface and forms a new carbon-bone structure.

A long period of time wlll be needed to properly develop and gain acceptance of CCC materials in the biomedical field. About six years are needed to design and develop the appropriate material and configuration. An additional two to three years are then required for clinical evaluations which involve a controlled and limited number of implantations to establish in-vivo behavior. Optimization activities may then be required to alter the material composition, construction, and design. After obtaining significant positive results, a minimum of 500 operations and two to three years of clinical evaluations may be needed to obtain high confidence in the materials and techniques. Material certification costs are about U.S. $1M.

Clinical testing of CCC materials for biomedical applications has been conducted mainly in France, Germany, England, Brazil, and the former USSR. Little has been done in the United States. Most of the work appears to have been centered on artificial hip joints. Further testing of hybrid CCC hip joints has been abandoned due to stem breakage (low material torsional and shear properties). Optimization of CCC prosthetic devices has yet to be accomplished. Any such efforts will require the close cooperation of the physician, part designer, and the CCC fabricator.

Further evaluation of CCC and hybrid CCC materials for biomedical uses is being pursued elsewhere in the world, but at a slow pace. Hybrid CCC materials appear to offer the greatest flexibility in bone implant design, especially for tailored elastic modulus and wear resistance. These and many other factors need to be further evaluated, including the (a) complex loading conditions, (b) potential for environmental degradation, (c) biocompatibility effects, (d) composite design and manufacturing, and (e) other factors.

4.8.15.1 Chronology of Biomedical CCC Components

Table 59 lists CCC prototypes of biomedical components. The number of CCC prototypes is relatively small but very important from a medical and technical point-of-view.

A more complete bibliography of the use of CCC materials in biomedical applications is given in Table 60.

4.8.15.1.1 The 1970s

The use of bio-CCC materials was apparently initiated in Europe in the mid-1970s. Up to this point in time, it was recognized that isotropic pyrolytic carbons were useful and that CCC materials may possibly offer improved mechanical properties. Pins for joining bonded areas, reinforcing bone plates and rods for extension of bones were fabricated with CCC materials and successfully demonstrated in various mammals (sheep, rabbits, others). This biomedical pioneering research was carried out in England and Germany.

4.8.15.1.2 The 1980s

Initial success using CCC materials for bone plates and pins led to their evaluation for various biomedical uses including hip prostheses, osteosynthesis plates,

TABLE 59
FIRST CCC PROTOTYPES FOR BIOMEDICAL APPLICATIONS

YEAR	PROTOTYPE	ORGANIZATION
1976	Pins for joining human bones	University College of Swansea/Wales/UNITED KINGDOM
1977	Artificial hip joint replacement for humans (shaft section)	Schunk & Ebe/Schunk Kohlenstofftechnik GmbH/ GERMANY
1978	Plates and pins for mending animal bones	Atomic Weapons Research Establishment (AWRE)/ ENGLAND
1980	Artificial knee joints	Societe Europeenne de Propulsion (SEP)/FRANCE
1983	Artificial heart components for animals	Societe Europeenne de Propulsion (SEP)/FRANCE
1983	Ventilation tubes for human middle ears	-

TABLE 60
CHRONOLOGY OF CCC MATERIALS AND COMPONENTS FOR BIOMEDICAL APPLICATIONS

YEAR	EVENT	SIGNIFICANCE	ORGANIZATION
1976	CCC pins for joining bones	Biocompatible material available for bone stretching and adjustment	University College of Swansea/Wales/ UNITED KINGDOM Centro Tecnico Aerospacial Sao Jose dos Campos/BRAZIL
1977/82	Biocompatible CCC parts fabricated for evaluation as human hip joints	Higher-performance bone replacement materials became available for endoprosthetic uses	Schunk & Ebe/Schunk Kohlenstofftechnik GmbH/GERMANY
1978	CCC bone plates and Steinmann pins were fabricated for biocompatibility experiments	CCCs evaluated for various orthopedic uses	Atomic Weapons Research Establishment/ ENGLAND
1978	Prototype 2-D CCC bone plates fabricated for osteo synthesis and endo prostheses animal experimentation	Biocompatibility of CCC bone structures demonstrated in living animals Enhanced prospects for ultimately using CCC bone replacements in humans	Universitat Karlsruhe/GERMANY
1980	CCC developed for various biomedical uses including hip prostheses, osteosynthesis plates, and knee joints	Specialty CCC exhibited excellent biomedical compatibility with living tissue and thus had potential for use as bone and dental prostheses in animals and humans	Societe Europeenne de Propulsion (SEP)/ FRANCE
1982	Silicon-carbide coated CCC double-cup prostheses prototype developed	Wear-resistant, long-life hip replacement available for clinical tests	Schunk & Ebe/Schunk Kohlenstofftechnik GmbH/GERMANY Universitat Karlsruhe/GERMANY
1982	CCC proposed for human bone implants	First disclosure of Soviet interest in CCC for bone replacements	State Research Institute of Graphite/ RUSSIA
1983	CCC parts fabricated for animal artificial heart parts	Demonstrated potential of specialty CCC for critical biomedical applications	Societe Europeenne de Propulsion (SEP)/ FRANCE
1984	3-D CCC designed and fabricated for prosthetic devices	Alternate materials for biocompatible applications	Fiber Materials, Inc./USA
1989	Analytical and experimental design of composite materials for hip stems	CCC prosthetic hip stems were redesigned to optimize strength and stiffness	Stanford University/USA

and knee joints. These experimental trials were conducted in France and the former USSR, but few details have been reported. Most of the work involved 2-D reinforced CCC materials, but with the advent of 3-D CCC materials, research interest shifted to this class of composites. Structural advantages of 3-D CCC materials were investigated in the U.S., but follow-on clinical research apparently was not initiated.

4.9 APPLICATIONS

CCC materials have been successfully transitioned from the prototype stage to operational use in over 40 different applications. Table 61 lists the major application areas. Current operational uses in one or more countries of the world include: (a) aircraft brake discs for both military and commercial aircraft, (b) rocket nozzle throats and exit cones for solid propellant motors, (c) nosetips of strategic missile reentry vehicles, (d) nosecap and leading edges for hypersonic atmospheric flight vehicles, (e) brake discs and clutches for racing cars, (f) clutches for heavy equipment, (g) protective cannisters for space power generators, (h) transfer systems for molten glass, (i) molds and dies for high-temperature compaction of ceramic and metallic materials, (j) medical prosthetics like hip bone replacements, (k) furnace insulation, (l) furnace metallic sintering trays, and (m) substrates for ceramics (electronic) manufacturing.

4.9.1 Current Uses

The major application outlet for CCC materials has been aircraft braking systems, as previously noted. Both 2-D and short fiber 3-D reinforced composites are being used. Each year the number of aircraft using CCC frictional materials increases, so the future of CCC materials is highly dependent upon their continued success and application in the aircraft frictional materials market. Uses of 3-D and 4-D CCC missile nosetips and rocket nozzle throats have been reported in the literature. CCC materials have been employed in other defense applications, but the open literature on these uses is limited in number and content. Nevertheless it is apparent that most of the "high technology" nations have active CCC materials development and evaluation programs to satisfy future defense needs. Commercial uses of CCC materials continue to lag behind defense uses, except for CCC brake discs of commercial aircraft. The high cost of the materials, compared to other graphitic or refractory materials, tends to slow their use in new systems or for component retrofit purposes.

TABLE 61
CURRENT APPLICATIONS OF CCC MATERIALS

- BRAKE DISCS AND CLUTCHES
- SOLID ROCKET MOTOR NOZZLES AND EXIT CONES
- MISSILE NOSETIPS
- SHUTTLE NOSECAPS, LEADING EDGES, AND OTHER COMPONENTS
- FURNACE ELEMENTS
- HOT GLASS TRANSFER UNITS
- HOT PRESSING TOOLS AND DIES
- SEMICONDUCTOR MANUFACTURING COMPONENTS

4.9.2 Systems Benefits

CCC materials are used in various components and systems because they provide one or more key systems benefits. Based on the application experiences to date, the major systems benefits are as given in Table 62.

The major systems or componentry benefits have included (a) higher-temperature performance than with other refractory materials, (b) significant weight savings due to low composite density, (c) improved durability or extended life, (d) increased survivability particularly in ultrahigh temperature and radiation environments, (e) component size reduction due to higher operating temperatures and less insulation, (f) mission flexibility due to great tolerance in withstanding a wide range of environmental conditions, (g) increased longevity with lower life-cycle costs, (h) higher reliability due to properties generally in excess of requirements, and (i) not a critical or strategic material but one that is domestically produced by numerous sources. Naturally, the type and degree of benefits to be gained will vary with the specific application being considered.

4.9.3 Future Applications

Many CCC materials have been prototyped, successfully tested, and are awaiting a production decision. These potential future uses of CCC components are listed in Table 63. Most of the uses include (a) components for limited-life and man-rated gas turbine engines, (b) propulsion gas shields for aircraft, (c) flight control surface components for hypersonic aerodynamic vehicles, and (d) defense space structures and (e) expanded uses in aircraft brake systems. Potential industrial uses such as (a) frictional materials for high-speed train and automobile braking systems, (b) furnace heating elements, structural frames and muffles, (c) forging dies for superplastic forming of high-temperature metals, (d) nonreactive crucibles for melting elements and compounds, (e) electrodes, separators and containers for energy fuel cells, (f) components and structures for fusion nuclear reactors, (g) prosthetic implants and devices, (h) space survivable structures, (i) thermal planes for electronic PWBs, (j) heat pipes and radiators for spacecraft, and (k) many more components not reported due to their proprietary nature.

4.10 BUSINESS ORGANIZATION AND MARKETING

4.10.1 Business Organization

The CCC materials industry is a highly segmented business in the United States. There are at least seven different sectors, including (a) carbon fiber suppliers, (b) organic matrix

TABLE 62
SYSTEMS BENEFITS OF CCC MATERIALS

- HIGHER-TEMPERATURE PERFORMANCE
- GREATER WEIGHT SAVINGS
- INCREASED DURABILITY (EXTENDED LIFE)
- GREATER SURVIVABILITY (THERMAL, IMPACT, & RADIATION)
- REDUCED COMPONENT SIZE
- GREATER MISSION FLEXIBILITY
- INCREASED LONGEVITY
- LOWER LIFECYCLE COSTS
- HIGHER RELIABILITY
- NOT A CRITICAL MATERIAL

TABLE 63
FUTURE USES FOR CCC MATERIALS

- WET LUBRICATED PARTS
- THERMAL PLANES FOR ELECTRONIC PRINTED CIRCUIT BOARDS
- SPACECRAFT RADIATORS, ANTENNAS & STRUCTURES
- HYPERVELOCITY ATMOSPHERIC FLIGHT VEHICLE NOSECAPS, LEADING EDGES, & CONTROL SURFACES
- FUSION POWER REACTOR COMPONENTS
- LIQUID PROPELLANT ENGINE COMPONENTS
- GAS TURBINE COMPONENTS
- PLANETARY ENTRY SHIELDS

suppliers, (c) fibrous fabric and preform weavers, (d) fibrous carbon prepreggers, (e) composite manufacturers, (f) substrate coaters, and (g) end-item users. Many companies participate in more than one business segment; a few integrated companies participate in all of the business segments. Suppliers of carbon fibers sell their products to fabric and preform weavers or prepreggers. Suppliers of organic matrix materials sell to prepreggers or to manufacturers. Weavers may also supply manufacturers. CCC producers either coat their own products or contract for these services with external specialized companies. Manufacturers sell completed articles to systems users and, in certain instances, service or refurbish the article during its application life. Organizations participating in the CCC marketplace have expertise in one or more of the seven business segments. Most organizations enter the CCC market with an area specialty and then, by forward or backward integration, enter one or more of the other sectors. Four avenues have been taken for participating in the CCC materials business. They are (a) internal development, (b) technology licensing, (c) acquisition, and (d) joint ventures. Most of the CCC manufacturers have developed their own technology and products via internal developments. The U.S. Textron Specialty Materials is but one example. Funding for the development of CCC technology and products has usually been provided by the Government, especially in the case of defense components. Dual-use products, like CCC disc brakes for military and civilian aircraft, were developed largely with corporate funding. Commercial products, of course, were brought to the marketplace with corporate funding. Some producers of CCC materials, which possessed a limited technology base, broadened their capabilities by licensing additional technology from other sources.

4.10.2 Marketing

4.10.2.1 Properties of Importance

The sales of CCC materials involve a large number of considerations. In general CCC materials are selected for various applications because (a) no other available material will satisfy the specific demanding requirements of the part design or (b) they possess a unique property or combination of properties not found in any other class of engineering materials. Most CCC markets are in the high-temperature area where thermal and thermophysical properties dominate. Frequently the component being considered has been able to take advantage of both thermal properties and other specialized materials properties (like friction coefficient). CCC brake discs are a prime example.

Any application that requires the properties and characteristics of carbonaceous or graphitic materials should examine the potential benefits of CCC materials.

Three or more factors are usually involved in this materials selection. They are (a) material performance, (b) costs, and (c) delivery times. Compared to polycrystalline graphitic materials, CCC materials offer superior mechanical and thermal properties but at the expense of higher cost. CCC materials, however, offer a great range of properites not found in polycrystalline or monolithic materials. By proper selection of constituents and processing conditions, CCC properties can be varied both directionally and over wide values. This unique design-to-use capability, which is inherent in all composite materials, has been advantageously used in many applications. The intrinsic flexibility of composite design has also played a major role in the development of CCC parts and components. Specific and detailed material requirements are generally not known in the early phases of part design. The part requirements usually change with time, but composite materials can generally and quickly adapt to the revised needs by (a) altering the constituent materials, (b) changing orientation of the constituents, or (c) revising the processing conditions. Monolithic materials, on the other hand, are characteristically limited in these respects.

4.10.2.2 Production Quantities and Sales

CCC materials are a relatively small business area when compared to other engineering materials. Company production numbers are rarely cited in the open literature, but reasonable estimates have been obtained from private discussions with leading market managers and business analytical sources.

Some worldwide, Western nations and U.S. CCC material costs and production figures are given in Table 64.

World production of CCC materials in 1985 was reported to be about 230,000 kg (506,000 lb). Sales were estimated at about U.S. $150-175M. Approximately 80 percent of world production was sold in the United States. The majority of worldwide sales were for aircraft brake systems. More specifically, the sales were divided as follows: (a) 63 percent for aircraft brake discs, (b) 14 percent for military and space rocket propulsion systems, (c) 11 percent for military reentry vehicle nosetips, and (d) 12 percent for all other applications including industrial uses. In 1990 a revised production and sales study was performed. It was reported that CCC materials for aircraft brake systems had increased to about 65-75 percent of total production weight, but the dollar sales were only 30 percent of the total sales figures. The CCC frictional brake materials were priced at about U.S. $110-$440/kg ($50-$200/lb), while other forms of CCC materials were sold at significantly higher prices.

TABLE 64
CHRONOLOGY OF CCC MATERIALS COSTS AND SALES

YEAR	EVENT	IMPORTANCE
1974	Structural 2-D CCC materials were U.S. $3300/kg ($1500/lb)	High material costs limited uses to high-performance defense components
1974	Developmental coated 2-D CCCs were U.S. $8800/kg ($4000/lb); coating cost 33%, substrate cost 40%, and inspection cost 20%	Coated 2-D CCC materials were high priced and labor was the dominant cost factor
1976	Available 3-D CCC nosetip materials cost about 30 times that of aerospace polycrystalline graphite materials	Significant CCC materials cost reduction required to enhance prospects for reentry vehicle uses
1977	Developmental grade 3-D fine-weave CCC billets were U.S. $6600/kg ($3000/lb)	High billet costs indicated a need for automated preform weaving and fewer matrix densification cycles
1978	Production 3-D fine-weave pierced fabric CCC billets were U.S. $2640-3080/kg ($1200-1400/lb)	Volume production reduced materials costs by about one-half
1978	Volume production of 2-D CCC brake discs reduced costs to U.S. $275-385/kg ($125-175/lb)	CCC discs became affordable for medium-to-large commercial aircraft brake systems
1983	Large 3-D CCC ITEs cost over U.S. $100,000 with preform preparation 80% and densification 20% of total materials and processing costs	Automated preform weaving needed for significant cost reduction
1985	Worldwide CCC sales were 37% for nosetips/ nosecaps; 31% for rocket nozzles and 31% for brakes	Defense material sales were a major fraction of total sales
1987	Shuttle orbiter nosecap and leading edge components were U.S. $24,000/kg ($10,909/lb)	Oxidation-protected CCC components for man-rated flight vehicles were very expensive
1990	Western nations CCC sales estimated at U.S. $150M-$175M	Annual sales continued to increase
1990	Large volume material costs were: brake discs, U.S. $176-264/kg ($80-120/lb); nozzle ITEs, U.S. $1760-2400/kg ($800-1090/lb); missile nosetips, U.S. $3300/ kg ($1500/lb)	Major manufacturing improvements and volume production produced significantly lower-cost materials

4.10.2.3 Present and Future Markets

During the past two decades, the major markets for CCC materials have been for military applications and defense technology programs. In these uses the ultimate in performance was required, and cost considerations were of secondary importance. Major defense applications included (a) military aircraft brake systems, (b) solid propellant rocket nozzle ITEs and exit cones, and (c) missile reentry vehicle nosetips. The aircraft brake disc market has been and is expected to continue domination of the CCC marketplace. This trend should extend at least into the next century. Virtually all new medium-to-heavy commercial and military aircraft will use structural CCC brake discs, unless the available brake system volume is extremely limited by design. CCC materials typically occupy slightly more volume than competing steel-cermet frictional materials, but CCC discs are lighter weight and more efficient. With time, steel-cermet brake systems in use will wear out and be retired. The flying fleet will thus be composed of an increasing number of aircraft carrying CCC brake systems. In the near term military aircraft sales are expected to decline significantly. This trend will produce a lesser demand for CCC frictional materials in military aircraft brake systems. On the other hand, orders for commercial aircraft are expected to continually rise. At present aircraft orders have been stretched out, but the demand is expected to increase in the late 1990s. The only major new commercial aircraft presently scheduled for production is the U.S. Boeing 777. The aircraft was flight qualified in 1995. Like other large aircraft it contains a CCC brake disc system. In view of the size and quantity of CCC brake discs required for this and similar aircraft, any qualified CCC material supplier can be confident of many years of applicable production and sales. However being a major supplier of CCC frictional materials for new aircraft does not come without major expenses and manufacturing expertise. A dedicated production plant (or major segment of the plant) with surplus capacity is generally needed to accommodate the cyclic demands of the brake industry.

CCC materials will continue to be developed for other machine uses, but the demand is expected to remain relatively small. Brake pads for high-performance cars are an important application, but due to the number of Formula One cars and the small size of the brake pads, total production needs can easily be satisfied with current production facilities. CCC clutch sales will also remain limited. Secondary braking systems for very high-speed trains constitute yet another future market. The CCC brakes have been designed to decelerate a fast-moving train to a speed where conventional brakes can take over. CCC volume and sales in this area will likewise be relatively small. Truck braking systems represent an enormous potential market. Major roadblocks to using CCC frictional materials are (a) high initial material costs, (b) high maintenance and inspection costs, and (c) the need for improved performance. CCC materials for

"wet" or lubricated applications also represent a large but relatively unexplored applications area. In the field of solid rocketry, CCC parts have been standard for many years in nozzle throats and exit cones. Defense production of CCC nozzle parts is presently at a near standstill, and replacement parts may represent the only significant market in the near future. The use of CCC materials in large expendable solid rocket motors, like the French Ariane V, will provide some relief for the CCC propulsion industry. Emphasis will likely shift from the use of CCC materials in large rockets to new applications in smaller tactical motors. The latter field is essentially a new business application area for CCC materials, provided they can be made less expensive. In the field of strategic reentry systems, 3-D and 4-D CCC nosetips are expected to remain the material of choice for nosetips and ultrahigh temperature control surfaces. Few replacement parts for the existing strategic forces will be needed. In fact CCC nosetips on missiles to be destroyed have useful lives greatly exceeding the life of the missile system. Other conventional applications using CCC materials include (a) nosecaps and leading edges for Shuttle Orbiter-like flight vehicles, (b) industrial furnace components, (c) hot pressing dies and molds, (d) hot glass transfer units, (e) containers for radioactive nuclear materials, and (f) other specialized uses too numerous to name.

Other important future applications for CCC materials were previously discussed in section 4.9.3 - Future Applications.

In summary, future CCC markets in the defense sector will continue to be driven by performance and weight considerations. Future commercial uses will be guided mainly by economic factors.

4.10.2.4 In-Stock Materials

A small number of CCC compositions and constructions in simple configurations (flats, rods, etc.) are stockpiled against future orders. For the most part, however, CCC material or component manufacture does not begin until an order is received. Virtually all applications require the composite to be designed and manufactured in accordance with specific performance needs and standards.

4.10.2.5 Delivery Times

The length of time from a material or component order to delivery is characteristically long. It may range from two to twelve months (very large parts). Constituent materials needed for the composites are typically in-stock items, and shipping times are short. Most of the manufacturing time is expended in labor-intensive processes or multiple process

steps. At any given time there may be many parts in various stages of completion (like CCC brake discs). Another disadvantage of long fabrication and processing times is associated with replacing defective CCC materials and components. Part rejection should occur at the earliest phase of manufacture in order to minimize the value added (and lost) during latter stages of production. High material costs argue against production overruns to accommodate in-process losses. Lastly the final manufacturing steps like inspection and machining can be accomplished in reasonably fast operations.

4.10.2.6 Impediments

The knowledge base associated with emerging CCC materials is perhaps the greatest impediment to their marketing and uses. Most of the knowledge is "empirically based," although this situation is rapidly changing. CCC publications are widely scattered in the open literature, somewhat difficult to retrieve, and generally deal with empirical relationships instead of constituent materials:processing:composite property:part performance relationships. Material performance:trade studies for selected applications have been few in number. As a result designers are more comfortable with advocating other state-of-the-art materials they understand. New materials pose unknown and nonquantified risks. In the case of man-rated systems, the risks are generally too high because of the available databases and the accuracy of life prediction models. Many of the CCC materials appear to be in a constant state of evolution as new constituents and processing methods are being developed. Mature CCC materials have limited databases. Most of these databases are either (a) property of the Government or (b) company proprietary. These and other factors tend to inhibit the consideration of CCC materials for new applications.

International marketing of CCC materials has also been restricted by the materials being listed on the CoCOM International Trade and Arms Regulations (ITAR). In 1977 CoCOM nations specified that certain CCC technology, materials, data, and equipment be controlled in its transfer from one individual or organization to another. Basic research was specifically excluded from Governmental control. The basic reason for placing CCC materials on the CoCOM ITAR list was its use in critical strategic systems and limited use in the industrial sectors. CCC materials were thus controlled along with other munition materials. It should be emphasized that this ITAR regulation did not preclude the transfer of technology among interested parties. It just delayed the process until an appropriate Government license was obtained. By this procedure the CoCOM countries were able to maintain an awareness and approval authority over what was being transferred. In spite of this limiting factor, CCC technologists have been able to maintain an understanding of the total technology through

(a) access to "limited distribution" technical documents, (b) attendance at "controlled" technical meetings, (c) unrestricted "open literature" publications, (d) detailed disclosures in patents of the world, (e) joint ventures, and (f) technology transfers.

There will likely be a freer exchange of CCC materials technology in the future. Except for critical defense applications, CCC materials will become more of an internationally-used material. Impacting this situation is the availability of CCC materials from NIIGrafit of Russia to any interested party. Now for the first time, CCC materials have become available and subject only to the agreements of the parties involved. Over 20,000 manufacturing people are reportedly on-site for the development and production of materials and articles. Licensing agreements and joint ventures are being solicited, and NIIGrafit offices have been established in the U.S. and Europe to accommodate anticipated business. One U.S. company has acquired certain CCC marketing rights, except in Russia and the Ukraine.

Lastly, future sales of CCC materials are highly dependent upon the willingness of designers to exploit the attributes of these materials. Substitution design should be an approach of the past, and the new design-to-use philosophy will likely become a routine procedure of the future. If properly implemented, dramatic component improvements can be expected in performance, weight, size, reliability, and other system considerations.

Internally, the CCC industry should examine and re-examine its total developmental and manufacturing capabilities. Most production processes were originally scaled from laboratory sizes and without regard to process economics. Although this was a logical approach for maximum performance defense articles, it left much to be desired for future commercial and industrial uses. There are presently some thoughts and actions concerning the conversion of the defense CCC industry to commercial uses. While this is a noble and useful thought, it appears to be greatly limited. Economical processing and dual-use materials should be selection criteria in the development of future CCC materials, not afterthoughts. Nevertheless, the existing CCC community has previously demonstrated great innovation and will likely continue to accommodate national needs in a most responsive and affordable manner.

SECTION 5
LESSONS LEARNED

The development of CCC materials during the first two decades involved a great deal of empiricism and little science. The absence of a "science-based" program in the USA was due to (a) critical developmental schedules that did not permit research studies, (b) limited presence of the carbon industry in the development of CCC materials, and (c) nonavailability of university courses on applicable subjects. Materials developers, evaluators, manufacturers, and managers were left to slowly develop their knowledge base and technical skills. During these early years many valuable lessons were learned but not documented for the benefit of succeeding technologists. Now for the first time, many of the important "lessons learned" by CCC pioneers will be reported. These valuable experiences should also be useful for application to other areas of materials development.

Table 65 is an outline of the valuable lessons learned during some 35 years of involvement in carbon-carbon science, technology, manufacturing, and applications. These "headliners" are further discussed in the following paragraphs.

5.1 PROGRAM PLANNING AND MANAGEMENT

An analysis of hundreds of CCC materials programs, as well as over 35 years experience in this field, has given rise to the following axioms.

5.1.1 A Critical Need Existed

In general, the need for a CCC material was created by the unacceptability of all other engineering materials for the application being considered. This situation had the enormous advantage of a "ready-made" market for the material to be developed. There was a strong "pull" from the customer and interest in all phases of development. This situation is in strong contrast to the creation of a CCC material without an obvious application outlet. Many of these types of composites were created through discovery or original thoughts. Their development was most difficult, often lacking the proper advocacy, program direction, material property generation, etc.

A systems or component need was often expressed in very general terms. These needs had to be translated into specific materials requirements which is a most difficult task. Moreover, it was common for the systems or component needs to change with time. Fortunately, carbon-based composite materials were able to accommodate these changes due to the intrinsic design flexibility of composite materials.

TABLE 65
LESSONS LEARNED

- ***PLANNING AND MANAGEMENT***
  - A CRITICAL NEED EXISTED
  - A PLANNING ROADMAP WAS REQUIRED
  - QUANTITATIVE GOALS WERE ESSENTIAL
  - A STRONG ADVOCATOR WAS A MUST
  - PROGRAM OWNERSHIP WAS VITAL
  - LONG-TERM FUNDING WAS HELPFUL
  - OVERSEAS PROGRAMS HAD COMMONALITIES WITH DOMESTIC EFFORTS
- ***MANUFACTURING***
  - PROGRAM INTEGRATION PRODUCED TIMELY AND COST-EFFECTIVE MATERIALS
  - INTERDISCIPLINARY TEAMS WERE MORE PRODUCTIVE
  - TECHNOLOGICAL BREAKTHROUGHS COULD NOT BE PREDICTED NOR SHOULD THEY BE EXPECTED
  - MATERIALS:FABRICATION:PROPERTY:PERFORMANCE STUDIES GREATLY AIDED MATERIALS DEVELOPMENT
  - MATERIALS RESPONSE AND PERFORMANCE SHOULD BE PREDICTED PRIOR TO SPECIMEN/PROTOTYPE TESTING
  - BOTH SUCCESSES AND FAILURES SHOULD BE EXPECTED
  - DOCUMENTED TECHNOLOGY WAS NOT ALWAYS READILY AVAILABLE
  - LOWER COST AND FASTER PROCESSED MATERIALS WERE NEEDED
  - DUAL-USE (Defense and Commercial) MATERIALS DEVELOPMENT REQUIRED GREATER EMPHASIS

TABLE 65 (Concluded)
LESSONS LEARNED

- *TECHNOLOGY TRANSITION AND APPLICATIONS*
  - MATERIAL USE WAS DICTATED BY UNIQUE PROPERTIES OR A BALANCE OF PROPERTIES
  - DESIGN-TO-USE APPROACH TOOK ADVANTAGE OF INTRINSIC MATERIAL PROPERTIES
  - TIMELY AVAILABILITY OF A MATERIAL WAS CRITICAL
  - UNANTICIPATED AND NONQUANTIFIED RISKS DELAYED THE USE OF A NEW OR IMPROVED MATERIAL
  - A LARGE MATERIAL DATABASE WAS GENERALLY NEEDED
  - PROTOTYPES INCREASED CONFIDENCE IN THE USE OF NEW AND IMPROVED MATERIALS
  - GROUND-BASED TEST FACILITIES DID NOT ALWAYS UNCOVER MAJOR MATERIAL PERFORMANCE PROBLEMS

5.1.2 A Planning Roadmap was Required

The creation of a master technology "roadmap" was certainly one of the most difficult planning operations. This planning roadmap contained (a) all of the key activities in their proper time frame, (b) the interrelationship and dependency of individual tasks upon each other as well as needed external technology, (c) the length of time for each major task, (d) annual and total resources required, and (e) expected major milestones and decision points. This type of planning roadmap was essential for convincing management that the program (a) was well thought out, (h) was properly integrated, (c) recognized the major problems and issues, (d) had realistic goals, and (e) was reasonably priced. In addition the roadmap permitted an assessment of anticipated results versus existing requirements. The roadmap provided the key document for dialogue between management, program supervisor, and laboratory personnel.

5.1.3 Quantitative Goals were Essential for Later Measuring Program Progress

Many materials development programs contained only generalized and nonquantified goals. This situation was due to the uncertainties associated with specific component needs, and the nonpredictability of future research and development accomplishments. However, program success was greatly increased with (a) the selection of a baseline "state-of-the-art" material and (b) quantitative goals whenever possible. The baseline material and its properties served as a reference point from which developmental progress was measured. Quantitative goals pertaining to properties, characteristics, processing, economic, and other factors served to measure progress being made and to establish an end point for the program.

5.1.4 A Strong Advocator was Essential

An important ingredient to every successful program was a strong advocator. This person (a) was personally convinced of the program's need, (b) believed in its ultimate success, and (c) spent an enormous amount of time recommending and defending the effort. Without such a person most projects were not approved for initiation or later died due to lack of support and reallocation of funds to other projects.

5.1.5 Program Ownership was Vital

Ownership of successful programs involved both management and technical personnel. Senior management provided the general direction for the effort. The first-level program manager was responsible for more detailed program guidance. The supporting technical personnel were responsible for accomplishing the detailed work. Unless management felt some

degree of "ownership" of a program, it was likely to be terminated due to lack of attention and support. A number of programs died a slow death due to (a) wavering support by existing or new managment or (b) declining interest by technical personnel as the depth of problems became clearer and the technical options became fewer in number.

5.1.6 Long-Term Funding was most Helpful

Program funding has also been a major factor in program support. Both adequate and long-term funding greatly helped in producing an acceptable product. Annual funding of multi-year projects, which is common in U.S. Government programs, often reflected a lack of vision and commitment. Annually-funded programs generally failed to attract top technical talent, and the results were often obvious. On the other hand overseas CCC programs were routinely funded for the entire length of the effort.

5.1.7 Overseas Programs had some Commonalities with Domestic Efforts

CCC programs originating outside the U.S. had some common objectives, often different technical approaches, but resulted in new materials satisfying systems needs. For example, the requirements for throat regions of U.S. large solid propellant motor nozzles have been satisfied with 3-D CCC material. In France a similar requirement resulted in the development of 4-D CCC materials. These overseas programs were also characterized by (a) greater government involvement in the selection of CCC projects and developmental sources, (b) national integration of best available talent in which competitive organizations were frequently made a part of the team, (c) close involvement of both systems and materials organizations, (d) less critical delivery schedules, and (e) mandatory use of the newly-developed material product. Overseas CCC programs often involved (a) shorter developmental cycles, (b) fewer resources, and (c) greater flexibility in matching developmental achievements with systems needs. These overseas programs, however, were often assisted by a general knowledge and results of previous U.S. programs.

5.2 TECHNOLOGY DEVELOPMENT

Once a project was approved for initiation, the program burden shifted from the planning phase to the accomplishment phase. Important lessons from previous efforts are further discussed in the following text.

5.2.1 Program Integration Produced more Timely and Cost-Effective Materials

The early years of CCC materials development were characterized by each discipline (designer, developer, analyst, tester, etc.) contributing a portion of the total developmental cycle. Each discipline produced the best possible product, but little consideration was given to (a) any potential follow-on problems and (b) the overall situation. The product of each group was a technical report, possibly a presentation or an article. Without an existing integration plan, much time was often lost in transitioning the product from one contributing group to its successor. In more recent times the total materials cycle has been integrated and displayed in a technology roadmap. The impact of these integrated programs has been significant. New and improved materials have been more likely to be delivered on time, with the desired properties and characteristics and within the allocated resources.

5.2.2 Interdisciplinary Teams were more Productive

Many projects were staffed with technical personnel having the same general eduction and experience. The performance of these teams tended to be rather predictable, if not limited. Interdisciplinary teams, on the other hand, were usually (a) more inquisitive, (b) dynamic, and (c) productive. The team individuals often had a better grasp of the problem, synthesized a solution from widely diversified technological facts, proceeded in a rather unconventional manner, but arrived at a workable solution.

5.2.3 Technological Breakthroughs could not be Predicted

The goals of some CCC programs have greatly exceeded available resources and development, thus only a materials breakthrough could insure success. Breakthroughs, however, cannot be predicted nor produced on a timely basis. They have occurred occasionally in the development of CCC materials, often when least expected. The possibility for a materials breakthrough was frequently enhanced with (a) an interdisciplinary team or (b) an enormous amount of resources.

5.2.4 Materials:Property:Performance Trade Studies Greatly Aided Materials Development

Composite constituents, constructions, and processing methods offered great flexibility in tailoring developmental materials to the general needs of a given component. Guidance is needed throughout a materials development, however, in order to obtain the necessary material properties. Trade studies involving material properties:performance features

have proven to be very helpful in (a) identifying the most important composite properties, (b) providing a focus on limiting properties, (c) establishing a balance between properties and performance, and (d) aiding the materials developer in making the proper choices. Unfortunately there have been few of these types of programs during materials development. Such programs have typically been initiated during advanced development or just prior to a manufacturing technology demonstration.

5.2.5 Material Performance should be Predicted Prior to Testing

Analytical codes served to calculate properties of new material analogues without the time and expense of associated empirical work. A subsequent correlation of predicted versus experimentally-determined properties indicated the (a) degree of acceptability of the computer code or (b) need for further code upgrading. Experience gained in this manner (a) greatly improved confidence in existing codes, (b) highlighted code deficiencies, and (c) helped build a sounder technological base. Likewise, the performance of a CCC material should be predicted prior to testing in simulated or actual service environmental conditions. After correlation of predicted versus experimental results, the test data were used to upgrade the computer code. This particular approach was very helpful in formulating reliable life prediction codes, although much additional work remained in this area.

5.2.6 Both Successes and Failures should be Expected

The successes in every program were routinely highlighted. The failures and causative factors were often ignored. But in every program, both successes and failures were inevitable. Often much was learned by analyzing failures. As the number of unproductive approaches began to grow and progress slowed, the future of the project began to be put in doubt. Human tendency was to cancel the project and invest in another "more-promising" or "more-fashionable" effort. In most cases, however, it was found that the new effort being considered was more attractive only in theory. Its many deficiencies, impediments, and issues had yet to be uncovered by actual developmental work.

5.2.7 Documented Technology was not Always Readily Available

For every CCC program there was a wealth of technical information documented in the literature. Its retrieval, however, was very difficult even with the availability of computerized searching. Fast-paced programs typically have not taken the time to retrieve useful information, approaches, data, etc. Corporate-funded research and development have been rarely made available to the general public. Corporate proprietary information has sometimes been

shared with designated partners, but for the most part it remained the exclusive property of a single company. In the U.S. most CCC technology, manufacturing, and equipment (except for basic research) information has been restricted to Government-approved sources. Little has been exchanged on an international basis, although important sales of technology and manufacturing know-how have taken place between friendly nations. All of these informational retrieval and exchange impediments have slowed the international development of CCC materials.

5.2.8 Lower-Cost and Faster-Processed Materials were Needed

CCC materials often contain expensive constituents, are produced with lengthy and many process steps, and thus have had high delivered materials costs. Great progress had been made in lowering the costs of constituents, but manufacturing has remained complex and lengthy. Most of the existing manufacturing processes were based on scaling up laboratory processes, and little thought was given to the ultimate material costs. This situation was not too critical since the major outlets were for high value defense componentry. Commercial and industrial products, on the other hand, require lower-cost composites to compete with existing materials. Dramatic progress will be required to obtain low-cost CCC materials of widespread interest to the industrial world.

5.2.9 Dual-Use Materials Required Greater Emphasis

Most CCC materials have been designed for high-performance applications. These specialized materials have thus been quite costly and of little interest to the industrial world. 2-D and pseudo-3-D CCC frictional materials have been developed for both military and commercial uses. Essentially the same types of material are used for the brake discs of military and civilian aircraft, racing car discs, clutches, etc. The CCC frictional industry has thus been able to accommodate the cyclic needs of the military and industrial worlds with two types of common materials. CCC organizations that have specialized in high-performance materials, such as 3-D composites, have experienced great difficulties in transitioning these materials to commercial uses. The price was simply too high and the manufacturing times were too long. These organizations have experienced significant downsizing as military production programs slowed to a trickle. New CCC materials developments, however, have given greater emphasis to dual-use materials. One example has been thermal planes for electronic circuit boards. With significant cost reduction in mesophase carbon fibers, high thermal conductivity planes are expected to be widely used in both military and civilian spacecraft.

5.3 TECHNOLOGY TRANSITION AND APPLICATIONS

Transitioning a new or improved CCC material to an application outlet has been a difficult, frustrating, but most rewarding experience.

In the past defense CCC materials were not used unless absolutely required by the demanding requirements, and all other candidate materials failed to satisfy the specification. As greater experience is gained in engineering CCC materials for applications, this family of materials should become more competitive with other classes of high-performance materials. For example, frictional CCC materials have been found to offer superior properties at competitive prices compared to cermet-steel materials in aircraft and racing car braking systems.

5.3.1 Material Use was Dictated by its Unique Properties or Balance of Properties

The application outlet for any given CCC material was dictated by its unique properties or a combination of properties and characteristics. Reentry missile nosetips and rocket nozzle throats relied on the very high thermal stability (low recession), thermostress resistance, and high-temperature mechanical properties. The directional thermal conductivity of certain CCC materials has led to various thermal management applications, like thermal planes for electronic circuit boards. Other applications have no thermal requirements. The use of CCC materials in medical prostheses and bone implants has advantageously used their outstanding chemical resistance to body fluids coupled with adequate structural properties.

5.3.2 Design to Use Took Full Advantage of Intrinsic Material Properties

First-generation design efforts with CCC materials involved a "materials substitution" philosophy. Components containing metallic or high-temperature ablative materials were essentially reproduced with CCC materials. Rocket nozzle throats were replaced with identical 2-D CCC throats. Reentry missile heatshields of carbon fabric-reinforced phenolic materials were replicated with 2-D and 3-D materials. While this design approach aided greatly in the introduction of CCC materials, it was also limiting and failed to take full advantage of the many intrinsic properties of the materials. This design philosophy was eventually replaced with a "design-to-use" approach. One example was the 3-D CCC plug nosetip which replaced the graphite shell design. Another example was the 3-D CCC integrated throat-entrance section (ITE) which replaced multisectioned and bonded ablative materials. Yet another example of great importance was the design of a full rotor and stator of CCC material rather than the use of frictional pads on structural brake elements.

5.3.3 Timely Availability of a Material was Critical

Component and systems materials selection dates have frequently been set without adequate consideration of the probable availability date for the needed CCC material. Consequently many CCC materials achieved state-of-the-art status after the passing of a critical material selection date. This situation had the undesirable effects of (a) delaying the delivery of a component, (b) necessitating component redesign, (c) using an alternate and lower-performance material, and (d) obtaining only a partial return on investment. Conversely some CCC materials have been developed before a need arose. Much time was lost in finding a proper application outlet and tailoring the material properties to the end item requirements.

5.3.4 Unanticipated and Nonquantified Risks Delayed Use of a New Material

There was a great reluctance for designers to use new and improved CCC materials in components and systems because they represented unknown and nonquantified risks. Material properties were not measured in adequate numbers and depth; predictive codes were inadequate for reliable performance or lifetime forecasts; performance trade studies were not available on the specific or similar components; and most important, there was no previous flight test or actual use experience. All of these factors (and others) inhibited progress, but eventually, the potential performance payoff of CCC exceeded the risks involved. The necessary applications-oriented activities were then initiated, and for most cases the CCC material was successfully used.

5.3.5 A Large Database was Generally Needed

Materials properties and performance data are required at every stage of development to (a) guide composite development, (b) identify potential uses, (c) perform trade studies, (d) conduct design efforts, and (e) other reasons. The type and extent of a materials database needed at each stage of material development and application has been resolved in the U.S., but in general there never seems to be enough data to satisfy the users. Material developers have routinely measured only the most important and limiting properties, and the database has been spread over many versions of the material. Designers, on the other hand, have preferred a statistical database on only a few materials. Inadequate databases were most obvious for the design of man-rated components, where expensive and extensive "A" basis allowables were needed. One example of the latter was the design of the nosecap and leading ledges for the U.S. space shuttle orbiter.

5.3.6 Prototypes Increased Confidence in the Use of New Materials

CCC prototypes were typically made available during an advanced development program, an engineering development program, or a manufacturing development program. Prototypes fabricated during manufacturing technology programs usually focused on scale-up and process economic issues. Prototypes manufactured during advanced development or engineering development phases typically focused on performance features of subscale or full-scale articles in simulated or actual service environments. In any case the prototypes greatly increased confidence in the utility of a given CCC material because it necessarily involved the services of designers, fabricators, evaluators, and analysts.

5.3.7 Ground-Based Test Facilities did not Alwavs Uncover Major Materials Problems

Ground-based testing of CCC prototypes was an essential element of the total developmental cycle. Simulation of actual service conditions was frequently imperfect, in spite of the use of all available technology. Performance could only be guaranteed by a prototype in the actual service environment. The rocket nozzle industry, for example, relied heavily on the use of an instrumented CCC part to acquire data and verify performance acceptability. Missile nosetip designers, on the other hand, have employed elaborate ground-based air arc heaters for simulation and testing of CCC materials. One class of intermediate density, 3-D CCC nosetip material passed all of the available ground checks, yet it failed in flight. Fortunately data acquisition of the reentry flight provided the cause of material failure. Subsequent development of a more appropriate ramp heating test for the high-pressure air arc heater and certain adjustments in materials construction and processing provided satisfactory solutions.

SECTION 6
SUMMARY

6.1 THE TECHNOLOGY BASE

Summary statements on the technology of CCC materials are given in Table 66. Carbon-carbon composites (CCCs) are members of the advanced composite materials family. They are composed of a carbonaceous (sometimes graphitizable) matrix, a carbonaceous (usually a fibrous) reinforcement, and occasionally other constituents to impart specialized properties. CCC materials are sometimes classified with the family of ceramic-matrix composites, but they possess many properties quite unlike other ceramic matrix composites.

CCC materials were largely an American invention. Three different organizations in the United States created various forms of these materials during the 1960/1961 era. Several hundred types of CCC materials have since been created, with most of the developmental work taking place in the U.S., France, England, Germany, and Russia. Materials are now available with a wide range of properties, due to the intrinsic versatility of composite design, available constituents, and various processing methods. Composites have been fabricated with 1-D to 11-D fibrous reinforcements and various resinous chars, pitch cokes, or pyrolytic carbon matrices. 2-D, 3-D, and 4-D-reinforced composites have been the most widely used. These types of composites have been fabricated as uncoated or coated materials or as oxidation-protected composites. Both structural and nonstructural versions of CCC materials have been developed. Ablative (nonstructural) CCC technology has been highly developed and it is relatively mature. Structural CCC technology, however, requires additional advances.

CCC materials have a unique combination of properties which can be varied over wide ranges. In the absence of oxidizing species, they retain their room-temperature mechanical properties at over 2225°C (4037°F). For uses in oxidizing environments, the material constituents must be protected. Refractory ceramic coatings are often used for this purpose, but their upper-use temperatures are about 1650°C (3002°F). CCC materials also exhibit high thermal conductivity and low thermal expansion which in turn gives them exceptional resistance to thermal shock and thermally-induced stresses. All of the properties of CCC materials are influenced greatly by the type, amount, and orientation of the constituents and the processing conditions they experience in being transformed into a composite material.

Perhaps the greatest limitation of CCC materials is their susceptibility to oxidation. High-temperature air and strong oxidizing media may erode the solid carbonaceous materials or greatly

TABLE 66
CCC TECHNOLOGY BASE SUMMARY

- CCC WAS AN AMERICAN INVENTION, BUT OTHER NATIONS LATER PROVIDED IMPORTANT CONTRIBUTIONS
- CCCs WERE THE PRODUCT OF 35 YEARS OF EVOLUTIONARY DEVELOPMENT
- COMPOSITE DESIGN ENABLED A WIDE RANGE OF PROPERTIES AND GROWTH POTENTIAL
- CCCs HAVE A UNIQUE BALANCE OF HIGH-TEMPERATURE, STRUCTURAL, DIMENSIONAL, FRICTIONAL, AND OTHER PROPERTIES
- COMPOSITE PROPERTIES HAVE BEEN GREATLY UPGRADED WITH NEW CONSTITUENTS AND IMPROVED PROCESSING
- HYBRID (CERAMIC-MATRIX) COMPOSITES OFFER INTRINSIC OXIDATION RESISTANCE

alter other useful properties. Ceramic coatings have been developed to impede the flow of oxidizing species to the susceptible substrate, and a variety of oxidation scavengers, particulates, and other noncarbon materials have been developed. Much progress has been demonstrated, but additional achievements are needed. If successful, many new applications outlets will be developed for oxidation-protected composites.

CCC materials, like other forms of composite materials, should be designed and fabricated to meet specific engineering requirements. For that reason there are few off-the-shelf materials available to the customer. Design-to-use, however, requires the concurrent engineering efforts of the design engineer, manufacturing specialist, and materials scientist. Such coordinated efforts will generally produce the desired material satisfying all of the technical, manufacturing, economic, and availability concerns of the customer.

Empirical approaches were used to create the first generation of CCC materials. These efforts were surprisingly successful, but as the field matured, it became painfully apparent that a more scientific foundation was required to further advance the technology. Material constituents:fabrication:processing:property: performance relationships were needed. Some relationships were developed in later years, but today these relationships are still not well understood. The "science" of CCC materials has yet to be generated, although the scientific principles of "carbonaceous" materials have greatly aided the development of related composite materials. Virtually all key scientific aspects of CCC materials have yet to be researched in depth, and many years will be needed for such activities to be accomplished.

The development of CCC materials has been supported by both experimental and analytical activities. Unique test facilities were developed to measure materials behavior in extreme environmental conditions. High-pressure air arc heaters, for example, were designed to measure the ablation characteristics and specimen shape history during exposure to simulated reentry heating conditions. High-temperature test facilities were also built to quantify the properties of CCC materials. These properties were later used to guide materials development and component design. Modeling of materials performance was also highly developed to describe the thermal, mechanical, physical, and chemical responses. Such models greatly assisted in materials development, failure analysis, and performance predictions. Nondestructive inspection and evaluation methods were adapted for use with CCC materials to identify anomalies and defects and to assess the general quality of the material. Computer-aided tomography (CAT) has proven to be most helpful, but much additional work remains to relate material defects with property alterations. Materials developmental progress to date has been rapid and significant but

important needs remain. The most important needs appear to be (a) lower-cost composites and (b) wider-temperature range, longer-life oxidation composites.

6.2 MANUFACTURING AND PRODUCTION

Table 67 contains brief statements on CCC materials manufacturing. CCC manufacturing has been accomplished primarily by the United States, France, England, Russia, and to some extent Germany. Current worldwide production has been difficult to determine, but it is estimated that about 0.23 Mkg (0.51 Mlb) to 0.45 Mkg (0.99 Mlb) of CCC materials are being fabricated on an annual basis. These products have considerable economic importance. Worldwide annual sales have been on the order of $150-$225 million or more. About 90 to 95 percent of current CCC production has been for brake discs of commercial and military aircraft. This application area is expected to become even more important as CCC defense sales decline and aircraft sales increase. Since the mid-1970s, CCC technology has been highly controlled for both defense and proprietary reasons. Nevertheless, a number of technology sales and joint ventures have accelerated the transfer of manufacturing know-how between the leading world manufacturers. CCC materials of the past have been very high priced compared to other engineering materials, but significant progress has been made in reducing costs and improving quality. Today large volume materials cost about $176-264/kilogram ($80-120/pound) for 2-D frictional CCC, about $3300/kilogram ($1500/pound) for 3-D fine-weave orthogonal CCC, and approximately $1760-$2400/kilogram ($800-1090/pound) for 3-D cylindrical CCC materials. Ceramic-coated 2-D CCC materials cost even more. Lastly, manufacturing processes for lower-cost and faster-processed materials appear to be the most critical need.

6.3 APPLICATIONS

Summary statements are given in Table 68 concerning the applications of CCC materials. CCC materials are important to the national security of high technology countries. They are important to the growth and competitiveness of certain nation's aerospace and technology base. The materials have been used in specialty defense, aerospace, industrial, and other applications. Over 125 types of prototypes have been fabricated to date, and over 40 of them have been transitioned to operational use. The use of CCC materials as either substitutes for existing materials or as designed-to-use materials has enabled great advances in components and systems. The first CCC prototypes (1962/1963) were used in solid motor nozzle throats and exit cones. Low erosion, thermostructural survivability, less weight, and other desirable features were demonstrated. Today virtually all medium-to-large diameter solid propellant motors contain a

TABLE 67
CCC MANUFACTURING BASE SUMMARY

- WORLD'S LEADING MANUFACTURERS ARE IN THE UNITED STATES, FRANCE, AND RUSSIA
- WORLDWIDE PRODUCTION ESTIMATED AT ABOUT 230,000-450,000 kg (506,000-990,000 lb)
- WORLDWIDE ANNUAL SALES ARE U.S. $150-250M OR MORE
- ABOUT 90-95% OF CURRENT PRODUCTION IS FOR AIRCRAFT BRAKE SYSTEMS
- JOINT VENTURES HAVE ACCELERATED THE TRANSFER OF MANUFACTURING KNOW-HOW
- LARGE VOLUME MATERIAL COSTS ARE ABOUT U.S. $176-264/kg ($80-120/lb) FOR 2-D CCC; $3300/kg ($1500/LB) FOR 3-D FW CCC; AND $1760-2400/kg ($800-1090/lb) FOR 3-D CYLINDRICAL CCC

TABLE 68

CCC APPLICATIONS SUMMARY

- CCC MATERIALS ARE IMPORTANT TO THE NATIONAL SECURITY OF HIGH TECHNOLOGY COUNTRIES
- CCC MATERIALS ARE IMPORTANT TO THE GROWTH AND COMPETITIVENESS OF CERTAIN NATIONS' AEROSPACE AND TECHNOLOGY BASE
- CCC MATERIALS HAVE BEEN USED IN SPECIALTY DEFENSE, AEROSPACE, INDUSTRIAL AND OTHER APPLICATIONS
- CCC MATERIALS HAVE ENABLED GREAT ADVANCES IN CERTAIN SYSTEM AND COMPONENT PERFORMANCES
- OVER 125 DIFFERENT PROTOTYPES HAVE BEEN FABRICATED AND OVER 40 TYPES TRANSITIONED TO OPERATIONAL USES
- FIRST PROTOTYPES (1962/63) WERE NOZZLE THROATS AND EXIT CONES
- NEXT-GENERATION APPLICATIONS ARE EXPECTED TO FOCUS ON THERMAL MANAGEMENT, OXIDATION PROTECTION, AND WET LUBRICATION USES

CCC integral throat-entrance (ITE) section. Other state-of-the-art applications include (a) brake discs and clutches for heavy mass vehicles, (b) missile nosetips, (c) leading edges and control surfaces of hypersonic flight vehicles, (d) furnace heater elements and insulation, (e) wall components of fusion power reactors, (f) thermal planes of electronic printed-circuit boards, and (g) many, many more uses. Future components are expected to involve various thermal management, oxidation-protected, and wet-lubricated frictional parts.

SECTION 7
CONCLUDING REMARKS

Table 69 provides a number of conclusions and concluding remarks concerning CCC materials. CCC materials technology, manufacturing and applications will continue to be dominated by French, United States, and possibly Russian efforts. Germany had an outstanding research effort in the 1970s and 1980s, but the program has been diminished due to slow progress in commercializing CCC materials. As the major world powers have increased demilitarization efforts, defense markets for CCC materials have shrunk. The defense supplier base has thus been greatly reduced, and some organizations have left the business. Research and development, which historically has been funded by defense organizations, has been on the downturn. It is perhaps time for the major industrial users of CCC materials (i.e. frictional materials) to share a greater fraction of CCC research and development costs and also share the information with the rest of the industry. Defense conversion of CCC manufacturing capabilities for industrial uses has not been attempted, and it would likely not succeed. Commercial and industrial needs are simply not sufficiently great to warrant such expenditures. Dual-use materials, however, appear to be a very attractive approach for the future. Material performance could be degraded somewhat to achieve major decreases in material costs. There appears to be sufficient "high-performance" CCC materials in an "off-the-shelf" category for near-term needs. The development of new dual-use CCC materials would require cooperative agreements between defense and industrial organizations. Together, both groups could look forward to new and improved materials satisfying their needs and at an affordable cost.

TABLE 69
CONCLUDING REMARKS ON CCC MATERIALS

- CCC TECHNOLOGY, MANUFACTURING AND APPLICATIONS WILL CONTINUE TO BE DOMINATED BY FRENCH AND UNITED STATES EFFORTS
- WORLD TECHNOLOGY AND MANUFACTURING TRANSFERS HAVE BEEN MUTUALLY PRODUCTIVE
- DEFENSE SUPPLIER BASE IS SHRINKING AS DEMILITARIZATION INCREASES
- COMMERCIAL AND INDUSTRIAL CCC USERS SHOULD SHARE A GREATER FRACTION OF RESEARCH AND DEVELOPMENT COSTS
- DUAL-USE MATERIALS AND TECHNOLOGY PROGRAMS MAY PROVIDE THE GREATEST BENEFITS
- LOWER-COST AND FASTER PROCESSED MATERIALS ARE CRITICAL TO EXPANDING USES

SECTION 8
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SECTION 9
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Thousands of articles, presentations, patents, book chapters, reports, and books on CCC materials (and their constituents) have been published during the past three and one-half decades. Many of these documents are in the "open literature" for all to retrieve and read. Many of the documents are also "limited in distribution" to safeguard defense or proprietary considerations. The unrestricted literature has been difficult to locate because of the diverse nature of the publications. Even after locating the desired literature, there are essentially too many publications to read. To assist those new to the science and technology of CCC materials, a selected bibliography of overviews and key publications has been prepared. Readers interested in more details should examine the references given in each publication.

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9.2 APPLICATIONS

Only a limited number of articles have been published on the applications of CCC materials because of (a) company proprietary considerations and (b) defense considerations. Nevertheless a number of publications have been found, and they are listed according to the specific applications area.

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APPENDIX 1
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Amorphous Carbon	A carbon material without long-range crystalline order.
Anisotropic	Not isotropic; exhibiting different properties when tested along axes in different directions.
Axial Strain	The linear strain in a plane parallel to the longitudinal axis of the specimen.
Biaxial Woven Fabrics	Fabrics with interlaced yarns oriented along the 0°/90° axes.
Braid	A narrow tubular or flat woven fabric produced by intertwining a single set of yarns according to a definite pattern.
Braiding	A fabric or preform formation process that intertwines.
Brittle	Characteristic of a material denoting relatively low elongation or deformation prior to fracture.
Carbon	The element 6 of the periodic table.
Carbon-Carbon Composite (CCC)	A composite material consisting of a carbon or graphite fiber in a carbon or graphite matrix.
Carbon Fiber (CF)	Filaments consisting of nongraphitic carbon obtained by carbonization either of organic, synthetic or natural fibers and subsequent heat treatment.
c-Direction	The direction perpendicular to the basal planes in a crystalline graphitic material.
Carbonization	Process of formation of material with increasing carbon content from an organic material, usually by pyrolysis.
Catastrophic Failure	A totally unpredicted failure of a mechanical, thermal, or electrical nature.
Ceramic Matrix Composite (CMC)	A material consisting of a ceramic fiber surrounded by a ceramic matrix, such as a silicon carbide fiber-reinforced silicon carbide matrix.
Char	Carbonization product of a natural or synthetic organic material which has not passed through a fluid stage during carbonization.
Characteristic	A distinguishable feature of a material which is partially dictated by environmental parameters.
Chemical Vapor Deposition (CVD)	The process which involves the thermal pyrolysis of a chemical compound or compounds, thereby producing a vapor and subsequent condensation of a single element or combination of elements in solid form.
Chemical Vapor Infiltration (CVI)	A chemical vapor deposition process in which a single element or combination of elements in solid form are deposited into a porous material like a fibrous preform.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Coefficient of Expansion	A measure of the change in length or volume or an object specifically measured by the increase in length or volume of an object per unit length or volume.
Coefficient of Friction (COF)	A ratio of the tangential force that is needed to start or to maintain uniform relative motion between two contacting surfaces to the perpendicular force holding them in contact.
Coke	A highly carbonaceous product of pyrolysis of organic material at least part of which has passed through a liquid or liquid-crystalline state during the carbonization process.
Composite Material	A combination of two or more materials differing in form or composition on a macroscale; the constituents retain their identity in the newly-formed composite; the constituents can usually be physically identified in the composite, and they exhibit an interface between one another.
Compressive Modulus	Ratio of compressive stress to compressive strain below the proportional limit; theoretically equal to Young's modulus determined from tensile experiments.
Compressive Strength	The ability of a material to resist a force that tends to crush or buckle; the maximum compressive load sustained by a material divided by the original cross-sectional area of the material.
Conductivity	The thermal or electrical conductance of a unit cube of a given material, i.e., conductivity per unit volume.
Constituent	An element of a larger grouping; the principal elements in a composite material like a fiber, matrix, or filler.
Corrosion Resistance	The ability of a material to withstand contact with a surrounding material or atmosphere without degradation or change in properties.
Creep	The change in dimensions of a material under load over a period of time, not including the initial instantaneous elastic deformation; the time-dependent part of strain resulting from an applied stress.
Crystallite	Very small, imperfectly-formed crystal in which the unit cell repeats itself in a continuous manner.
Damping	The decay with time of the amplitude of free vibrations of a specimen.
Deformation	A change in the shape of a specimen caused by the application of a load or force.
Delamination	The separation of the layers of material in a laminate.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Densification	Process of increasing the density of a material, usually through externally applied thermal or thermal stresses or by filling accessible pores.
Density	The mass per unit volume.
Dimensional Change	A generic term for changes in length, width, or thickness of a material subjected to specified conditions.
Dimensional Stability	Ability of a material to retain the precise shape to which it was fabricated or machined.
Elastic Modulus	Ratio of the stress or load applied to the strain or deformation produced in a material that is elastically deformed.
Elongation	Deformation caused by stretching; the fractional increase in length of a material when stressed in tension.
Elongation at Break	The elongation at the moment of material rupture; also known as strain-to-failure.
Fabric	Any nonwoven, woven, knitted, or braided fibrous structure or three-dimensional fibrous assembly.
Fatigue	The failure or reduction of mechanical properties after repeated applications of stress.
Felt	A textile (fabric) characterized by the densely matted condition of most or all of the fibers of which it is composed.
Fiber	A general term used to refer to filamentary materials; the finite length is at least 100 times its diameter.
Filament	The smallest unit of a fibrous material.
Filament Winding	A process for fabricating a composite in which the continuous reinforcement (with or without a matrix) is placed over a rotating and removal mandrel; the shape of the product is generally a surface of revolution.
Fill	Yarn oriented at right angles to the warp in a woven fabric.
Filler	A solid material, usually in particulate form, which is added to a matrix to obtain specialized composite properties.
Fine Woven	A fibrous preform in which the yarns or tows are of small diameter and closely spaced.
Flexural Strength	The unit resistance to the maximum load just before failure in bending.
Fracture	The separation of a material.
Fracture Toughness	The damage tolerance of a material containing initial flaws or cracks.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Graphite (G)	An allotropic form of the element carbon; a material consisting essentially of graphitic carbon.
Graphitizable Carbon	A nongraphitic carbon which upon high heat treatment converts into graphitic carbon.
Graphite Fiber (GF)	A fiber composed of the element carbon and made by the oxidation, carbonization, and graphitization of a precursory organic fiber.
Graphitization	A solid-state transformation of thermodynamically unstable nongraphitic carbon into graphite by thermal activation.
Harness Satin (HS)	A fabric weaving pattern which produces a satin appearance; 8-harness means the warp tow or yarn crosses over seven fill tows (or yarns) and then under the eighth in a repeating manner.
Heat Treated (HT)	A material processed at a temperature above its normal process temperature to improve thermal stability, dimensional stability, density, thermal conductivity, and other properties.
Highly-Oriented Pyrolytic Graphite (HOPG)	Pyrolytic graphite with angular spread of the c-axes of crystallites of less than one degree.
High-Pressure-Impregnation-Carbonization (HIPIC)	A PIC process carried out at high pressures, usually between 35 MPa (5.1 ksi) and 105 MPa (15.2 ksi).
Hoop Strength	The circumferential strength in a material of cylindrical form subjected to internal or external pressure.
Hybrid Matrix Composite	A material consisting of a carbonaceous fiber surrounded by a noncarbonaceous matrix, such as a carbon fiber-reinforced silicon carbide matrix composite.
Impact Strength	The ability of a material to withstand shock loading.
Inhibitor	A substance that retards a chemical (like oxidation) reaction.
Interface	The boundary or surface between two different media, like the contact area between a fiber and a matrix.
Interlaminar	An object, event, or potential field referenced as existing or occurring between two or more adjacent laminae.
Interlaminar Shear	Shearing force tending to produce a relative displacement between two laminae in a laminate along the plane of their interface.
Involute Composite	A two-directional fabric lay-up used to produce a closed-shape cylinder or conical structure in which each fabric layer leading edge is at the inner diameter surface and the trailing edge at the outer diameter surface is rotated about 110° from the leading edge.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Isostatic	Equal in all directions.
Isotropic	Having uniform properties in all directions.
Izod Impact Strength	Energy absorbed by shock loading a notched specimen bar which is held at one end and broken by striking.
Laminate	To join laminae with a bonding material, usually with heat and pressure.
Linear Expansion	The increase in a given dimension measured by the expansion or contraction of material subjected to a thermal gradient or changing temperature.
Mass	The quantity of matter in a body.
Matrix	A homogeneous material in which the fibrous reinforcement is imbedded.
Mesophase	An intermediate phase in the formation of carbon from a thermoplastic organic matrix like pitch.
Microcracking	Small cracks formed in composites when thermal stresses locally exceed the strength of the matrix.
Microstructure	A structure with heterogeneities that can be seen through a microscope.
Modulus	The slope of the initial straight portion of a stress-strain or load-elongation curve.
Modulus of Elasticity	The ratio of the stress or load applied to the strain or deformation produced in a material that is elastically deformed.
Multidirectional Reinforcements	Fibrous reinforcements providing structural properties in at least three, but different, axes.
Multifilament Yarn	A large number of fine filaments usually with some twist in the yarn to facilitate handling.
n-Directional (n-D) Composite	A composite material in which substantially all of the reinforcing fibers are oriented in four or more directions, such as a 4-directional composite.
Needled Felt	A textile composed of fibers physically interlocked by the action of a needle loom.
Nondestructive Evaluation (NDE)	The analysis of nondestructive inspection finds to determine whether the material is acceptable for its function.
Nondestructive Inspection (NDI)	A process or procedure for determining the quality or characteristics of a material, part, or assembly without permanently altering the material or its properties.
Nongraphitic Carbons	All varieties of substances consisting mainly of the element carbon with two-dimensional long-range order of the carbon atoms in planar hexagonal networks but without any measurable crystallographic order in the third direction apart from more or less parallel stacking.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Nongraphitizable Carbons	No homogeneous development of the graphitic structure upon heating to 3000°C (5432°F).
Off-Axis	At some angle to the major reinforcement.
Orthogonal Nonwoven Fabric (Preform)	A three-directional fabric manufactured by mutual fiber placement in three or more orthogonal directions with no interlacing.
Orthotropic	Having three mutually perpendicular planes of elastic symmetry.
Oxidation	Generally refers to any chemical reaction in which electrons are transferred; the removal of carbon by oxidizing species; the stabilization of precursor polymeric fibers with the infusion of oxygen.
Oxidation-Inhibited Carbon-Carbon Composite	Same as oxidation-protected carbon-carbon composite.
Oxidation-Protected Carbon-Carbon Composite	A CCC material that contains one or more discrete phases (coating, filler, etc.) to improve its resistance to oxidation.
Parallel Laminate	A laminate of woven fabric in which the plies are aligned in the same position as originally aligned in the fabric roll.
Percent Elongation	The increase in length of a specimen expressed as a percentage of the original length.
Pierced Fabric (PF)	Woven fabric penetrated with fibers in a direction perpendicular to the fabric axes.
Pitch	A high molecular weight material obtained from the destructive distillation of coal or petroleum products. Used as the precursor matrix for CCC materials and for the manufacture of certain carbon fibers.
Plane Weave (PW)	The simplest of the fundamental weaves in which each filling yarn passes alternately under and over each warp yarn; both faces of the woven material are identical.
Ply	A single layer of prepreg.
Polyacrylonitrile (PAN)	The precursor material used in the manufacture of certain carbon fibers.
Porosity	A condition of trapped air, gas, or vacuum within a solid material.
Precursor	A starting material which is changed chemically and physically to yield a new material having greatly different properties.
Preform	A preshaped fibrous reinforcement in the approximate contour and thickness desired in the final part.
Prepreg	Ready to process material in which the reinforcement has been impregnated with a resin or other organic material.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Pressure-Impregnation-Carbonization (PIC)	A densification process for CCC materials involving hot pitch impregnation and carbonization under high temperatures and isostatic pressure conditions; the process is typically carried out in special hot isostatic presses (HIP) equipment.
Property	A distinguishable feature of a material.
Protected Carbon-Carbon Composite	A CCC material that contains a coating or a filler to increase its environmental resistance.
Pyrocarbon (PC)	A solid carbonaceous material formed by the pyrolysis of a carbon-containing precursor.
Pyrographite (PG)	A solid graphitic material formed by the pyrolysis of a carbon-containing precursor.
Pyrolysis	A thermal process in which an organic material is converted into a carbonaceous residue.
Pyrolytic Carbon (PC)	Monolithic carbonaceous material obtained by chemical vapor deposition onto suitable substrates from volatile hydrocarbon compounds at temperatures ranging from 725°C (1337°F) to 1825°C (3317°F).
Quasi-Isotropic Laminate	A laminate approximating isotropy by orientation of plies in several or more directions.
Random	No fixed pattern.
Reinforcement	A strong material used to increase the strength and modulus of a composite.
Resin	A solid organic material, usually of high molecular weight, that is used to form the matrix in plastic composites.
Roving	A number of ends, tows, or strands collected into a parallel bundle with little or no twist.
Satin Weave	A type of fabric weaving in which one warp end is woven over several successive fill yarns and then under one fill yarn.
Shear Modulus	The ratio of shearing stress to shearing strain within the proportional limit of the material.
Shear Strength	The maximum shear stress that a material is capable of sustaining; the maximum load during a shear or torsion test based on the original cross-sectional area of the specimen.
Short Beam Shear (SBS)	A flexural test of a specimen having a low test span-to-thickness ratio such that the failure is primarily in shear.
Size	A material applied to a fibrous product to protect its surface and aid in handling.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Specification	A precise statement of a set of requirements to be satisfied by a material.
Specific Gravity	The density (mass per unit volume) of any material divided by that of water at a standard temperature.
Specific Heat	The quantity of heat required to raise the temperature of a unit mass of a substance one degree under specified conditions.
Specific Properties	Material properties divided by the material density.
Stabilization	A process used to render precursory organic fibers infusible prior to carbonization.
Staple Fibers	Fibers of spinnable length manufactured directly or by cutting continuous filaments to short lengths.
Stiffness	A measure of modulus; the ratio between the applied stress and resulting strain.
Strain	The strain produced in a material by given loading conditions and before creep occurs.
Strand	An untwisted bundle or assembly of continuous filaments, such as tows, ends, and yarns.
Stress	The internal force per unit area that resists a change in size or shape of a body.
Stress Graphitization	A solid-state transformation of nongraphitic carbon into graphite by heat treatment combined with the application of mechanical stress.
Substrate	The region of a composite which is below the original surface.
Surface Treatment	A fiber treatment process used to enhance bonding between the fiber and the matrix.
Symmetrical Laminate	A composite laminate in which the sequence of plies below the laminate midplane is a mirror image of the stacking sequence above the midplane.
Tape	Unidirectional prepreg or woven broad goods manufactured in specified widths.
Tape Wrapped (TW)	Prepreg fabric tape (usually bias cut) is heated and wrapped onto a rotating mandrel and subsequently cooled to firm the surface prior to application of the next tape layer.
Tensile Strength	The maximum load or force per unit cross-sectional area within the gage length of the specimen.
Tensile Stress	A normal stress caused by forces directed away from the plane on which they act.
Tension	The force or load that produces a specified elongation.

APPENDIX 1 (Continued)
GLOSSARY OF TECHNICAL TERMS

Term	Definition
Thermal Conductivity	Ability of a material to conduct heat; the physical constant for the quantity of heat that passes through a unit cube of material in unit time when the difference in temperature of two faces is one degree.
Thermoplastic	Capable of being repeatedly softened by an increase of temperature and hardened by a decrease in temperature.
Thermoset	A plastic that, when cured by the application of heat or chemical means, changes into an infusible and insoluble material.
Three-Directional (3-D) Composite	A composite material in which substantially all of the reinforcing fibers are oriented in three mutually perpendicular directions, such as an orthogonal or pierced fabric lay-up structure.
Torsional Stress	The shear stress on a transverse cross section caused by a twisting action.
Tow	An untwisted bundle of continuous filaments.
Toughness	The energy required to break a material; this energy value is equal to the area under the stress:strain curve.
Triaxial Weave	Woven fabric characterized by yarn orientation in the 90°±60° axes.
Two-Directional (2-D) Composite	A composite material in which substantially all of the reinforcing fibers are oriented in two directions, such as a flat laminate, tape-wrapped laminate, or a fabric lay-up in a closed cylindrical or conical lay-up structure.
Ultimate Elongation	The elongation at rupture.
Ultimate Tensile Strength (UTS)	The final (highest) stress sustained by a specimen in a tension test.
Unidirectional Composite (UDC or 1-D)	A laminate in which substantially all of the fibers are oriented in the same direction.
Volume Fraction	Fraction of a constituent material based on its volume.
Warp	A yarn running lengthwise in a woven fabric.
Weave	The specific manner in which a fabric is formed by interlacing yarns.
Weft	The transverse fibers in a woven fabric.

APPENDIX 2
LIST OF ACRONYMS

Acronym	Definition
ACC	advanced carbon-carbon composite
AEC	Atomic Energy Commission
AF	Air Force
AFWAL	Air Force Wright Aeronautical Laboratory - U.S.
ASRM	advanced solid rocket motor
ASTHMA	axisymmetric transient heating of material ablation computer program
BLT	boundary layer transition
BPX	burning plasma experiment
BRV	ballistic reentry vehicle
CAT	computer-aided tomography
CBCF	carbon-bonded carbon fiber
CCC	carbon-carbon composite
CEA	Commissariat A L'Energie Atomique - France
CMA	charring material ablation computer program
CMC	ceramic matrix composite
COCOM	Coordinating Committee for Multi-Lateral Export Controls
COF	coefficient of friction
CRAD	contractor research and development
CVCM	collected volatile condensable materials
CVD	chemical vapor deposition
CVI	chemical vapor infiltration
CW	continuous wave
DC	direct current
DCAP	degraded composites analysis program
DNA	Defense Nuclear Agency - U.S.
DOD	Department of Defense - U.S.
DOE	Department of Energy - U.S.
DPO	digital pulse echo
EAR	export administration regulation
EC	exit cone
EDM	electric discharge machining
EEC	extendable exit cone
ESA	European Space Agency
FFTF	fast flux test facility
FMI	Fiber Materials, Inc.
FSU	former Soviet Union
FW	filament wound
FWPF	fine-weave pierced fabric

APPENDIX 2 (Continued)
LIST OF ACRONYMS

Acronym	Definition
GASKET	graphite surface kinetics
GEO	geosynchronous orbit
GIS	graphite impact shell
GPHS	general-purpose heat source
HFIR	high flux isotope reactor
HIP	hot isostatic press
HIPIC	high-pressure-impregnation carbonization
HM	high modulus
HS	high strength or harness satin
HSW	harness satin weave
HT	heat-treated or high tensile strength
HTR	high-temperature reactor
ICBM	intercontinental ballistic missile
IM	intermediate modulus
IPSM	improved performance space motor
IRAD	independent research and development
ITAR	international traffic-in-arms regulations
ISP	specific impulse
ITE	integral throat-entrance cap
ITEC	integral throat-exit cone
ITER	international thermonuclear experimental reactor
IUS	inertial upper stage
JET	joint European Torus
JP-4	hydrocarbon fuel used by gas turbine engines
LDEF	long-duration environmental flight
LDI	low-density matrix indications
LEO	low-earth orbit
LIP	liquid infiltration process
LOPIC	low pressure-impregnation-carbonization
LOX	liquid oxygen
LPI	low-pressure infiltration
LWRHU	lightweight radioisotope heater unit
MaRV	maneuvering reentry vehicle
MEIT	momentum/energy/integral technique
MMC	metal-matrix composite
MOTA	materials open test assembly
MX	missile-X
NASA	National Aeronautics and Space Administration - U.S.

APPENDIX 2 (Continued)
LIST OF ACRONYMS

Acronym	Definition
NASP	national aerospace plane
NAT	nozzle aerothermochemistry computer program
NDE	nondestructive evaluation
NDI	nondestructive inspection
NDT	nondestructive testing
NSTS	national space transportation system
NT	nosetip
OPCCC	oxidation-protected carbon-carbon composite
OPR	overall pressure ratio
ORCCC	oxidation-resistant carbon-carbon composite
PAM	payload assist module
PAN	polyacrylonitrile
PC	pyrolytic carbon
PCB	printed circuit board
PEEK	polyetherether ketone
PG	pyrolytic graphite
PIC	pressure-impregnation-carbonization
PMC	polymeric-matrix composite
PRC	People's Republic of China
PVD	physical vapor deposition
PW	plain weave
PWB	printed wiring board
RCC	reinforced carbon-carbon
R&D	research and development
RHU	radioisotope heater units
ROM	rule of mixtures
RP	repetitively pulsed
RTG	radioisotope thermoelectric generator
RV	reentry vehicle
S/C	spacecraft
SDIO	Space Defense Initiatives Organization - U.S.
SEM	standard electronic module, or scanning electron microscopy
SICBM	small intercontinental ballistic missile
SRM	solid rocket motor
SSTO	single-stage-to-orbit
STS	space transportation system
TEM	transmission electron microscopy
TEOS	tetraethyl-orthosilicate

APPENDIX 2 (Concluded)
LIST OF ACRONYMS

Acronym	Definition
TFTR	Tokàmak fusion test reactor
TM	trademark
TP	thermal plane
TRIT	turbine inlet temperature
TVC	thrust vector control
UDC	unidirectional composite
UHM	ultrahigh modulus
US	United States
USSR	Union of Soviet Socialist Republic
UV	ultraviolet
VKK	Vozdushno Kosmicheskiy Korabl - Russia
V/STOL	vertical takeoff and landing aircraft
1-D	one-directional
2-D	two-directional
3-D	three-directional
4-D	four-directional
11-D	eleven-directional
n-D	multidirectional

APPENDIX 3
LIST OF ABBREVIATIONS

Abbreviation	Definition
atm	atmosphere (pressure)
Btu	British thermal unit
cal	calories
calc	calculated
cc	cubic centimeters
cm	centimeter
D	deuterium
db	decibel
dc	direct current
dpa	displacements per atom
ft	foot
g	gram
gal	gallon
GPa	gigapascal
h	hour; height
ID	inside diameter
in	inch
J	joule
k	kilo, conductivity
K	Kelvin
keV	kiloelectron volts
kg	kilogram
km	kilometer
kPa	kilopascal
ksi	1000 pounds per square inch
kw	kilowatt
l	liter
lb	pound
lbf	pounds force
lbs	pounds
m	meter
M	million
MeV	million electron volts
Mg	megagram
micro	one millionth of a meter
mils	one thousandth of an inch
min	minute; minimum

APPENDIX 3 (Concluded)
LIST OF ABBREVIATIONS

Abbreviation	Definition
Mrad	millirads
mm	millimeter
MPa	megapascal
mph	miles per hour
Msi	one million pounds per square inch
MW	megawatt
n	neutron
N	Newton
nm	nanometer
OD	outside diameter
oz	ounce
P	applied load; pressure
Pa	pascal
ppb	parts per billion
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
rad	100 ergs of radiation per gram of receptor
rf	radio-frequency
RH	relative humidity
rpm	revolutions per minute
RT	room temperature
s	second
T	temperature; tenacity; tritium
torr	a unit of pressure necessary to support a column of mercury one mm high at 0°C
UTS	ultimate tensile strength
vol	volume
vol %	volume percent
W	watt
We	watt (electrical)
wt	weight
wt %	weight percent
yd	yard
yr	year

APPENDIX 4
LIST OF SYMBOLS

Abbreviation	Definition
a	same as ab direction
ab	the direction of preferred layer orientation; the direction parallel to the substrate surface in a CVD deposit; the basal plane direction in a crystallite; or the direction parallel to the fiber, yarn, tow, felt, or fabric layers in a composite
ag	across the grain direction
c	the direction perpendicular to the basal planes in a crystallite; the direction perpendicular to the substrate surface in a CVD deposit; or the direction perpendicular to the fiber, yarn, tow, felt, or fabric layers in a fiber-reinforced composite
C	carbon
D	deuterium
SiC	silicon carbide
Si_3N_4	silicon nitride
T	tritium
X	the direction parallel to the fabric warp or major reinforcing plane
Y	the direction perpendicular to the fabric warp
Z	the direction perpendicular to the major reinforcing plane, usually the through-the-thickness plane, or the atomic number
°C	degrees Celsius (centigrade)
°F	degrees Fahrenheit
0°	fiber direction
90°	perpendicular to fiber direction
=	equals
-	minus
x	diameters (magnification); multiplied by
/	per
%	percent
+	plus; position ion charge
$	dollar

APPENDIX 5
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section A. U.S. Academic Organizations	
Alfred University Center for Advanced Ceramics Technology Alfred, NY 14802 USA	Research Studies • Oxidation Kinetics
Auburn University Department of Mechanical Engineering Auburn University, AL 36849 USA	Research Studies • Damping
California State University Department of Civil, Industrial & Applied Mechanics Northridge, CA 91330 USA	Research Studies • Dampening Characteristics • Modulus at High Temperature
Case Western Reserve University 10900 Euclid Avenue Cleveland, OH 44106 USA	Research Studies • Property Measurements • Oxidation Behavior
Clarkson University Microstructure and Mechanics Laboratory Potsdam, NY 13699 USA	Research Studies • Composite Microstructure • Fatigue Characteristics
Clemson University 123 Earle Hall Clemson, SC 29634-0907 USA	Research Studies • High Purity Pitches • Pitch-Based Carbon Fibers • Fiber Properties • CVD
Dartmouth College Thayer School of Engineering Hanover, NH 03755 USA	Research Studies • Deformation Mechanisms under Mechanical Loadings
Drexel University 32 & Chestnut Street Philadelphia, PA 19104 USA	Research Studies • n-D Woven Preforms • NDE Techniques
Kansas State University 146 Durland Hall Manhattan, KS 66506 USA	Research Studies • Fiber Topography: Oxidation Relationships
Massachusetts Institute of Technology Department of Mechanical Engineering Cambridge, MA 02139 USA	Research Studies • Emittance of Coated CCC
Massachusetts Institute of Technology Department of Physics Cambridge, MA 02139 USA	Research Studies • Electronic Properties • Microstructure • Intercalated Fibers & Composites
Ohio State University Materials Science and Engineering 2041 N. College Road Columbus, OH 43210 USA	Research Studies • Oxidation-Resistant Coatings

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section A. U.S. Academic Organizations (Continued)	
Pennsylvania State University Department of Materials Science & Engineering University Park, PA 16802 USA	Research Studies • Carbonization • Materials Response Modeling • Work-of-Fracture • Air Oxidation • Boron-Containing Polymers
Purdue University School of Aeronautics & Astronautics West Lafayette, IN 47907 USA	Research Studies • Thermal Stress Analyses
Purdue University Thermophysical Properties Research Laboratory 2595 Yeager Road West Lafayette, IN 47906-1398 USA	Research Studies • Thermophysical Property Measurements
Rensselaer Polytechnic Institute Materials Engineering Department Troy, NY 12180-3590 USA	Research Studies • Chemical Vapor Deposition • Chemical Vapor Infiltration
Southern Illinois University Materials Technology Center Carbondale, IL 62901-4303 USA	Research Studies • Microstructure • Property Measurements
Southern Methodist University Engineering & Applied Sciences Dallas, TX 75275-0001 USA	Research Studies • Structural Response Modeling
Texas A&M University College Station, TX 77843-3123 USA	Research Studies • Damping • Dynamic Young's Modulus • Composite Damage • Oxidation Resistance
Tuskegee University Mechanical Engineering Department Tuskegee, AL 36088 USA	Research Studies • Fracture Toughness • Failure Mechanisms
University of California-Los Angeles Materials Science & Engineering Department 405 Hilgard Avenue Los Angeles, CA 90024-1595 USA	Research Studies • Materials Modeling • Damage Mechanisms • Constituent Properties • Fiber Studies
University of California-Santa Barbara Materials Department 705 Ashley Road Montecito, CA 93106	Research Studies • Overviews & Analyses • Matrix Microstructure • Thermal Conductivity

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section A. U.S. Academic Organizations (Continued)	
University of California-San Diego Department of Mechanics & Engineering Sciences 9500 Gilman Drive LaJolla, CA 92093 USA	Research Studies • Mesophase Pitch Matrices • Fatigue Mechanisms
University of Colorado Denver, CO 80217 USA	Research Studies • Gas Phase Air Oxidation
University of Delaware Center for Composite Materials Department of Mechanical Engineering Newark, DE 19716 USA	Research Studies • 3-D Composite Modeling • 2-D CCC
University of Illinois Department of Materials Science & Engineering Champaign, Urbana, IL 61801 USA	Research Studies • High Char Resinous Matrices
University of Illinois PO Box 4348 Chicago, IL 60680 USA	Research Studies • CCC Oxidation Inhibition
University of Kentucky Center for Applied Energy Research 3572 Iron Works Pike Lexington, KY 40511-8433 USA	Research Studies • Microstructural Characterization
University of Lowell Mechanical Engineering Department Lowell, MA 01854 USA	Research Studies • Process-Induced Stresses • Composite Modeling
University of Notre Dame Department of Chemical Engineering Notre Dame, IN 46556 USA	Research Studies • CVD Process Fundamentals
University of Pennsylvania 34th & Spruce Street Philadelphia, PA 19104 USA	Research Studies • Site-Specific Reactions of Carbon and Oxygen
University of Washington Department of Chemical Engineering Seattle, WA 98195	Research Studies • Pyrolysis Mathematical Models • Coated CCC Processing
University of Wyoming Composite Materials Research Group PO Box 3295 Laramie, WY 82071 USA	Research Studies • Failure Mechanics • Damage Mechanisms • Mechanical Properties
Virginia Polytechnic Institute & State University Engineering Science & Mechanics Department Blacksburg, VA 24001 USA	Research Studies • Structural Response Modeling

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section A. U.S. Academic Organizations (Concluded)	
Wright State University Mechanical & Materials Engineering Dayton, OH 45435 USA	Research Studies • Attachment and Joining
Section B. U.S. Research Institutes & Federal Contract Research Centers	
Aerospace Corporation Materials Sciences Laboratory PO Box 92957 Los Angeles, CA 90009-2957 USA	Research Studies • Property Measurements • Failure Analyses • Particle Erosion • Fiber Properties
Battelle Columbus Laboratories 505 King Avenue Columbus, OH 43201 USA	Process Development and Composite Properties • HIPIC Densification • Property Measurement and Analyses
Battelle Pacific Northwest Laboratories Richland, WA 99352 USA	Research Studies • Vitreous Carbon Matrices • Neutron Effects
California Research & Technology, Inc. 6269 Variel Avenue Woodland Hills, CA 91367 USA	Research Studies • Particle Impact Modeling and Damage
Illinois Institute of Technology Research Institute Materials & Processing Technology 10 West 35th Street Chicago, IL 60616 USA	Materials Development & Properties • Low-Cost Moldable Composites • Mechanical Test Methods • Property Measurements
Southern Research Institute 2000 Ninth Avenue South PO Box 55305 Birmingham, AL 35255-5305 USA	Materials Property Measurements • Materials Modeling • Failure Analyses • Mechanical/Thermal Properties
Southwest Research Institute 6220 Culebra Road PO Drawer 28510 San Antonio, TX 78284 USA	Research Studies • Stress Profiles • High Velocity Particle Damage
University of Dayton Research Institute 300 College Park Avenue Dayton, OH 45469-0168 USA	Research Studies • Mechanical Property Measurements • Static and Fatigue Properties • New Property Measurements • Mechanics Analyses • Crack Techniques and Void Imaging
University of Dayton Research Institute AF Phillips Laboratory Edwards Air Force Base, CA 93523-5000	Materials:Process:Properties Studies • Mechanical Behavior and Response • Nonproprietary Processing • Carbon Matrix/Fiber Studies

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations	
Abex Corporation New York, NY	Materials Development • High-Temperature Friction Materials • Aircraft Brake Materials
AdTech Systems Research, Inc. 1342 N. Fairfield Road Dayton, OH 45432-2698 USA	Materials Modeling and Mechanics • Computerized Material Designs • Turbine Engine Blade Analyses
Advanced Material Technologies 3611 South Harbor Blvd. Santa Ana, CA 92704-6928 USA	Materials Development Requirements • Performance/Property Trade Studies
Advanced Research & Application Corporation 425 Lakeside Drive Sunnyvale, CA 94086-4704 USA	Nondestructive Inspection/Evaluation • X-ray Computed Tomography (CT)
Advanced Technology Materials, Inc. 7 Commerce Drive Danbury, CT 06810	Research Studies • Boron-Containing Polymeric Precursors
Aerojet Composites, Inc. PO Box 2908 San Rafael, CA 94902 USA	Component Manufacturing and Tests • Rocket Motor Parts • Engine Parts
Aerotherm Corporation 580 Clyde Avenue PO Box 7040 Mountain View, CA 94039-7040 USA	Materials Modeling, Development & Test • Ablation and Erosion Predictive Codes • Fast Densification Processes • Instrumented Models and Tests • Shape Stable Missile Nosetips
Aircraft Braking Systems 1204 Massillon Road Akron, OH 44306-4186 USA	Component Design, Manufacturing & Test • Frictional Characteristics • 2-D Resin/Char & CVI Composites • Aircraft Brake Discs
Albany International Research Company 777 West Street PO Box 9114 Mansfield, MA 02048-9114 USA	Constituent Materials Development • 2-D & 3-D Braided Preforms
Allied-Signal Aerospace Company Aircraft Landing Systems 3520 Westmoor Street South Bend, IN 46628-1373	Component Design, Manufacturing, & Test • 3-D Nonwoven Preforms • Friction Characteristics • Aircraft Brake Discs
Allied-Signal Aerospace Company Garrett Engine Division 111 South 34th Street PO Box 5217 Phoenix, AZ 85010 USA	Component Design & Test • Turbine Rotors

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
Amoco Performance Products, Inc. PO Box 849 Greenville, SC 29602 USA	Constituent Materials Development • PAN-Based Carbon/Graphite Fibers • Pitch-Based Carbon/Graphite Fibers • Rayon-Based Carbon/Graphite Fibers
Applied Sciences, Inc. Cedarville, OH 45314 USA	Research Studies • Vapor-Grown Carbon Fibers • High Conductivity Composites
Ashland Oil, Inc. Ashland Carbon Fibers Division PO Box 391 Ashland, KY 41114 USA	Constituent Materials Development • High Char, Processible Pitches
Atlantic Research Corporation 5945 Wellington Road Gainesville, VA 22065-1699 USA	Materials Development & Manufacturing • Braided Preforms & Composites • Property Measurements
Bendix Advanced Technology Center 9140 Old Annapolis Road/MD 108 Columbia, MD 21045 USA	Research Studies • Frictional Characteristics
BFGoodrich Aerospace Engineered Products Group 9921 Brecksville Road Brecksville, OH 44141-3289 USA	Materials & Process Development • Frictional Characteristics • Lower Cost, Faster Processes • Material:Process Relationships
BFGoodrich Aerospace Carbon Products 500 William White Blvd. Pueblo, CO 81001 USA	Component Manufacturing • Brake Disc Production
BFGoodrich Aerospace 11120 S. Norwalk Blvd. Santa Fe Springs, CA 90670-3830 USA	Materials/Component Design & Manufacturing • CVI Pyrolytic Graphite Composites • High Thermal Conductivity Composites • Aircraft Brake Discs • Airframe Components
BFGoodrich Aerospace Aircraft Wheel and Brake Operations PO Box 340 Troy, OH 45373 USA	Component Design & Test • Properties Measurement • Brake Disc Design • Frictional Tests
Boeing Defense & Space Group PO Box 3707 Seattle, WA 98124-2207 USA	Nondestructive Inspection/Evaluation • X-ray Computed Tomography (CT) • Composite Density Gradients

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
Carborundum Company Graphite Products Division PO Box 1054 Niagara Falls, NY 14302 USA	Materials Development & Manufacturing • Low Friction Materials • Aircraft Brake Discs • Industrial Components
Carbon Carbon Advanced Technologies (CCAT) 7445 E. Lancaster Fort Worth, TX 76112 USA	Component Manufacturing • Turbine Engine Nozzle Parts
Chromalloy American Corporation Chromalloy Research & Technology Division Blaisdell Road Orangeburg, NY 10962 USA	Component Manufacturing • Silicon Carbide Coatings
Calspan Corporation Advanced Technology Center Box 400 Buffalo, NY 14225 USA	Research Studies • Ablation Tests
CUMAGNA Corporation Norristown, PA 19403 USA	Constituent Materials Manufacturing • 3-D Braided Preforms
DuPont Lanxide Composites, Inc. 1300 Marrows Road PO Box 6077 Newark, DE 19714-6077 USA	Materials Development & Manufacturing • Hybrid Carbon Fiber/Silicon Carbide Matrix Composites • Titanium Carbide-Coated CCCs
Effects Technology, Inc. 5383 Hollister Avenue Santa Barbara, CA 93111 USA	Materials Modeling & Tests • Hypervelocity Particle Erosion
Failure Analysis Associates, Inc. 149 Commonwealth Drive Menlo Park, CA 94025 USA	Nondestructive Inspection/Evaluation • Eddy Current Evaluation • Composite Defects
Fiber Materials, Inc. Biddeford Industrial Park 5 Marin Street Biddeford, ME 04005-4497 USA	Materials/Development & Manufacturing • Automated 3-D and n-D Preform Manufacturing • Automated Manufacturing Processes • Property Measurements • Missile Nosetips and Nozzle Components • Insulation
Foster-Miller, Inc. 350 Second Avenue Waltham, MA 02154-1196 USA	Materials & Process Development • Advanced Preforms • Process Science Instrumentation • Brazing Processes

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
General Atomics Advanced Materials Technology Division 3550 General Atomics Court San Diego, CA 92121-1194 USA	Constituent Materials Development • Oxidation Inhibitors • Glass Sealants • Multilayered Coatings
GenCorp Aerojet Aerojet Solid Propulsion PO Box 15699 Sacramento, CA 95852-1699 USA	Component Design, Manufacturing & Test • Composite Failure Criteria • Nozzle Components & Test • Engine Components & Test
GenCorp/Aerojet Electronic Systems Division PO Box 296 Azusa, CA 91702 USA	Constituent Materials Development • Intermetallic Coating Process
General Dynamics Fort Worth Division PO Box 748 Fort Worth, TX 76101 USA	Component Design & Tests • Flight Vehicle Structures Design • Actively Cooled Structures Design
General Dynamics Space Systems Division PO Box 85990 San Diego, CA 92138-5357 USA	Component Design & Tests • Space Optical Mirror Structures • 3-D Joints
General Electric Aircraft Engines One Neumann Way PO Box 156301 Cincinnati, OH 45215-6301	Component Design & Tests • Oxidation Screening Tests • Gas Turbine Engine Parts
General Electric Company Re-Entry Systems Operation 3198 Chestnut Street Philadelphia. PA 19101-0001 USA	Materials/Components Design & Manufacturing • HIPIC Densification Processes • CVD/CVI Densification Processes • Missile Nosetips and Nozzle Components • Turbine Engine Rotating Parts
General Electric Company Corporate Research and Development PO Box 8 Schenectady, NY 12301	Research Studies & Materials Development • Oxidation Analyses • Borate Additives • Coatings
Harris Corporation Government Aerospace Systems Division PO Box 94000 Melbourne, FL 32902-0001 USA	Component Design & Test • Hinges
Hercules Aerospace Company Bacchus Works PO Box 98 Magna, UT 84044-0098 USA	Component Design, Manufacture, & Test • CVI & Pitch HIPIC Densification • Nozzle Exit Cones and ITEs • 3-D Fibrous Preforms

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
Hitco Technologies, Inc. Advanced Materials Division 13722 Harvard Place Gardena, CA 90249-2529 USA	Component Design & Manufacturing • Aircraft & Commercial Brake Discs • Motor Exit Cones • Engine Thrust Chamber & Nozzle Parts
Hoechst Celanese Corporation 86 Morris Avenue Summit, NJ 07901 USA	Constituent Materials Development • Oxidation-Resistant Fibers
Hughes Aircraft Company PO Box 902 El Segundo, CA 90245-0902 USA	Constituent Materials Development • High Char Resin Impregnants
Jortner Research & Engineering, Inc. Cloverdale, OR 97112-0219 USA	Materials Modeling & Tests • 2-D Delamination Failure Model • Micromechanical Models • Shear Test Methods
Kaiser Aerotech 880 Doolittle Drive PO Box 1678 San Leandro, CA 94577-0801 USA	Component Design & Manufacture • Nozzle Exit Cones • Space Structures • Flight Vehicle Airframe Structures
Kaiser Marquardt 16555 Saticoy Street Van Nuys, CA 91406-1739 USA	Materials Manufacturing & Component Design • CVI PG Composites • CVI Hybrid Fiber/Matrix Composites
Kaman Sciences Corporation PO Box 7463 Colorado Springs, CO 80933 USA	Property Measurements • High Strain Rate Properties • Nuclear Weapons Effects • Electron Beam Heating Effects
Kline & Company, Inc. 330 Passaic Avenue Fairfield, NJ 07006 USA	Market Analyses • Business Studies and Forecasts
Ktech Corporation 901 Pennsylvania NE Albuquerque, NM 87110-7403 USA	Property Measurements • Dynamic Mechanical Properties • Nuclear Weapons Effects
Lockheed Martin Missiles & Space 1111 Lockheed Way PO Box 3504 Sunnyvale, CA 94088-3504 USA	Component Design & Test • 2-D Filament-Wound Composites • Particle Erosion Tests • Space Structures • Space Radiators
Loral Aeronutronic Ford Road Newport Beach, CA 92658-9983 USA	Materials Development & Test • 2-D and 3-D Composites • Thermostructural Tests • Nozzle and Thrust Chamber Tests

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
Loral/Space Systems 3825 Fabian Way Palo Alto, CA 94303 USA	Component Design & Test • Antenna Reflectors
LTV Aerospace & Defense Company Missiles Division PO Box 650003 Dallas, TX 75265-0003 USA	Materials/Components Development & Test • Coated and Uncoated 2-D/3-D Composites • Shuttle Nosecap and Leading Edges • Airframe and Turbine Engine Parts
Magnaweave, Inc. 26 S. Wakefield Road Norristown, PA 19403 USA	Constituent Materials Development • Multidirectional Woven Preforms
Martin Marietta Space Systems PO Box 179 Denver, CO 80201 USA	Component Design & Test • Space Solar Array Structure • Microstructure:Property Relations
Materials Sciences Corporation Suite 250 500 Office Center Drive Fort Washington, PA 19034-3213 USA	Materials Modeling & Tradeoff Studies • Micromechanical Analyses • In-Process Thermostructural Modeling • 3-D Architectural Design Guidance • Processing Failure Analyses
Materials & Systems Research, Inc. 67 East Cleveland Avenue Salt Lake City, UT 84115 USA	Component Design & Tests • High Temperature Battery Components
McDonnell Douglas Aerospace PO Box 516 St. Louis, MO 63166-0516 USA	Materials/Component Development & Test • Braided Composites • Thrust Chambers • High Pressure Ablation Tests
McDonnell Douglas Aerospace 5301 Bolsa Avenue Huntington Beach, CA 92647-2048 USA	Materials Development, Design, & Test • Advanced Fibers and Matrices • Design Criteria • Nuclear and Space Environmental Tests
MSNW, Inc. PO Box 715 Blue Bell, PA 19422 USA	Research Studies • Mathematical Modeling
Nuclear & Aerospace Materials, Inc. 16716 Martincoit Road Poway, CA 92064-1629 USA	Materials Development • X-ray Resistant Composites • High Thermal Conductivity Composites • Neutron Irradiation
Oak Ridge National Laboratory PO Box 2003 Oak Ridge, TN 37831-7294 USA	Materials Development & Testing • HIPIC Preform Densification • High Temperature Coatings • Low Density Carbon Insulation

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
PDA Engineering 2975 Redhill Avenue Costa Mesa, CA 92626 USA	Materials Modeling & Tradeoff Studies • Materials Development Guidance • Thermostructural Analyses • Modeling and Failure Analyses
Pfizer, Inc. 640 N. 13th Street Easton, PA 18042 USA	Materials Development & Manufacturing • CVD/CVI Coatings/Infiltrants
Raytheon Company Research Division Waltham, MA 02154 USA	Materials Development & Manufacturing • Chemical Vapor Deposition
Refractory Technology Aerospace Components Co. (RTAC) 8207 West 3500 South Magna, UT 84044-1851 USA	Materials & Component Manufacturing • 3-D Composites • Coated Composites • Turbine Engine Nozzle Parts • Airframe Structures
Rockwell International Corporation North American Aircraft Operations 201 N. Douglas St. Los Angeles, CA 90009 USA	Component Design & Test • High Thermal Conductivity Composites • Airframe Structures
Rockwell International Corporation Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91303 USA	Component Design & Test • Space Engine Thrust Chambers • Space Radiators
Rockwell International Science Center 1049 Camino Dos Rios Thousand Oaks, CA 91360 USA	Research Studies • Electrical Conductivity • Property/Processing Relationships • Materials Modeling
Rohr, Inc. Foot of H Street PO Box 878 Chula Vista, CA 92012-0878 USA	Materials & Component Manufacturing • Coated Composites • Acoustic Fatigue Properties • Turbine Engine Nozzle Parts • Airframe Structures
Sandia National Laboratories PO Box 5800 Albuquerque, NM 87185 USA	Materials/Component Manufacturing & Test • Pyrolytic Graphite Matrix Composites • Materials:Process:Property Studies • Design Databases • Missile Heatshields and Flight Tests

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
Science Applications International Corp./ Material Sciences Operation 1720 East Wilshire Avenue Santa Ana, CA 92705-4615 USA	Materials Development & Manufacturing • Oxidation-Resistant Composites • Low Cost, Fast Processes • Process Science Studies • Planetary Vehicle Thermal Protection
Sparta, Inc. 9455 Towne Centre Drive San Diego, CA 92121-1964 USA	Composite Design & Test • Coatings Development • High Conductivity Composites
Spectracorp 599 Canal Street Lawrence, MA 01840 USA	Materials Development & Test • Specialty Composites
SPIRE Corporation One Patriots Park Bedford, MA 01730 USA	Materials & Process Development • Metallated Composites • Particle Erosion-Resistant Nosetips
Stackpole Fibers Company Foundry Industrial Park Lowell, MA 01852 USA	Constituent Materials Manufacturing • Low-Cost Carbon Fibers and Preforms
Systems, Science and Software PO Box 1620 La Jolla, CA 92038-1620 USA	Materials, Modeling, & Mechanics • Particle Erosion Impact Damage • Performance Prediction Codes
Teledyne CAE 1330 Laskey Road Toledo, OH 43612-0971 USA	Component Design & Test • Space Power Aeroshells
Textron Defense Systems 201 Lowell Street Wilmington, MA 01887-2985	Component Design & Test • Air Arc Reentry Tests • Component Design and Assembly
Textron Specialty Materials 2 Industrial Park Lowell, MA 01851-5199	Materials Development & Manufacturing • 3-D and 5-D Fibrous Preforms • Automated Preform Manufacturing • Preform Densification • Nosetips and Nozzles
Thiokol Corporation Elkton Division PO Box 241 Elkton, MD 21922-0241 USA	Component Design & Test • Space Motor Nozzle Design • Modeling and Performance Predictions • Ground and Flight Tests
Thiokol Corporation Wasatch Division PO Box 707 Brigham City, UT 84302-0707 USA	Component Design & Test • Strategic/Tactical Missile Motor Designs • Performance Predictions and Failure Modes • Ground-Based Nozzle Tests

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Continued)	
TRW, Inc. Applied Technology Division One Space Park Redondo Beach, CA 90278 USA	Component Design & Test • Space Structural Deployment Boom
TRW, Inc. Ballistic Missile Division PO Box 1310 San Bernardino, CA 92402-1310	Component Design & Analyses • Short-Beam Shear Properties • Nonlinear Stress-Strain Behavior • Launch Vehicle Nozzle Analyses • Assessments & Tradeoff Studies
Textile Technologies, Inc. 2800 Turnpike Drive Hatboro, PA 19040 USA	Constituent Materials Development • Advanced Fibrous Preforms
Ultramet 12173 Montague Street Pacoima, CA 91331 USA	Materials & Process Development • Oxidation-Resistant Coatings
United Technologies Chemical Systems Division PO Box 49028 San Jose, CA 95161-9028 USA	Component Design & Test • Motor Nozzle Designs & Tests • Nozzle Test Firings • Technology Assessment & Transfer
United Technologies/Pratt & Whitney Government Engine and Space Propulsion PO Box 109600 West Palm Beach, FL 33410-9600 USA	Component Design & Test • Turbine Engine Part Design and Test • Liquid Engine Translating Nozzle Cones
United Technologies Research Center 411 Silver Lane East Hartford, CT 06108 USA	Materials & Process Development • CVD Coatings • Fast Processed Composites • Turbine Engine Coated Rotors and Vanes
Westinghouse Electric Corporation 1310 Beulah Road Pittsburgh, PA 15235-5098 USA	Property Measurements • High-Temperature Properties
Williams International 2280 West Maple Road PO Box 200 Walled Lake, MI 48390-0200 USA	Component Design & Test • Materials Requirement Definition • Turbine Engine Part Design • Engine Combustor Parts and Nozzle Vanes
W. R. Grace & Company 7379 Route 32 Columbia, MD 21044 USA	Materials & Component Development • Unidirectional CCC • Mechanical Properties • Internal Combustion Engine Valves

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section C. U.S. Industrial Organizations (Concluded)	
Zoltek Corporation Carbon & Graphite Division 11 Missouri Research Park St. Charles, MO 63304 USA	Constituent Materials • Low-Cost Carbon Fibers
Section D. U.S. Government Organizations	
Air Force Arnold Engineering Development Center 678 Second Street Arnold AFB, TN 37389-4405 USA	Prototype Tests • High-Pressure Ablation Tests • Particle Erosion Tests • High Altitude Nozzle Tests
Air Force Ballistic Missile Organization/AFMC BMO/MYET Norton AFB, CA 92409-6468 USA	Prototype Assessments & Tests • Missile Component Assessments • Reentry Flight Tests • Motor Nozzle Tests
Air Force Development Test Center/AFMC 6586th Test Group Holloman AFB, NM 88330 USA	Materials & Prototype Tests • Subsonic and Supersonic Particle Erosion • Nosetip Erosion
Air Force Phillips Laboratory PL/VTS AFMC 3550 Aberdeen Avenue, S.E. Kirtland AFB, NM 87117-5776 USA	Space Components & Test • Component Fabrication and Test
Air Force Phillips Laboratory/SMSC/AFMC Directorate of Space and Missile Technology OLAC-PL/VTSC Edwards AFB, CA 93523-5000 USA	Component Tests & Failure Analyses • Rocket Nozzle Ground Tests • Propulsion Failure Analyses • CCC Research and Development
Air Force Wright Laboratory Flight Dynamics Directorate/AFMC WL/FIB Wright-Patterson AFB, OH 45433-7750 USA	Component Tests • Missile Nosetip Ablation Tests • Aircraft Brake Disc Tests • Hypersonic Flight Vehicle Tests • Structural Designs
Air Force Wright Laboratory Materials & Manufacturing Technology Directorates/AFMC WL/ML Wright-Patterson AFB, OH 45433-7750 USA	Advanced Materials & Processes • Composite Concepts • Process Science • Mechanics Analyses • Manufacturing Technology
Federal Aviation Administration FAA Technical Center Atlantic City International Airport, NJ 08405 USA	Prototype Tests • Turbine Engine Combustor Tests

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section D. U.S. Government Organizations (Continued)	
Jet Propulsion Laboratory Applied Mechanics Technology 4800 Oak Greeve Drive Pasadena, CA 91109 USA	Materials/Component Design & Analyses • PAN- and Pitch-Based Composite Evaluation • Materials:Process:Property Relationships • Thrust Chamber Evaluation
NASA Ames Research Center Thermal Protection Materials Branch Mail Stop 234-1 Moffett Field, CA 94035-1000 USA	Property Measurements • Laser Heating Effects • Air Arc Heater Testing
NASA Langley Research Center Materials Division Mail Stop 188B Hampton, VA 23681-0001 USA	Materials & Process Development • Materials:Process:Property Studies • Composite Oxidation Tests • Property Measurements
NASA Lewis Research Center Materials Division Mail Stop 106/5 21000 Brookpark Road Cleveland, OH 44135-3191 USA	Property Measurements • Frictional Characteristics • Engine Tests
NASA Lyndon B. Johnson Space Center Structures & Mechanics Division Mail Stop ES 32 NASA Road 1 Houston, TX 77058-0001 USA	Component Design & Analyses • Composite Design Verification • Shuttle Nosecap and Leading Edges Analyses • Thermal/Structural/Acoustic Tests • CCC Impact Tests
NASA Marshall Space Flight Center Materials and Processes Laboratory Mail Stop EH34 Marshall Space Flight Center, AL 35812 USA	Component Designs • Assessments and Tradeoff Studies
Naval Air Warfare Center Missile & Support Technology Code CO 253 China Lake, CA 93555 USA	Component Design & Test • Armor Protection
Naval Research Laboratory Materials Chemistry Branch Washington, DC 20375 USA	Research Studies • Glassy Carbons
Naval Surface Warfare Center Code K22 10901 New Hampshire Avenue Silver Spring, MD 20903-5640 USA	Materials/Component Evaluation • Thermostructural Analyses • Adhesives Evaluation • Matrices
Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000 USA	Research Studies • Fiber-Carbon Interfaces

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations	
Academy of Mining and Metallurgy Cracow, POLAND	Research Studies • Microstructure:Mechanical Property Relationships
Aerospatiale Establissement d'Aquitaine B.P. 11 33165 Saint-Medard-en-Jalles Cedex, FRANCE	Component Design, Fabrication & Test • 3-D Woven Fibrous Preforms • Preform Densification • Property Measurements • Ablation
Akebono Brake Industry Co. Ltd. 19-5 Nihonbashi Koami-cho Chuo-ku, Tokyo, JAPAN	CCC Brake Disc Systems • CCC Disc Manufacturing
Atomic Weapons Research Establishment Chemical Technology Division Aldermaston Reading RG7 4PR, ENGLAND	Materials Development & Evaluation • CVD and Resin Char Composites • Property Generation • Nuclear Irradiation
Beijing Research Institute of Materials & Technology No. 1 Nan DaHong Men Road PO Box 9211 Beijing 100076, P.R. CHINA	Materials & Process Developments • 3-D Preforms and CCC Materials • Fundamental Materials Behavior • Property Measurements
Beijing University of Aeronautics and Astronautics Department of Materials Science & Engineering Beijing, 100083, P.R. CHINA	Materials Development & Evaluation • Composite Fabrication • Oxidation-Resistant Coatings • Brake Discs
Boris Kidric Institute PO Box 522 11001 Belgrade, YUGOSLAVIA	Research Studies • CVI Deposition Processes • CVD/CVI:Property Relationships
Brochier SA 33, Avenue Franklin-Roosevelt BP 272, 69152 Decines Cedex, FRANCE	Constituent Materials Manufacturing • Automated 3-D Woven Preforms
Bulgarian Academy of Science Institute of Organic Chemistry ul. Acad. G. Bonchev 9 Sofia 1113, BULGARIA	Research Studies • Role of Carbon Fillers
Carbon Technology Unit Dr. K. S. Krishnan Road New Delhi, 110012, INDIA	Research Studies • CCC Oxidation Rates

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
CEA-CESTA BP 2 33114 le Barp, FRANCE	Research Studies • Laboratory Ablation • High-Temperature Properties
Centre de Recherches sur la Physico-Chimie des Surfaces Solides 24, Avenue du President Kennedy 68200 Mulhouse, FRANCE	Research Studies • CCC Oxidation Inhibition • Boron Oxide Inhibition
Centro Tecnico Aerospacial San Jose dos Campos, BRAZIL	Research Studies • Biocompatible Composites
Chinese Ceramic (Silicate) Society Baiwanzhuang Beijing 100831, P.R. CHINA	Research Studies • Hypervelocity Particle Erosion
Chungnam National University Department of Chemical Engineering Taejon 305-764, KOREA	Research Studies • Mesophase Pitch Separation Methods
Chung Shan Institute of Science & Technology (CSIST) PO Box 90008-8-1 Lung-Tan Taiwan, 32500, R.O.C.	Materials Development & Manufacturing • 3-D Woven Fibrous Preforms • HIPIC Processed Composites • Oxidation-Resistant Materials • Wear Behavior
Commissariat a l'Energie Atomique (C.E.A.) BP 12 91680 Bruyeres-le-Chatel, FRANCE	Research Studies • Carbon Insulation • Rapid Densification Processes • High-Temperature Properties
Commissariat a l'Energie Atomique (C.E.A.) CE/SACLAY 91.191 - Gif/sur/Yvette FRANCE	Research Studies • Plasma Sprayed Coatings • FAST Deposition Processing
CSIRO Division of Coal Research PO Box 175 Chatswood, New South Wales, AUSTRALIA	Research Studies • Pitch Mesophase Formation
Domaine Universitarie Centre de Recherches Paul Pascal du C.N.R.S. 33405 Talence Cedex, FRANCE	Research Studies • CVI Matrices • Oxidation Rates
Dunlop Limited/Aviation Division Holbrook Lane Coventry CV6 4AA, ENGLAND	Component Manufacturing • Brake Disc Design & Manufacturing

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Feng Chia University Department of Materials Science Taichung Taiwan, R.O.C.	Research Studies • Matrix Pyrolysis Fundamentals
Flexline B.V. Advanced Composites R&D Center Delfweg 50 2211 VN Noordwijkerhout THE NETHERLANDS	Materials Manufacturing • Lower Cost Processes
Government Industrial Research Institute (GIRI) of Kyushu Shuku-mach Tosu-shi, Saga-ken 841, JAPAN	Research Studies • Matrix Orientation:Composite Property Relationships
Harbin Institute of Technology School of Astronautics Harbin, 15006, P.R. CHINA	Research Studies • Notched Strength Measurements • Composite Properties
Hokkaido University N14, W8, Kita-ku Sapporo 060, JAPAN	Research Studies • Pitch Carbonization • Oxidation-Resistant Coatings
ICI Wilton Materials Research Centre Wilton, Middlesborough, Cleveland TS6 8JS ENGLAND	Materials Development • 2-D CCC Mechanical Properties • Inhibited CCC Properties
Institute of Aviation Materials Radio Street, 17 107005 Moscow, RUSSIA	Process Development & Applications • Advanced Composite Development • Materials & Component Testing • Prototype Design and Fabrication
Institute of Aviation Technology 27, Petrovka Street Moscow Centre, RUSSIA	Materials Development • Component Fabrication • Properties and Testing
Institute of Metal Research Academia Sinica Shenyang 110015, P.R. CHINA	Property Measurements • Biaxial Testing • 3-D CCC
Institute of Polymer Mechanics 23, Aizkraukles Street LVI006, Riga, LATVIA	Research Studies • Mechanics Analyses
Institute for Problems in Mechanics Moscow, RUSSIA	Research Studies • Aerospace Materials Evaluation • Applied Materials and Structures Problems • Simulated Reentry Heating Test

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CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Instituto Nacional del Carbon Apartado 73, 330880 Oviedo, SPAIN	Research Studies • Pitch-Property Relationships • Mesophase Pitch Carbonization
Israel Institute of Metals Technion Research and Development Foundation Technion City Haifa 32000, ISRAEL	Research Studies • Ceramic Coatings • Ceramic Infiltration
Israel Institute of Technology Department of Materials Engineering Haifa 32000, ISRAEL	Research Studies • Matrix Morphologies • Constituent Materials:Composite Property Relationships
Japan Atomic Energy Research Institute Tokai-mura Ibaraki, 319-11, JAPAN	Materials Evaluation • Nuclear Reactor Component Tests
Japan Railway Technical Research Institute JAPAN	Component Design & Tests • High-Speed Train CCC Brake Designs
Kawasaki Heavy Industries, Ltd. Gifu Works 1, Kawasaki-cho, Kakamigahara Gifu 504, JAPAN	Component Design & Fabrication • Prototype Shuttle Nosecap and Leading Edge Design
Kawasaki Steel Corporation High Technology Research Labs 1, Kawasaki-cho, Chuo-Ku Chiba 260, JAPAN	Materials Development & Tests • Process:Structure:Performance Relationships • Prototype Shuttle Nosecap and Leading Edge Materials
Kiev Polytechnic Institute pr. Pobedy, 37 Kiev-56, 252056, UKRAINE	Materials Research • CCC Oxidation • Silicon-Based Coatings
Kobe Steel, Ltd. 1-3-18 Wakinohama-cho, Chuo-ku Kobe 651, JAPAN	Component Designs • Oxidation-Resistant Structural Flight Parts
Korea Research Institute of Chemical Technology/ Polymer Lab PO Box 9 Daedeog-Danji, KOREA 305-606	Materials:Process:Property Studies • Heat Treatment Effects on Composites
Korea Advanced Institute of Science and Technology Department of Materials Science and Engineering PO Box 131 Cheongryang, Seoul, KOREA	Research Studies • Fracture Behavior • Oxidation of Hybrid Composites • Pyrolytic Matrices

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CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Kyushu University Institute of Advanced Material Study Department of Molecular Engineering 86 Kasuga, Fujuoka 816, JAPAN	Materials & Process Development • Hot Pressing Process for Short Fiber Composites
Laboratoire de Physicochimie Minerale 1 U.R.A. No. 116 Universite Claude Bernard Lyon I, 43, Boulevard du 11 Novembre 1918 69622 Villeurbanne Cedex, FRANCE	Research Studies • CVD Coated Fibers
Laboratoire Marcel Mathieu 2 Avenue du President P. Angot 64000 Pau, FRANCE	Research Studies • Carbonization • Microstructures
Lanzhou Carbon Industry Corporation Haishiwan Lanzhou 730084, P.R. CHINA	Component Manufacturing • Aircraft CCC Brake Disc Production • Frictional Properties
LEMTA URA C.N.R.S. 875 Avenue de la Foret de Haye 54516 Vandoeuvre-Les-Nancy Cedex, FRANCE	Research Studies • Thermal Diffusivity Measurements
McLaren International Woking, ENGLAND	Race Car Brake & Clutch Systems • Component Design
Mechanical Engineering Research Institute Griboedov Street 4 Box 5678 Moscow 101830, RUSSIA	Research & Property Measurements • Mechanical Properties • Microstructure Studies • Particle Erosion Effects
Messier-Bugatti Zone Aeronautique Louis Brequet F 78140 Velizy Villacoublay, FRANCE	Aircraft Brake Systems • Structural Carbon Brake Systems • Brake Disc Refurbishment
Ministry of International Trade & Industry (MITI) 3-1 Kasmuigaseki 1-chome, Chiyoda-ku Tokyo, JAPAN	Program Sponsor • Long-Range Materials Development
Mitsubishi Electric Company Petroleum Energy Center 1-1-57, Miyashimo, Sagamihara 229, JAPAN	Materials Development & Manufacturing • 1-D CVD PG Rods
Mitsubishi Gas Chemical Company, Inc. Chiyoda-ku Tokyo 100, JAPAN	Constituent Materials • Mesophase Pitches for Fibers and CCC Matrices

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Mitsubishi Heavy Industries (MHI) Nagoya Aerospace Systems 10, Oye-cho Minate-ku, Nagoya 445, JAPAN	Materials & Component Manufacturing • Prototype Turbine Engine Parts Fabrication and Tests
Mitsubishi Kasei Corporation 5-2 Marunouchi 2-chome Chiyoda-ku, Tokyo 100, JAPAN	Materials & Process Development • High Thermal Conductivity Composites • Pitch-Based CCC Materials • Frictional Materials
National Physical Laboratory K.S. Krishnan Road New Delhi 110012, INDIA	Research Studies • Fiber-Matrix Bonding • Fracture
National Research Institute for Metals 2-3-12 Nakameguro Meguro, Tokyo, JAPAN	Materials Modeling Predictions • Predictive Equation for Oxidative Materials Loss
National Space Development Agency of Japan (NASDA) Tsukuba Space Center 2-1-1 Sengen, Tsukuba-shi Ibaraki, 305, JAPAN	Component Designs • Spacecraft Part Design
National Taiwan University Institute of Materials Science & Engineering Taipei, Taiwan, R.O.C.	Research Studies • Multilayer Coatings
National Tsing Hua University Materials Science Center Hsin-Chu, Taiwan, R.O.C.	Research Studies • Fiber-Matrix Bonding • 2-D Composites • CVI Infiltrated CCC
NIIGrafit Moscow Office 2 Electrodnaya Street Moscow, 111524, RUSSIA	Materials Development & Manufacturing • Composite Development • Component Manufacturing
Nippon Oil Company, Ltd. Advanced Materials R&D Div. Central Technical Research Lab 8, Chidori-cho, Naka-ku Yokohama 231, JAPAN	Materials & Process Development • Multilayered, Oxidation-Resistant Coatings
Nippon Oil Company, Ltd. Central Technical Research Laboratory 8, Chidori-cho, Naka-ku Yokohama 231, JAPAN	Fiber Manufacturing • Pitch Mesophase • Pitch-Based 3-D Woven Fabrics

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CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Nippon Steel R&D Labs-I 1618 Ida Nakahara-ku Kawasaki 211, JAPAN	Property Measurements • Creep Rates
Nissan Motor Company, Ltd. 1 Natsushima Yokosuk Kanagawa 247, JAPAN	Component Design & Tests • Solid Rocket Motor Throats and Exit Cones
Northwestern Polytechnical University Department of Materials Science & Engineering Xian 710072, P.R. CHINA	Materials Modeling & Performance • Ablation Prediction Methods • Oxidation Resistant CCC
Office National d'Etudes et de Recherches Aerospatiales (ONERA) 29 Avenue de la Division Leclerc F 92322 Chatillon Cedex, FRANCE	Research Studies • Materials Properties • NDE/NDI Techniques • Ablation • Oxidation Behavior and Modeling
Osaka Gas Co., Ltd. 4-1-2, Hirano-machi, Chuo-ku Osaka 541, JAPAN	Materials Development • Oxidation-Resistant Materials
PETOCA Co., Ltd. #4 Touwada, Kamisu-cho, Kashima Ibaraki 314-02, JAPAN	Thermal Expansion Measurements • Carbonization Effects • Unidirectional Composites
Polymer Research Institute of Chemical Technology Daedeog-Danji 305-606 KOREA	Materials & Process Development • Filament-Wound CCC
Propellant, Explosives & Rocket Motor Establishment Westcott, Aylesbury, ENGLAND	Component Design & Test • Rocket Motor Parts
Sardar Patel University G. H. Patel Institute of Materials Science Vallabh Vidyanagar - 388 120 Gujarat, INDIA	Research Studies • Thermosetting Resin Pyrolysis
Schunk Kohlenstofftechnik GmbH PO Box 6420 W-6300 Giessen 1, GERMANY	Component Design, Fabrication & Tests • CCC Fabrication • Industrial Applications and Parts
Shaanix Nonmetallic Materials and Technology Institute PO Box 72 Xian, Shaanix, P.R. CHINA	Materials & Process Development • Low-Cost, Powder-Filled Composite Fabrication • 3-D HIPIC Processing

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CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Shikibo, Ltd. Industrial Textile Division 1500-5 Shibahara Minami, Yakaichi Shiga 527, JAPAN	Materials & Process Development • 3-D Preforms and Composite Fabrication
Showa Denko KK 2-10-12 Shiba Daimon Minato, Tokyo 105, JAPAN	Component Design & Tests • 3-D CCC Parts • Plasma Facing Component Designs and Testing
Sigri Elektrographit GmbH Werner-von-Siemens Strasse 18 Postfach 1160 D-8901 Meiting bei Augsburg, GERMANY	Materials & Component Manufacturing • Engine Vectoring Vanes • Reactor Heat Exchanger Tubes • Commercial Parts
Societe Europeenne de Propulsion Division Propulsion & Poudre et Composites LeHaillan - BP 37 F 33165 Saint Medard en Jalles, FRANCE	Materials & Component Manufacturing • 3-D and n-D Preforms and Composites • Rocket Nozzle Components • Brake Discs • Airframe Components • Property Measurements
Societe Le Carbone Lorraine B.P. 31-37-41, rue Jean-Jaures 92231 Gennevilliers, FRANCE	Materials & Component Manufacturing • Preform Densification • Commercial Products
SOREQ Nuclear Research Centre Plasma Physics Department Yavne 70600, ISRAEL	Materials Property Measurements • Laser-Induced Effects • Spallation
State Research Institute of Graphite 2, Electrodnaya Street Moscow, 111524, RUSSIA	Material Science & Process Development • Fundamental Behavior • Materials & Process Development • Materials Property Measurements • Materials & Component Manufacturing
Toho Rayon Company, Ltd. Mishima Plant 234 Kamitogari, Nagaizumi-cho Sunto-gun, Shizuoka 411, JAPAN	Component Manufacturing • Turbine Wheel with Integral Blades
Tokyo Institute of Technology Faculty of Engineering 2-12-1, Ookayama Meguro-ku, Tokyo 152, JAPAN	Research Studies • Fiber-Matrix Bonding • Hot Pressing Process

APPENDIX 5 (Continued)
CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
Tokyo Institute of Technology Research Laboratory of Engineering Materials 4259 Nagatsuta-cho Midori-ku, Yokohama 227, JAPAN	Materials:Process:Property Studies • Fiber-Matrix Bonding • Work-of-Fracture • Neutron Irradiation Effects
TONEN Corporation 1-3-1 Nishi-Tsurugaoka, Ohi-machi, Iruma-gun Saitama 354, JAPAN	Materials:Property Studies • Pitch-Based Graphite Fibers • Composite Strength Properties • Unidirectional Composites
Toyohasi University Department of Materials Sciences Tempaku-cho Toyohasi 440, JAPAN	Property Measurements & Research • Fracture Behavior
Universite de Bordeaux-I 351 U.R.A. C.N.R.S. Cours de la Liberation 33405 Talence Cedex, FRANCE	Research Studies • Hybrid Composites • Property Measurements • Damage and Failure
University of Bath School of Materials Science Bath, BA2 7AY, ENGLAND	Materials:Process:Property Studies • Flexural Strength after Oxidation • Dynamic Elastic Modulus
University of P. et M. Curie Laboratoire de Mecanique et Technologie 61, Avenue du President Wilson Cachan Cedex, FRANCE	Research Studies • CCC Damage Modeling
Universitat Wien Institut fur Festkorperphysik Boltzmanngasse 5, A-1090 Vienna, AUSTRIA	Research Studies • Composite Pore Structure • Small-angle X-ray Scattering
University of Ibaraki Faculty of Engineering Hitachi 316, JAPAN	Research Studies • Neutron Irradiation Effects • Erosion, Thermal Shock, and Fracture
Universitat Karlsruhe Institut fur Chemische Technik Kaiserstrasse 12 7500 Karlsruhe, GERMANY	Research Studies • CCC Overviews • Fiber-Matrix Bonding Materials:Process:Property Studies • Oxidation-Resistant Coatings • Pitch Viscosity
University of Manchester Manchester Materials Science Centre Manchester, ENGLAND	Research Studies • Thermal Conductivity Measurements • Thermal Diffusivity Measurements

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CONTRIBUTORS TO CCC TECHNOLOGY

Organization	Area of Contribution
Section E. Non-USA Organizations (Continued)	
University of Newcastle Upon Tyne Northern Carbon Research Laboratories School of Chemistry Newcastle Upon Tyne, ENGLAND	Basic Research • High Carbon Matrices
University College of Swansea Swansea, Wales, UNITED KINGDOM	Research Studies • Biocompatible Materials
University of Technology Department of Chemical Engineering Loughborough, Leicestershire LE11 3TU, UNITED KINGDOM	Research Studies • CCC Void Structure
University of Tokyo 22-1 Institute of Industrial Sciences Roppongi 7-chome Minato-ku, Tokyo 106, JAPAN	Research Studies • Low-Cost, Fast Processes
University of Tokyo Department of Materials Science Hongo, Bunkyo-ku Tokyo 113, JAPAN	Process:Property Studies • Heat Treatment Effects • Mechanical Properties • Coating:Substrate Microstructures
Universitat Ulm Department of Surgery D-7900 Ulm, GERMANY	Research Studies • Clinical Implants
Vaikram Sarabhai Space Centre Government of India Department of Space ISRO, Trivandrum 695013, INDIA	Research Studies • Fiber-Matrix Bonding
Waseda University Department of Mechanical Engineering Tokyo, JAPAN	Research Studies • CCC Fracture Toughness