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Presented herein are results of research conducted at Chemetal Corp. under Cont. No. F49620-77-C-0086 during the period from April 1977 to December 1978. The purpose of this research was to investigate the CNTD (Controlled Nucleation Thermochemical Deposition) process developed at Chemetal as it applies to the microstructural properties of silicon carbide. A general parametric study was conducted of the silicon carbide chemical vapor deposition system with emphasis on parameters which might influence directly the mechanism of CNTD. An iterative approach was employed which related deposition conditions to room temperature		

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tensile strength and microstructure. It was hypothesized that conditions which effected minimum grain size with a probable minimum flaw population in deposits would result in increased strength.

CNTD silicon carbide deposits with average grain sizes of 500-1000Å were obtained. Room temperature flexural strengths in excess of 3000 MPa (435 kpsi) were recorded on wire samples. Strength was found to be strongly dependent upon microstructure and probably on composition of the deposit.

Unexpectedly high fracture toughnesses were observed (~~15 to 16 MPa√m~~ in some samples) and were associated with the presence of chlorine during preliminary studies. Widely varying strengths were observed in furnace deposited bend bar samples indicating that the deposition conditions for CNTD SiC on directly heated wire substrates require significant changes when deposition is done in a hot wall furnace.

Written by


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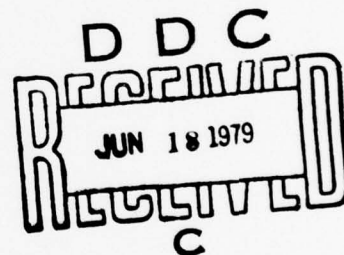
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AN INVESTIGATION OF THE CNTD MECHANISM
AND ITS EFFECT ON MICROSTRUCTURAL PROPERTIES

CONTRACT NUMBER F49620-77-0086

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This Final Technical Report, covering the period from 15 March 1977 to 15 December 1978 was prepared by Chemetal Corporation under Air Force Office of Scientific Research Contract F49620-77-C-0086. Major Wilbur C. Simmons is the Program Monitor.

The Principal Investigator is Mr. Robert A. Holzl. The Program Managers were Dr. Jacob J. Stiglich and Mr. Brian G. Zeale. Experimentation and evaluation was conducted by Messrs. Ben H. Tilley, Sam H. Rustomji, and Deepak Bhat.

The research is being coordinated with other government agencies. Joint investigations have been made with and data shared with the following:

Air Force Materials Laboratory, Dr. Henry Graham
NASA-Lewis Research Center, Dr. Sunil Dutta
Naval Research Laboratory, Dr. R. W. Rice

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I. INTRODUCTION

AFOSR CONTRACT No. F49620-77-C-0086

I. INTRODUCTION

Silicon carbide has been the object of much research and development attention in recent years because of its potential as a structural material to be used in high temperature, erosive, corrosive environments such as gas turbine engines. Chemical Vapor Deposition (CVD) silicon carbide is thought to have potential because it is made without additives which detract from its intrinsic strength, oxidation resistance and other properties.

A process has been developed at Chemetal which is generically similar to CVD. The microstructures of the resultant deposits are significantly different, however, in that the columnar grains which are typical of CVD materials are replaced by non-columnar deposits averaging 500-1000Å in grain size. This process has been referred to as Controlled Nucleation Thermochemical Deposition (CNTD).

The primary goal of the present program has been to achieve a better understanding of the CNTD mechanism as applied to SiC*. It has been assumed that the most desirable structure for a brittle ceramic such as silicon carbide would be that which has minimum flaw size, minimum flaw population, and minimum grain size. Thus, the emphasis during the present project has been on measuring room temperature flexure strength and the effects of various deposition parameters on it. Other characterization data obtained are hardness, fracture toughness (by indentation), surface topography and microstructure, and chemical composition (by energy dispersive x-ray analysis).

*The effort has spanned roughly 1-3/4 years. The present report covers the entire period although a summary report (1) was issued following the initial nine month period.

II EXPERIMENTAL EQUIPMENT AND PROCEDURE

During the Phase I (9 mos.) experiments deposits were made on tungsten wires directly heated by passing a current through them. In the second phase a hot wall graphite furnace was used to heat graphite bend bar substrates by radiation. Deposition parameters investigated included partial pressures of reactant species, total gas pressure, substrate temperature, gas preheat temperature, and various sources for silicon and carbon.

II. EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental system used in the first phase of this work is schematically depicted in Figure 1. The main deposition chamber was an air-cooled 75mm diameter quartz chamber. The majority of the tests used two 0.05cm diameter x 20.32cm long resistively heated tungsten wires as substrates. Preliminary tests were run also, using 2.54cm diameter x 15.24cm long graphite tubes heated by induction. Argon, hydrogen, silicon and carbon bearing gases* were introduced through an injector at the top of the chamber. A clamshell heater was used to regulate the pre-heat temperature of the reactant stream. The temperature in the reactant stream was monitored by placing a thermocouple 1.27cm from the filament and filament temperature was measured with a micro-optical pyrometer.

Methyltrichlorosilane (MTS)* was selected as the source of both carbon and silicon for the initial portion of the program. A gas metering system was used for MTS in which argon was used as a carrier gas. The carrier gas was passed through a vessel containing MTS, the amount of MTS carried being dependent upon the vapor pressure of the liquid.

*Properties of gases used are given in Appendix A.

Subsequently, the mixed stream was monitored through the use of a Hastings electronic mass flowmeter, and the flow of methyltrichlorosilane determined by measuring the difference between the flow of MTS with argon and the flow of argon alone. A similar system was used for silicon tetrachloride as the silicon source. In this case, the carbon source chosen was propane, which was dispensed as were the other gases through standard borosilicate glass rotameters with pressure gauges and needle type valves for maintaining constant metering pressure. The selection of deposition run time was made by choosing deposition rates and times to result in deposits of 0.05 to 0.065cm.

All deposits were characterized as to surface morphology, deposition rate, hardness and flexural strength. Modulus of rupture was determined by using a three point bend test. X-ray diffraction was used for phase identification, and energy dispersive analysis was used to determine the composition of the deposit. Fracture surfaces, as well as polished and etched surfaces, were examined metallographically with scanning electron microscopy to determine resultant microstructures. Several etching solutions were attempted with the most satisfactory results obtained by etching electrolytically using a solution of 5% chromic acid with 10cc HF in 100cc of solution.

Figure 2 illustrates the hot wall furnace system utilized during the Phase II (12 months) experiments. The furnace (an inductively heated graphite tube) was used to heat graphite bend bar substrates (2.54mm x 5.08mm x 76.20mm) and graphite cylinders (25mm diameter x 25mm long) from which

ring and disc samples could be cut after deposition. As in the wire experiments, a clam shell heater was used to control the preheat temperature of the gas stream. The graphite furnace temperature was monitored with an optical, disappearing filament, pyrometer.

In addition to the indirectly heated bend bar substrates, some runs were carried out on directly heated (by induction) graphite substrates 2.54cm diameter x 7.62cm long. The objective was to obtain 2.54cm diameter rings for burst tests. These results will be described below.

Argon was used as a carrier gas in conjunction with the various silicon bearing gases during the second phase experiments. Argon was passed through a boiler containing the silicon bearing liquid. The amount of liquid used was thus dependent on its vapor pressure, (i.e. the temperature in the boiler). The mass flow rates of reactants were obtained by means of standard borosilicate glass rotameters which were in turn calibrated against a Hastings electronic mass flowmeter. Silicon bearing gases used were SiCl_4 , SiHCl_3 , and methyltrichlorosilane (MTS). Propane was the carbon source as required. Deposit thickness was roughly determined by deposition time and rate.

During the course of the second phase, more than 100 experimental runs were made. The deposits were characterized as to surface morphology, hardness, fracture toughness (by indentation), flexural strength (in three point bending), or burst strength (in the case of rings). Chemical composition was assessed using energy dispersive x-ray analysis. X-ray

diffraction and scanning electron microscopy were used to examine as deposited surfaces, polished and etched surfaces and fracture surfaces.

Specific equipment and procedures used were as follows:

1. X-ray Diffraction A General Electric x-ray diffractometer was used incorporating CuK_α radiation with a Ni filter, a time constant of 2, and an intensity range (full scale) of 2000 cps. All peaks obtained matched the ASTM diffraction data file for β -SiC, however, intensities varied considerably over the course of the experiments. See Figure 3 for a typical x-ray diffractometer scan.
2. Scanning Electron Microscopy/EDS Equipment available at the University of Southern California was used: a Cambridge Steroscan S4-10 coupled with a Tracor Northern energy dispersive x-ray spectrometer.
3. Transverse Flexural Strength Room temperature flexural strength measurements were carried out on a Comten testing machine. Both 3 point and 4 point fixtures were available. Three point measurements were emphasized in the first phase experiments using tungsten wire substrates (span - 14.3mm). Specimens were approximately 1.8mm diameter x 40mm long; the wire diameter used was 0.5mm. Four point measurements were made on the graphite bend bar specimens used in the second phase (furnace) experiments. Coating thicknesses varied from 0.076mm to 0.50mm, span lengths were 1.90cm (inner) x 4.45 cm (outer).

III EXPERIMENTAL RESULTS AND DISCUSSIONS

4. Microhardness HV₅₀₀ were determined using a Leitz microhardness tester. Most values were in the range of 2500 to 3200 Kg/mm², but isolated values up to 4000 Kg/mm were noted. A magnification of 400X was used. No attempts were made to correlate hardness with microstructure. It is assumed that the fine grained, CNTD type microstructure is capable of some variation in hardness and that impurity effects may be present as well.
5. Fracture Toughness The critical stress intensity factor K_{1c} was deduced from microhardness indent fracture characteristics using the Leitz microhardness tester ⁽²⁾. Some values apparently higher than 10 MPa√m were obtained but could not be verified by an outside laboratory. They were, however, repeatable in-house in measurements done 5 months after the initial work in-house. The question of fracture toughnesses greater than 10 MPa√m must be considered unresolved until the effect is verified and then investigated by means of a thorough series of experiments.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The majority of investigations during the first phase of this study were conducted by depositing SiC on tungsten wires. The primary objective of this phase was to establish a set of operating parameters for reproducible manufacture of CNTD SiC. Subsequent investigations in the second phase were directed toward possible improvement from these baseline conditions and determining the sensitivity of the resultant deposit to variation in these parameters. It was determined that suitable conditions for CNTD SiC were:

total pressure

200-300 Torr

substrate temperature	1100-1150°C
MTS	250 ml/min
hydrogen	3360 ml/min
argon	800 ml/min
gas preheat temperature	540° - 640°C

Processed according to these conditions, CNTD silicon carbide was deposited at a rate of approximately 0.26 to 0.38mm an hour. A typical resultant deposit was near stoichiometric, having a composition, containing a slight excess of silicon, approximately $\text{SiC}_{0.95}$. The deposits were found to be free of the columnar crystal habit indigenous to most CVD products, and had an average crystallite size in the range of 500-1000Å. The surface topography was unusual, as compared with conventional CVD products in that it was quite smooth with a typical surface roughness of 2-5 RMS. At low magnification, the material appears quasi-vitreous. Higher magnification of metallographic sections reveals a laminar structure not unlike that characteristic of pyrolytic graphite. X-ray diffraction revealed a consistent preference for a (111) type texture in most of the deposits an example of which is shown in Figure 3. This effect may be explained by postulating that the SiC crystallites are deposited with (111) planes in the plane of the deposit, i.e. the growth direction is $[111]$. This growth is then interrupted repeatedly on a submicron scale; successive deposited material is not layed down randomly but retains its (111) texture. Transverse flexure strength values at room temperature as measured on a 3 point bend test, have been recorded in excess of 3100 MPa (464,000 psi). The Vickers Hardness of such material is typically 3600-4000 kpa as measured with a 500 gram weight. Critical stress

intensity factors (K_{Ic}), representative of fracture toughness as measured by indentation methods, are 5 to 6 MPa $\sqrt{m}$ in the growth direction and 4-5 MPa $\sqrt{m}$ normal to the growth direction. Consult Table 1 for representative data.

In the course of Phase 1 investigations, the following effects were observed while trying to define CNTD conditions:

1. At a constant mixture ratio of hydrogen to methyltrichlorosilane (approximately 13:1) only columnar deposits were produced at filament temperatures above 1250°C without regard to total pressure.
2. At these mixture ratios, deposits made below 200 torr were columnar without regard to filament temperature.
3. Noncolumnar deposits were made at filament temperatures in the range of 1100-1150°C at total pressures between 200-300 torr.
4. The nature of the deposit was not responsive to variation in the mixture ratio of hydrogen to MTS.
5. Lower deposition temperatures tended to promote the deposition of excess silicon and higher temperatures, the deposition of excess carbon.
6. All deposits were the cubic beta form of silicon carbide.

Having observed that deposition in the range of 1100-1500°C produced the desired structure, but that deposits tended to contain excess silicon, a slight modification in the system was introduced. A second active gas containing carbon was added. Propane proved to be a suitable additive. The addition of propane improved the stoichiometry, and in so doing appeared to improve the burst strength characteristics. Consult Table II Phase I Experiments for representative data.

Efforts were also conducted to produce deposits having similar characteristics to those obtained with MTS by using silicon tetrachloride as a silicon source and propane as a carbon source. These deposits, without exception, showed lower strengths and greater propensity toward a columnar crystal habit. The difficulties encountered during brief experiments with the silicon tetrachloride hydrocarbon system in Phase I were overcome during Phase II experiments.

Preliminary investigations were conducted on different substrates and shapes, to wit SX4 graphite tubes*, 2.54cm diameter x 15.24cm long. The SX4 graphite was selected owing to the fact that its coefficient of thermal expansion matches that of silicon carbide quite closely. Using essentially similar conditions to those used for the filament tests, fine grain non-columnar deposits of silicon carbide were achieved. Methyltrichlorosilane was employed as the silicon source with additions of propane to the gas stream to effect proper stoichiometry. Considerable difficulty was experienced, however, in maintaining uniform microstructure over the full 15.24cm length. This is attributed primarily to the buildup of the

* Airco, Speer, St. Marys, Pennsylvania

boundary layer on the surface of the part, which in turn, affects the pre-heat temperature of the gases and causes variation in the intermediate reaction products. Burst tests on rings formed during these experiments were unsatisfactory because of difficulty experienced in specimen preparation; values of 200 to 500 MPa (29-72.5 ksi) tensile strength were recorded. Failure always occurred from notches produced in cut-off so that intrinsic strength was never accurately measured. Data given in Table II.

In Phase II experiments rings cut from similar bars as just described were chamfered on the O.D. and oxidized for 2 hours at 900°C. Burst strengths after this procedure were 450 to 620 MPa (65 to 90 ksi). Strength values were quite consistent within each run using this ring preparation technique, the range of values being typically $\pm 10\%$ from the mean. Refer to Table II, Phase II, Experiments for a compilation of these data.

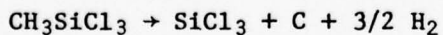
By far the most influential factor noted in the course of the investigations was the regulation of pre-heat temperature, particularly as it related to resultant microstructure and flexural strength of the deposit. For filament temperatures of approximately 1125°C, the best pre-heat temperature of the gas appeared to be 575°C, or a difference between the pre-heat temperature and filament temperature of about 550°C, as measured approximately 1cm from the deposition surface. Initial indications were that at higher substrate temperatures a larger difference than 550°C is required to maintain strength, whereas at lower filament temperatures, a smaller difference in temperature is indicated.

Figures 4,5 and 6 compare CNTD material and columnar material which is typical of high quality conventional CVD silicon carbide. The significant difference in the fracture surfaces is interesting and warrants further study. From metallographic sections, there is clearly evidence of a laminar structure in the CNTD material as depicted in Figures 7, 8 and 9. Figure 7 shows distinct bands, and is representative of specimens of lower flexural strength (≤ 700 MPa). In Figure 8, the bands are finer with some variation. These specimens demonstrate flexural strength in the range of 700-2000 MPa. The most finely banded structures, as shown in Figure 9, evidence the best strength. Further investigations are being conducted to identify the morphology of the banding. It is believed to be related to the gas temperature and the kinetics of the reaction. The presumption can be made, although not yet proved, that the material structure as shown in Figure 7 may be caused by the presence of excess silicon. There is some concern that such a banded structure may contain considerable internal stress. No specific investigations of this possibility have as yet been conducted.

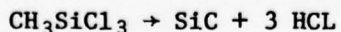
Experiments conducted by the CNTD process in the deposition of other materials have justified the conclusion that there is a basic difference between the mechanism of this process and that of conventional CVD (8). It has been hypothesized that an intermediate compound is actually deposited on the substrate and is subsequently thermochemically converted to the final product. The thermochemistry of the deposition of silicon carbide has been considered in light of this hypothesis.

Evidence of a lower chloride of silicon having a composition of $\text{SiCl}_{2.6}$ has been claimed (3). In fact, in the course of the subject investigations, such a material has been observed as an extremely low vapor pressure amber liquid (See Fig.15). To justify its existence as a liquid at elevated temperatures (circa 1000°C) under the pressure conditions in the reaction chamber, it must be postulated that the material is polymeric. Free energy data are not available for $(\text{SiCl}_{2.6})_x$, but it is believed by Chemetal to be an important intermediate product in the CNTD of silicon carbide. Such an assumption seems consistent with the experimental observations. When the deposition temperature is raised or the total pressure reduced, the CNTD product is not made. This is probably because these conditions tend to distill the intermediate and prevent its collection on the substrate.

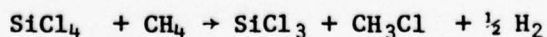
The effect of the gas pre-heat temperature and the difference between MTS and silicon tetrachloride as silicon sources may also be considered in light of the postulated deposition mechanism of an intermediate product. Compare the following reactions:



$$\Delta G_{800^{\circ}\text{K}} = - 2.950 \text{ kcal}$$



$$\Delta G_{800^{\circ}\text{K}} = - 0.84 \text{ kcal}$$



$$\Delta G_{800^{\circ}\text{K}} = + 38.935 \text{ kcal}$$

The free energy data used is from the JANAF Tables (4). This comparison

is made using SiCl_3 as the product since no free energy data are available for $(\text{SiCl}_{2.6})_x$.

It may be concluded that silicon trichloride is made more readily from MTS than it is from a mixture of silicon tetrachloride and a hydrocarbon at 800°K . Similarly, there is a slightly higher potential for the formation of silicon trichloride from MTS than there is for the formation of silicon carbide.

These data suggest that a pre-heat temperature of 800°K might be significant in the formation of the necessary intermediate deposit. The data also suggest that conditions for making a CNTD deposit from the silicon tetrachloride/hydrocarbon system would have to be substantially different from those used for the MTS system.

The main objective of the first phase was thus accomplished. A set of deposition parameters was determined which produced very high room temperature flexure strengths of deposits on tungsten wires. Modest exploration of parameter changes were made in anticipation of Phase 2 experiments.

It should be noted that during the time of the first phase work, samples of CNTD SiC deposited on tungsten wires were furnished to NASA (Lewis) Research Center for verification of their properties. Specimens from that batch in turn were given to Naval Research Lab. and to the Air Force Materials Laboratory for other property measurements. Chemetal room temperature flexure strengths were verified. In addition, elevated

temperature strengths showed unexpected behavior in that they were higher at 1300°C than at room temperature⁽⁵⁾. This result may be rationalized by postulating a residual tensile stress present at room temperature which is relieved at temperatures near the deposition temperature⁽⁶⁾. Room temperature flexure strengths (four point bending) were 1724 MPa (250,000 psi) while strengths measured at 1300°C in nitrogen varied widely but averaged approximately 2759 MPa (400,000 psi). These values generally confirm Chemetal in-house results at room temperature.

Second phase experiments began with explorations of different Si bearing gases in an attempt to generalize the conditions evolved in the first phase (9 month) study for CNTD SiC. Essentially the same experimental set-up as in the first phase was used (Fig. 1) for directly heated tungsten wires. See Table III for typical deposition conditions and Figures 10, 11 and 12 for graphical representation of the trends.

It was desired to explore alternative Si bearing gas systems. Therefore experiments were conducted using SiCl₄/H₂/ propane (24 runs) and SiHCl₃/H₂/ propane (5 runs). The results of these investigations may be summarized as follows:

1. The CNTD structure was observed throughout the experiments using SiCl₄ and SiHCl₃.
2. The SiHCl₃ system yielded much higher deposition rates than did the SiCl₄ system, up to 2X the rates under similar temperatures and pressures.

3. The most important parameter affecting the deposition rate in the SiCl_4 system was chamber pressure. Fig. 10 gives the combined effect of chamber pressure and part temperature for this system.
4. The effects of substrate temperature on strength and deposition rate are shown in Figures 10, 11 and 12.
5. In general, the CNTD structure was attained when:
 - a) The substrate temperature was ($\leq 1150^\circ\text{C}$), hydrogen flow was ($\geq 4000\text{cm}^3/\text{min}$), gas stream temperature was ($\geq 675^\circ\text{C}$), and chamber pressure was between 250 and 500 Torr.
 - b) The substrate temperature was ($\geq 1150^\circ\text{C}$) hydrogen flow was ($\leq 500\text{cm}^3/\text{min}$), the gas stream temperature was ($\leq 570^\circ\text{C}$), and chamber pressure ≥ 500 Torr.

After the initial explorations of various Si source gases, Phase II experiments continued with attempts to transfer CNTD technology from deposition on directly heated wires to deposition on substrates heated in a furnace. Attempts were made to use the SiCl_4/H_2 / propane system for initial furnace runs, but delamination and microcracking of the deposits and time constraints necessitated return to the MTS system. The reaction chamber was shown in Figure 2. Substrates were graphite (UT22, Ultracarbon Co.) bend bars having dimensions 76mm x 3.17mm x 6.35mm.

SiC deposits were made in an initial series of experiments which explored the effect of substrate temperature and the position of the substrate in the furnace chamber in an attempt to get uniform deposition over the 76mm length of the substrate. Substrate temperature varied from 1100°C to 1230°C as determined by an optical pyrometer sighting on the part in the furnace.

Deposits made at substrate temperatures between 1100° and 1150°C were mechanically weak. Better results were achieved between 1200°C and 1250°C, where the fracture toughness was observed to increase from values of 4 to 6 MPa $\sqrt{m}$ (at 1100°C to 1150°C) to 15 to 16 MPa $\sqrt{m}$. X-ray dispersive analysis of these samples showed the presence of chlorine which seemed to be associated with the increased fracture toughnesses.

The presence of measurable amounts of chlorine could be explained by postulating the presence of a polymeric liquid phase (e.g. SiCl_{2.6}) as described above which was not being completely reacted during the deposition process. Attempts were made to reduce or eliminate the chlorine content by increasing the hydrogen fraction in the gas stream. These experiments were successful in obtaining stoichiometric or silicon excess deposits but the fracture toughness returned to the range of 5 to 7 MPa $\sqrt{m}$. It became clear that the high fracture toughnesses were associated with silicon deficiency, and chlorine contents of 0.2 to 2 wt%.

Some elementary heat treatment experiments were carried out on selected samples in which the high fracture toughnesses had been observed. Data for these experiments is given in Table V. The purpose of these experiments was to obtain some data on the stability of the effect. Accordingly samples for which the fracture toughness and chlorine contents had been measured were heat treated at furnace temperatures of 1400° or 1550°C in flowing argon for times which varied from 1 hour to 3 hours. It can be seen from the data that hardnesses generally decreased after heat treatment, although high fracture toughnesses were still associated with chlorine contents between 0.2 and 2.0% by weight with an apparent maximum at about $1^{\text{wt}}/\text{o}$. Silicon contents for all high fracture toughness samples both before and after heat treatment were substoichiometric.

Time and program constraints prevented any other investigations of the anomalously high fracture toughness effects.

Fig. 13 shows the surface and interior structure of the SiC layer of sample (run) #751, for which pertinent data are given on Table: IV. The lack of visible microstructure until one reaches a magnification of 20,000X is apparent. The graphite substrate is visible in the split field bottom picture.

During the course of these studies, CNTD SiC was deposited on NC203 (hot pressed SiC, Norton Co.) flexure test bars to explore its effect on strength of the bars. Fig. 14 shows one of these deposits. The NC203

substrate is visible in the upper left view. The upper right view shows the structure at 20,000X. The bottom view shows a Vickers hardness indent made under a load of 2000 gms in attempt to compute a fracture toughness. The apparent hardness using this indent is $HV_{2000} = 3860 \text{ kg/mm}^2$. A 2000 gm indent at another location showed cracks from which a fracture toughness of $15.7 \text{ MPa}\sqrt{\text{m}}$ was calculated. The strength of the NC203 bars was raised from approximately 668 MPa (100,000 psi) to 828 MPa (120,000 psi) by adding the 0.015cm (0.006 in) CNTD SiC coating ⁽⁷⁾.

At the end of the experimental program, CNTD SiC was deposited on 2.54cm D. x 2.54cm long graphite substrates in a furnace using a range of deposition conditions as shown in Table VI. Six discs were cut 0.6cm from the top coated surface of these substrates; a-1 discs had a SiC layer of 0.51 to 0.65mm (0.020 to 0.025 in) on them. The discs were furnished to the Contract Technical Monitor for further evaluation.

IV CONCLUSIONS AND RECOMMENDATIONS FOR
FURTHER WORK

IV CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

1. CNTD silicon carbide having unusual strength and hardness characteristics can be made from active gas mixtures of:
 - a) methyltrichlorosilane/hydrogen
 - b) silicon tetrachloride/hydrogen/propane
 - c) trichlorosilane/hydrogen/propane
2. Proper control of deposition parameters such as substrate temperature, gas temperature, chamber pressure is important.
3. There is an apparent intermediate product formed, probably existing as a polymer of a lower chloride of silicon, which is an important precursor in the CNTD SiC process.
4. The presence of unexpected high fracture toughness values associated chlorine contents of 0.2 to 2.0 wt/o was observed.
5. Deposition of CNTD SiC on flexure test bars in a furnace has been demonstrated as a first step in scale up, but further work remains to extend scale up activities to larger and more complex geometries.
6. As scale up activities proceed and it is apparent that CNTD SiC is a candidate for high temperature structural applications, its elevated temperature mechanical properties (strength, creep, stress rupture, internal stresses) should be characterized.

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AFOSR Contract No. F49620-77-C-0086

7. Initial evidence for the existence of a SiC material having significantly higher fracture toughness than any bulk processed SiC has been obtained. This material, the conditions under which it is formed and its other properties should be characterized in a separate study.

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VI

APPENDICES

A Properties of gases

B Calculation of Flexural Strength
of a Rectangular Graphite Bend Bar

PROPERTIES OF GASES USED IN SiC EXPERIMENTS

<u>GAS</u>	<u>SUPPLIERS/GRADE/IDENTIFICATION</u>	<u>MINIMUM PURITY</u>
argon	Union Carbide, Linde Div. Liquid phase	99.998%
hydrogen	Union Carbide, Linde Div. Prepurified Grade	99.99%
nitrogen	Union Carbide, Linde Div. Liquid phase	99.997%
ammonia	Union Carbide, Linde Div. Specialty Gas Products Group, Anyhdrous Grade	99.98%
propane	local Southern California dealers heating quality	96%
methyltri- chlorosilane	Union Carbide, Chemicals and Plastics Div. A-154	98.5%
trichloro- silane	Union Carbide Chemicals and Plastics Div., A-19	99.9%
silicon- tetrachloride	Air Products and Chemicals, Inc., Specialty Gas Dept., Semi-Conductor Grade	99.7%

APPENDIX BCalculation of Flexural Strength of a Rectangular Graphite Bend Bar

Consider a composite beam of two materials A and B of different elastic moduli such that B forms a uniform coating around A. When this beam is subjected to flexure, the calculation of the flexure strength may be simplified by the method of equivalent section. By this method, the cross section of the substrate can be replaced by an equivalent section of the deposit such that at a given magnitude of axial strain, the force developed in the substrate and the equivalent section of the deposit are equal. Then the entire section can be treated as a single homogeneous material. It is assumed in this procedure that no slip occurs at the interface. The equivalent section is generated by changing the dimension of the substrate in the direction perpendicular to the direction of applied load.

For a given axial strain e , the force developed on the substrate is $F_s = eE_s A_s$, and that in the coating at the same point is $F_c = eE_c A_c$. For $F_c = F_s$, we have $E_c A_c = E_s A_s = nE_c A_s$ where $n = E_s/E_c$. Thus the equivalent area of the coating is equal to nA_s .

1. Rectangular Graphite Bend Bar

Consider now a rectangular beam of cross-section $b_1 \times h_1$ as shown in Fig. 1. A coating thickness t is applied uniformly on this substrate, so that

$$\frac{b_2 - b_1}{2} = \frac{h_2 - h_1}{2} = t$$

The area of the coating is $A_c (=b_2 h_2 - b_1 h_1)$ and that of the substrate is $A_s (=b_1 h_1)$. In the transformation of the area of the substrate, the dimension b_1 is changed to $n.b_1$.

In the case of a deposit of SiC or Si₃N₄ on graphite, we have the following: $E_{\text{graphite}} \approx 10$ GPa, $E_{\text{SiC}} \approx 450$ GPa and $E_{\text{Si}_3\text{N}_4} \approx 310$ GPa. Then, $n = E_s/E_c$ is equal to 0.022 and 0.032 for SiC and Si₃N₄, respectively. Thus, the equivalent area of the coating is only 2 to 3 per cent of the original substrate area. For all practical purposes, the graphite substrate is replaced by a void space. Then, the rectangular composite beam may be treated as a hollow beam.

For the purpose of calculating the moment of inertia, the hollow rectangular section is equivalent to an "I" section, as shown in Fig. 2. Thus,

$$I = b_2 h_2^3 - b_1 h_1^3$$

$$\text{and } \sigma_{\text{max}} = \frac{6 P h_2 a}{b_2 h_2^3 - b_1 h_1^3} \quad \text{where, } a = \text{length of moment arm}$$

2. Tungsten Wire Substrate

The coating of SiC on a tungsten wire substrate can also be analysed in a similar manner. For a circular section the transformation of the substrate leads to an elliptical equivalent section as shown in Fig. 3., where the minor axis is equal to $n \cdot d_s$ and the major axis is d_s .

For a deposit of SiC on tungsten, the modulus ratio, n is 0.87 ($E_w = 390$ GPa). Thus, as a first approximation, n may be taken as unity and the entire deposit may be treated as a single, homogeneous material. On the other hand, if an exact solution is sought, the moment of inertia of the transformed section is calculated as follows:

$$I_{\text{total}} = I_{\text{tubular section}} + I_{\text{elliptical section}}$$

$$= \frac{\pi}{64} (d_c^4 - d_s^4) + \frac{n\pi d_s^4}{64}$$

$$= \frac{\pi}{64} \{ d_c^4 - (1-n)d_s^4 \}$$

$$= \frac{\pi}{64} (d_c^4 - 0.13d_s^4)$$

Taking a typical example, $d_c = 1.5\text{mm}$ and $d_s = 0.5\text{mm}$ gives $I = 0.2481\text{mm}^4$ using the expression above, and $I = 0.2485\text{mm}^4$ if n is taken as unity. It is clear, therefore, that in the case of SiC on tungsten, the entire section can be treated as a single homogeneous material for the purpose of calculating the flexural strength.

It should be pointed out that in these calculations, the effect of the interface on the stress distribution in the material under flexural loading is neglected.

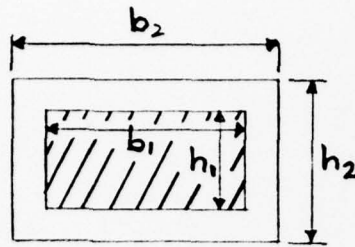
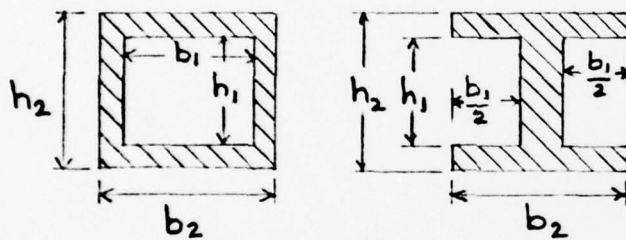


FIGURE 1



$$I = \frac{b_2 h_2^3 - b_1 h_1^3}{12}$$

FIGURE 2

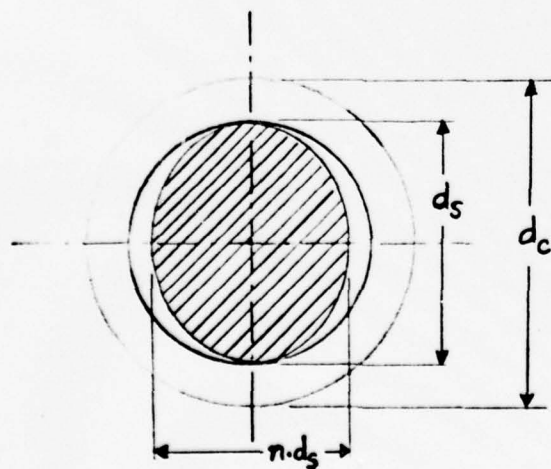


FIGURE 3
APPENDIX B

VII

FIGURES

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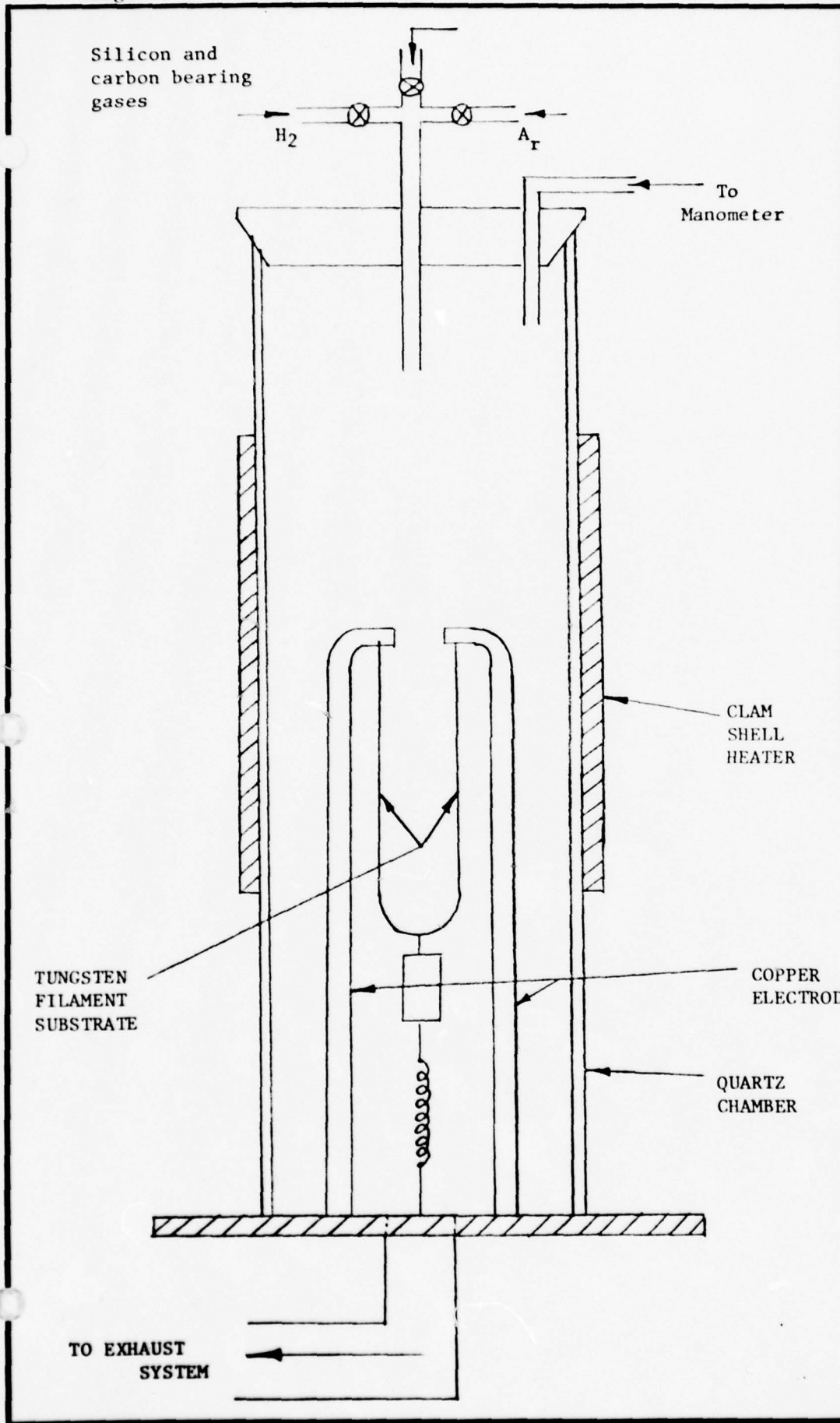


FIGURE 1 Schematic Diagram of SiC Deposition System used in Phase I

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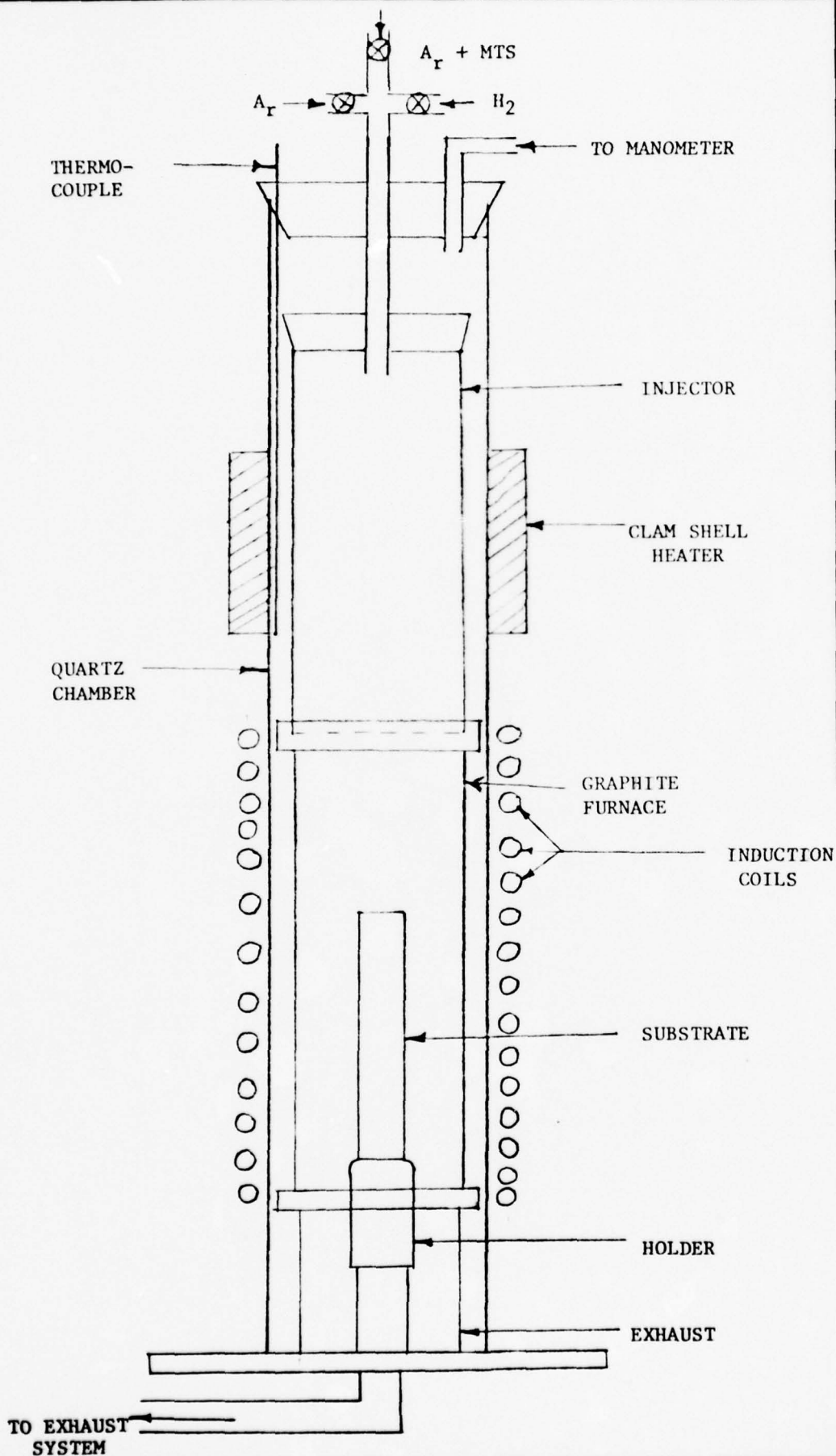


FIGURE 2 Schematic Diagram of SiC Deposition System used in Phase II

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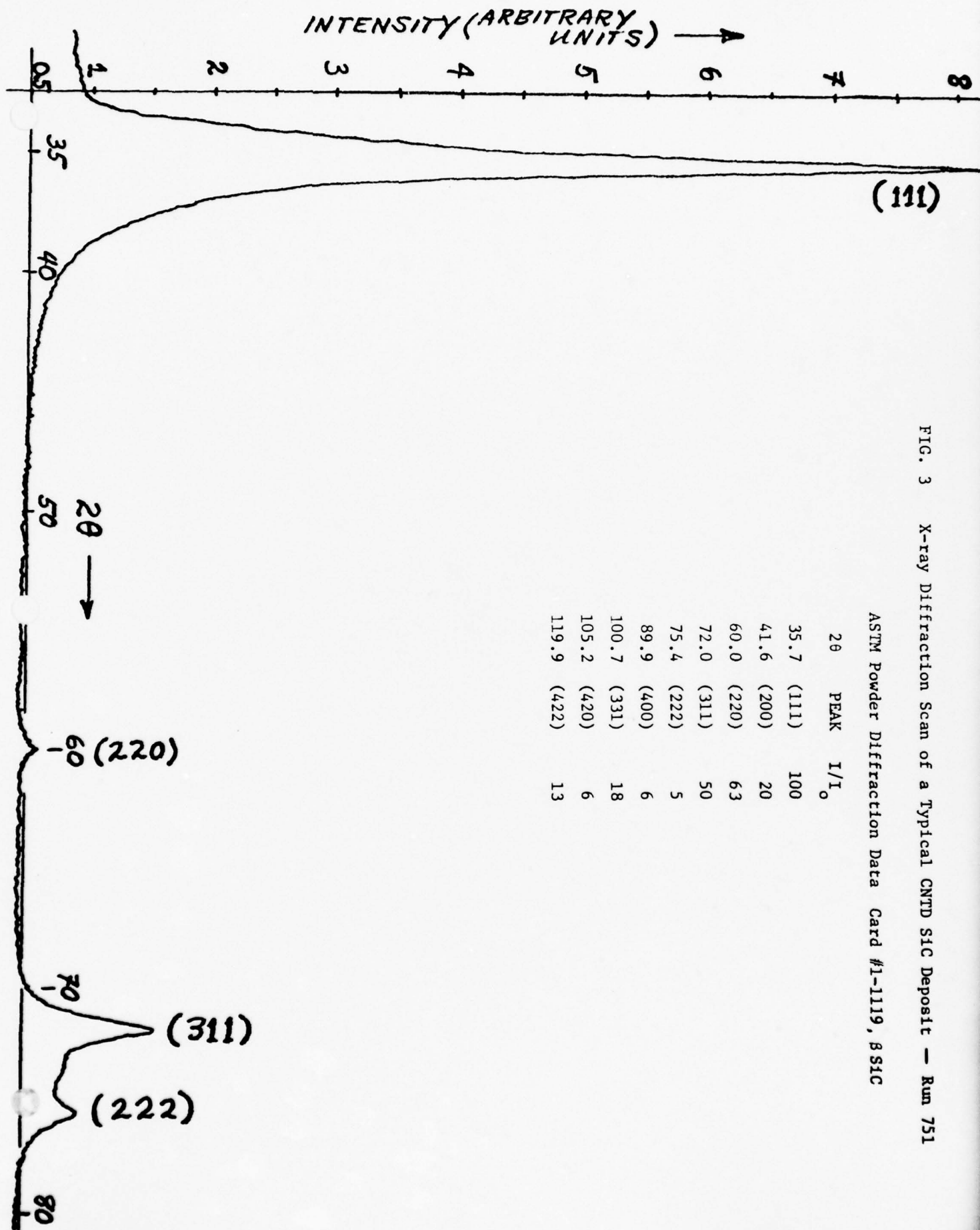


FIG. 3 X-ray Diffraction Scan of a Typical CNTD SiC Deposit — Run 751

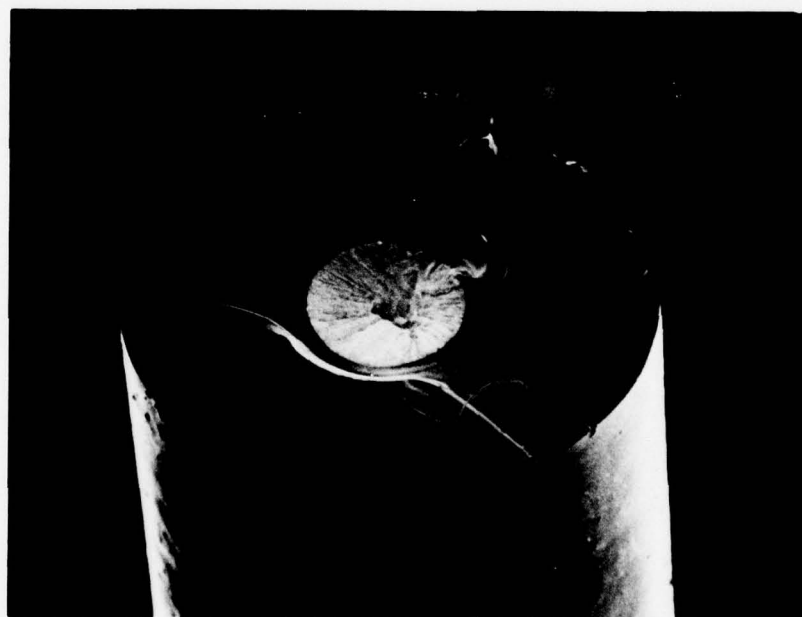
ASTM Powder Diffraction Data Card #1-1119, B SiC

FIGURE 4



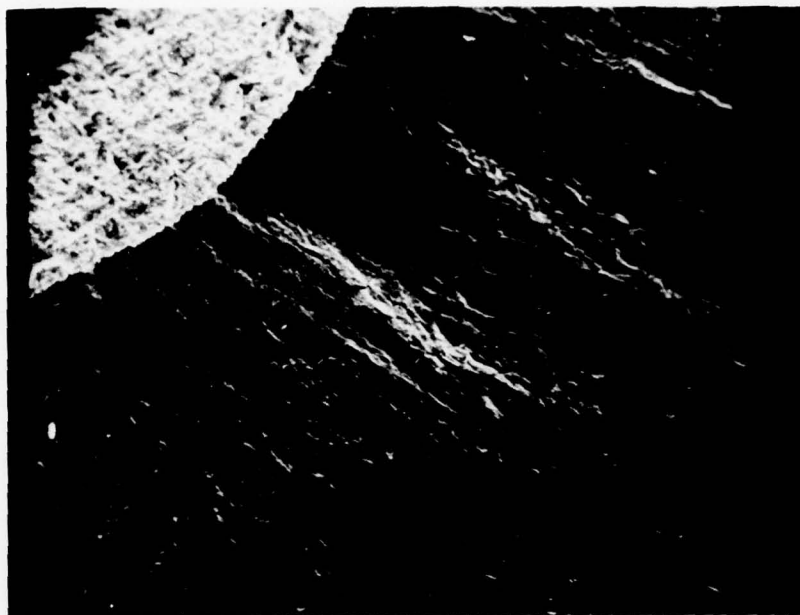
Fracture Specimen CVD SiC, 50X Magnification

FIGURE 5



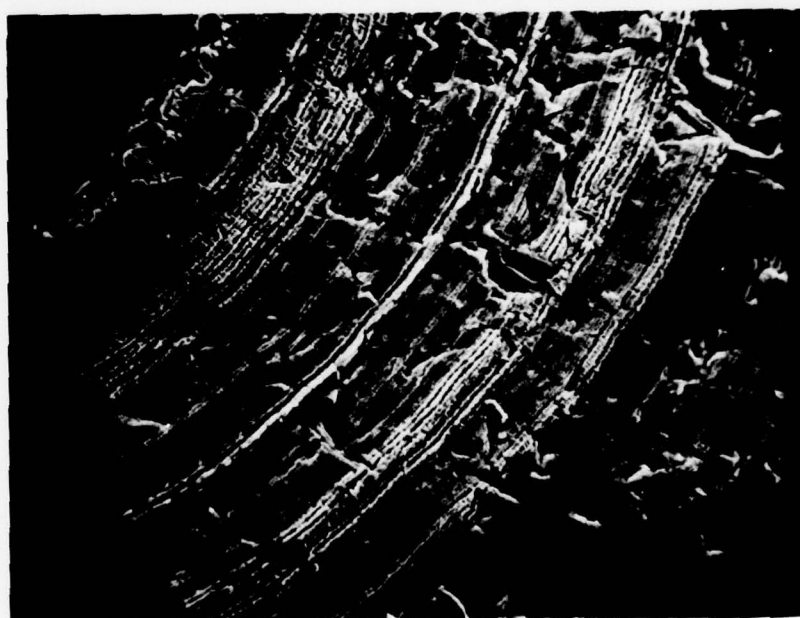
Fracture Specimen CNTD SiC, 50X Magnification

FIGURE 6



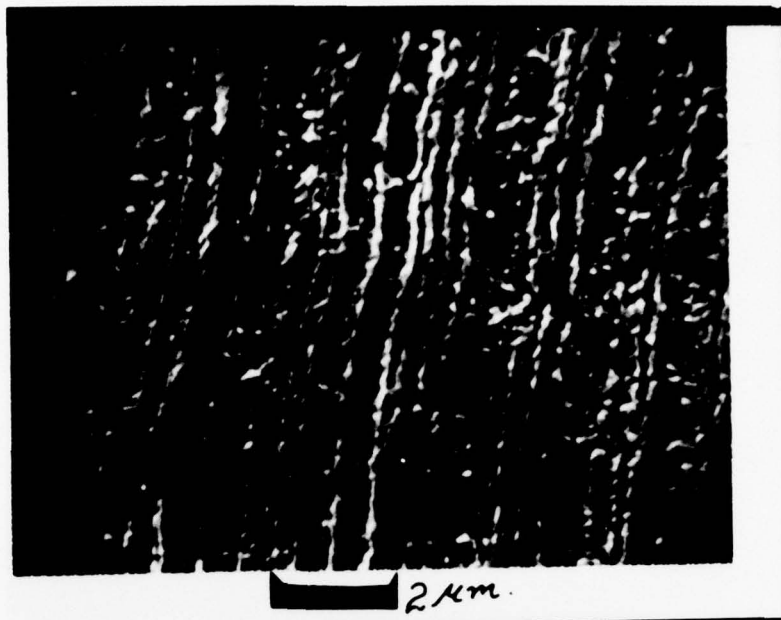
Section CVD SiC, 500X Magnification

FIGURE 7



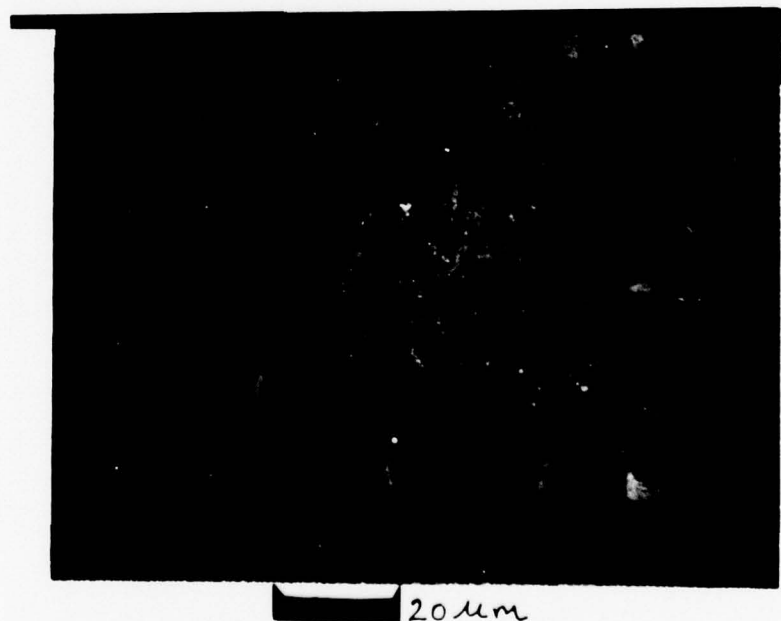
Section Low Strength CNTD SiC, 500X Magnification

FIGURE 8



Section Medium Strength CNTD SiC

FIGURE 9



Section High Strength CNTD SiC

FIG. 10 Chamber Pressure vs. Deposition Rate for Various Hydrog. Flows and Substrate Temperatures.

 $\text{SiCl}_4 = 300\text{ccs/min}$ $\text{C}_3\text{H}_8 = 68\text{ccs/min}$

S.T. = substrate temperature

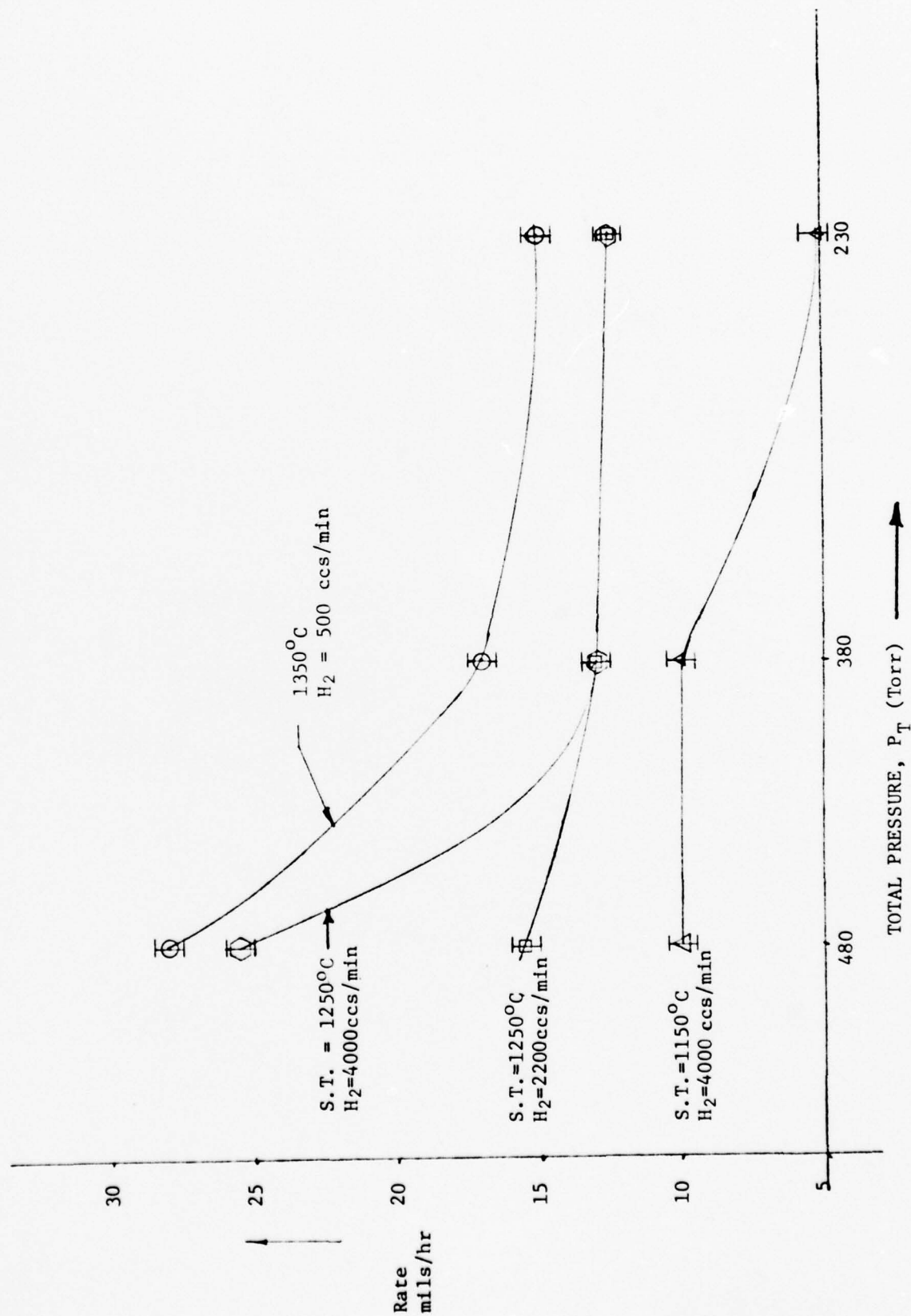


FIG. 11 Substrate Temperature vs T.R.S. for Two Chamber Pressures,
Low H₂ Flow.

SiCl₄ = 300ccs/min

C₃H₈ = 68ccs/min

H₂ = 500ccs/min

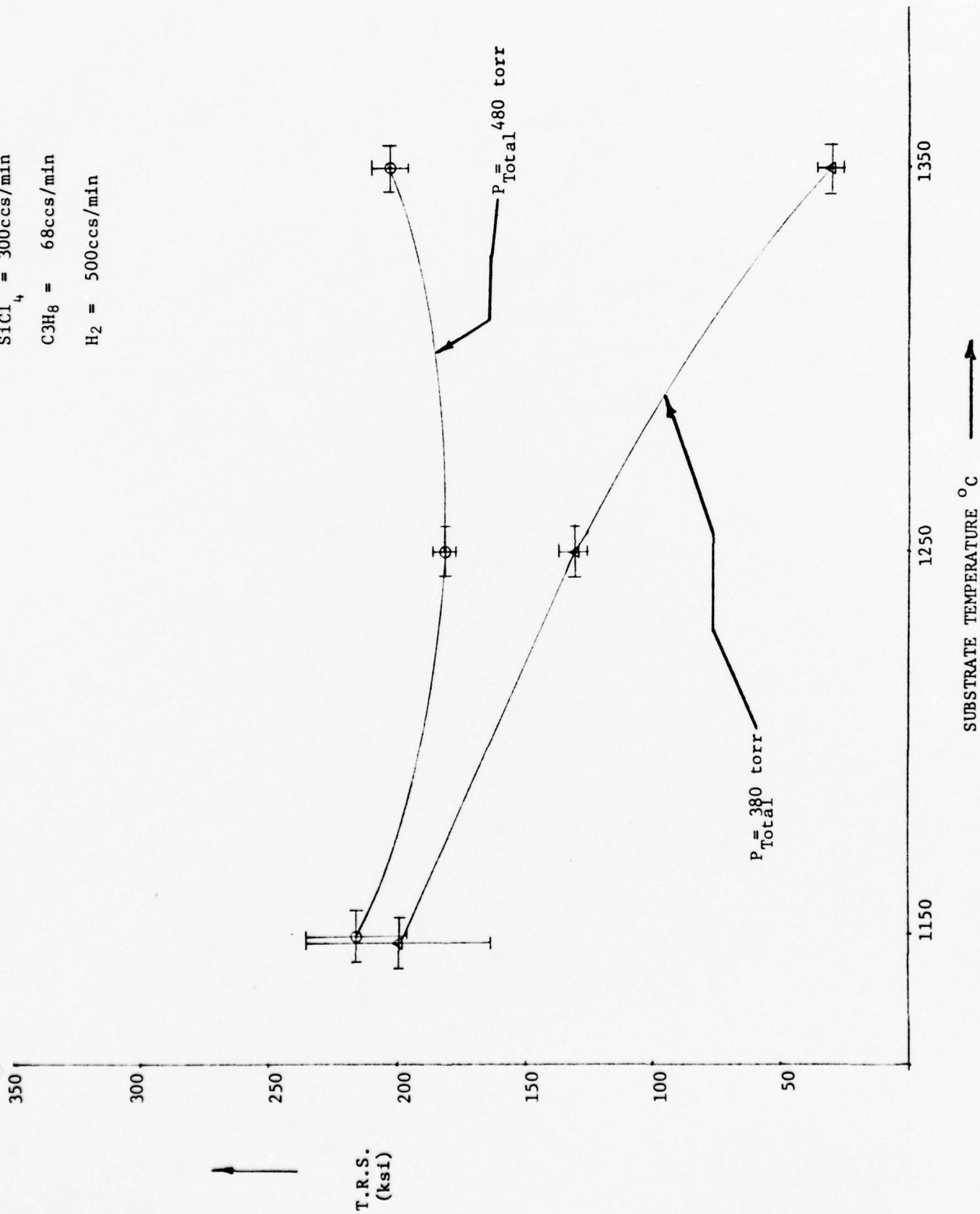
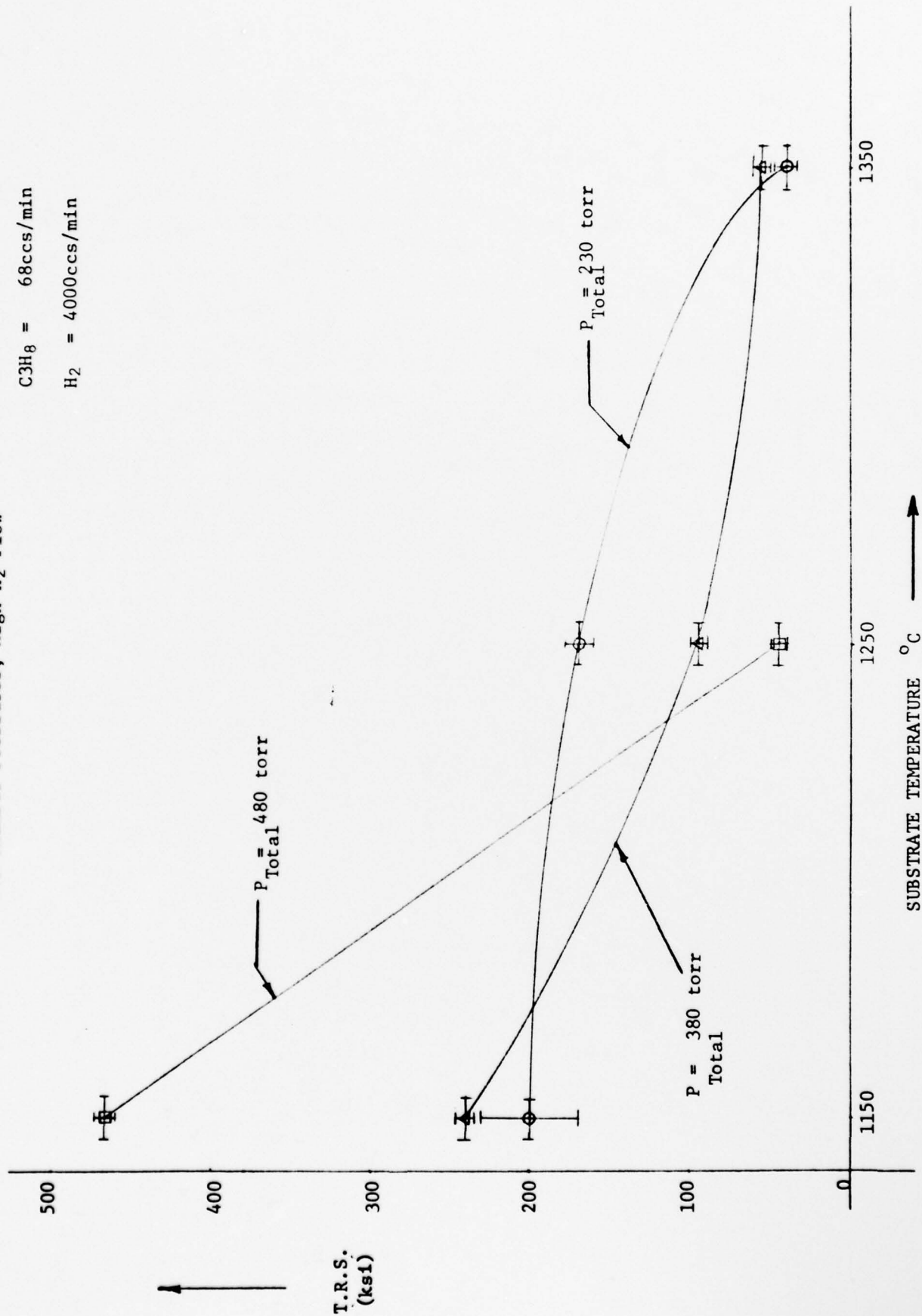


FIG. 12 Substrate Temperature vs T.R.S. for
Two Chamber Pressures, High H₂ Flow

SiCl₄ = 300ccs/min

C₃H₈ = 68ccs/min

H₂ = 4000ccs/min



SUBSTRATE TEMPERATURE °C →

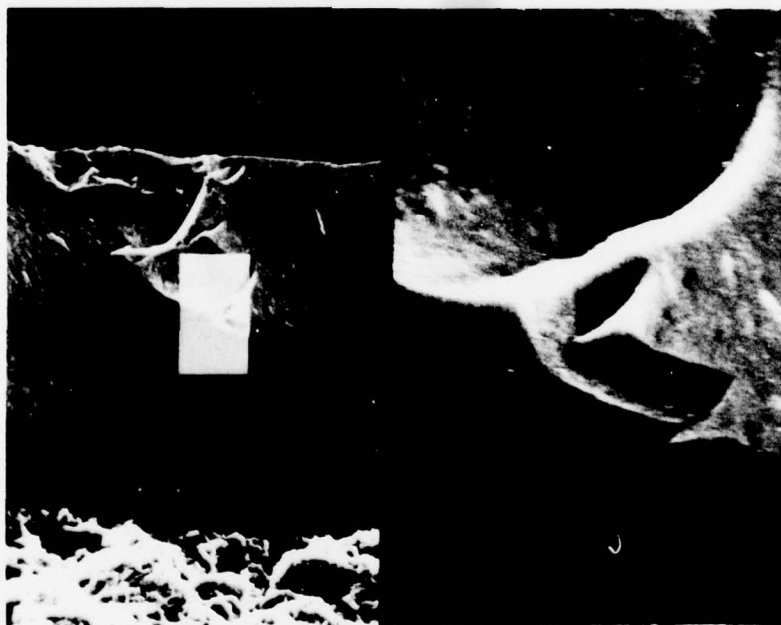
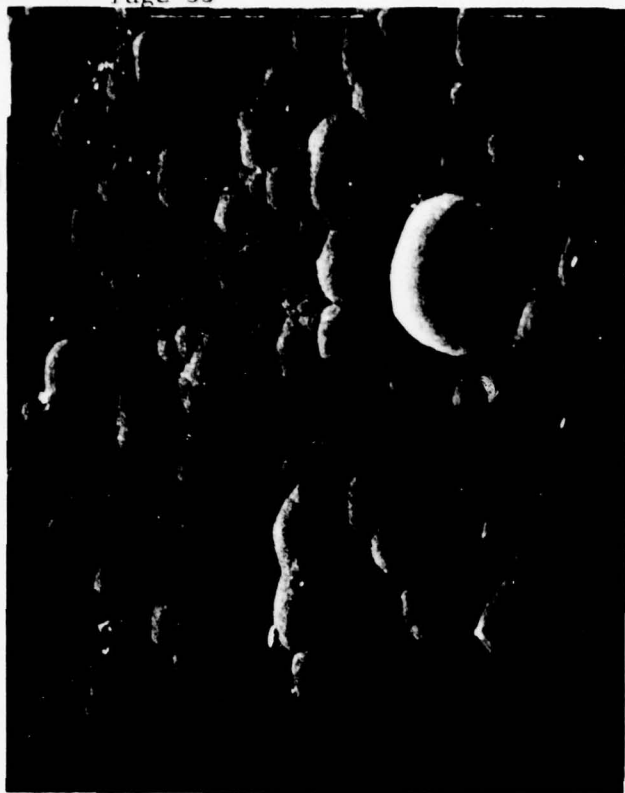


FIGURE 13 Sample (Run) #751, High Fracture Toughness CNTD SiC Deposit on Graphite (See Table IV). Upper Left-surface, 100X; upper right-coating interior, 20,000X; bottom-split view-coating interior, 200X/1000X.

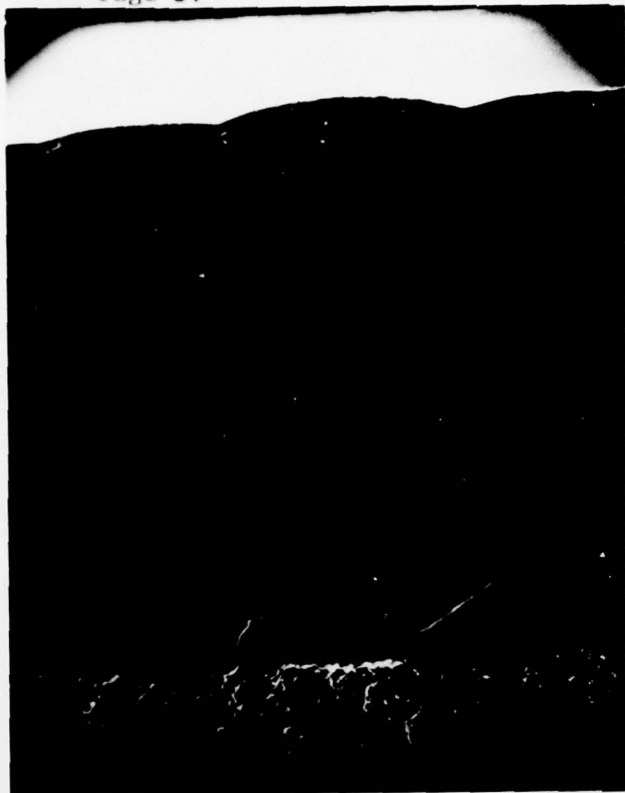


FIGURE 14

CNTD SiC Deposition on NC203 (Norton Co.) Hot Pressed SiC substrate. Upper left-coating section incl. substrate, 500X; upper right-interior of coating, 20,000X; bottom-Vickers indent. at 2000 gm load (no visible cracks), 1000X. A measurement at a different location gave $15.7 \text{ MPa} \sqrt{\text{m}}$. $\text{HV}_{2000} = 3860$.



FIGURE 15 "Frozen Liquid" appearing material
observed during deposition of SiC, 200X

VIII

TABLES

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TABLE I CNTD Silicon Carbide Deposition Conditions and Results Phase I Experiments

Specimen Number	Pressure (Torr)	Filament Temp. °C	Gas Temp. °C	Argon (cc/min)	Hydrogen (cc/min)	MTS (cc/min)	Additive (cc/min)	T.R.S.* (MPa)
136	367	1120	-	1400	2700	230	CH ₄ 75	1076
138	280	1110	-	960	2700	225	CH ₄ 70	1020
139	380	1110	-	960	2700	200	CH ₄ 70	414
144	380	1130	-	960	3500	225	C ₃ H ₈ 50	1083
148	380	1150	-	960	3500	200		1545
150	380	1150	-	960	3500	200		1558
154	380	1150	-	800	3500	200		1269
155	380	1150	-	850	3500	227		1269
158	405	1150	-	850	3500	230		841
161	380	1150	-	850	3500	225		75
176	127	1150	537	850	3360	250		60
180	127	1225	579	850	3360	250		65
182	127	1175	579	1160	3360	420		34
183	127	1175	579	1160	3360	420		834
184	127	1200	579	800	3360	420		65
186	253	1150	~600	800	3360	250		1790
189	228	Var.	537	800	3360	250		1531
192	253	Var.	607	800	3360	250		903
193	253	1150	579	800	3360	250		2069
194	253	1150	565	800	3360	250		1034
195	253	1150	593	800	3360	250		3448
196	253	1170	593	800	3360	250		1676
197	253	1140	593	800	3360	250		2090
198	253	1140	605	800	3360	250		1690
199	253	1140	580	800	3360	250		1924
200	253	1120	580	800	3360	250		1648
202	253	1120	593	800	3360	250		1379
203	253	1120	607	800	3360	250		2069
204	253	1120	624	800	3360	250		2414

*Transverse Rupture Strength, 3 pt. bending

TABLE 1 -- Cont'd.

Specimen Number	Pressure (Torr)	Filament Temp. °C	Gas Temp. °C	Argon (cc/min)	Hydrogen (cc/min)	MTS (cc/min)	Additive (cc/min)	T.R.S. (MPa)
205	253	1120	635	800	3360	250		3448
206	253	1110	635	800	3360	250		2415
207	253	1100	646	800	3360	250		1724
209	253	1100	646	800	3360	250		1303
210	253	1100	646	800	3360	250		1710
212	253	1110	646	800	3360	250		1669
214	253	1115	621	800	3360	250		1103
215	253	1115	616	800	3360	250		1586
224	253	1200	690	500	3100	350	C ₃ H ₈ 85	1200
226	253	1200	701	500	3100	350	C ₃ H ₈ 85	1324

TABLE II Ring Burst Test Conditions and Results, Phase I and II Experiments

Burst Test Specimen Dimensions: 0.064 cm wall thickness x 0.318 cm height x 2.54 cm I.D.

PHASE I EXPERIMENTS

Chambers Press. (Torr)	Substrate Temp. (°C)	Gas Temp. (°C)	MTS to Propane Ratio	Hydrogen Flow (cm ³ /min)	Burst Strength (MPa/psi)
253	1130	426	> 14.0	6500	269/39,000
253	1130	426	14.3	6500	332/48,200
253	1130	426	11.1	6500	300,43,500
253	1130	426	10.0	6500	389/56,400
153	1130	426	6.4	6500	414/60,000

PHASE II EXPERIMENTS, (*) Indicates I.D./O.D. of that sample chamfered, sample heated in air at 900°C for 2 hours

254	1140	450	11.1	6728	373/54,000 379,55,000 530/77,000	448/65,000* 373/54,000*
240	1120	510	11.1	5400	455/66,000 124,18,000	345/50,000 435/63,000*
240	1130	480	11.1	4000		248/36,000*
254	1130	500	11.1	6000	545/79,000* 503/73,000*	793/115,000* 448/65,000*
254	1110	465	11.1	6000		483,70,000*

TABLE III DEPOSITION CONDITIONS ON WIRES, PHASE II EXPERIMENTS

Run#	Pressure Torr	Part T	Gas T	Argon (ccs/min)	SiCl ₄ (ccs/min)	C ₃ H ₈ (ccs/min)	H ₂ (ccs/min)	T.R.S. (ksi)	Deposition Rate (mils/hr)
418	230	1150°C	1250°F	1500	300	68	4000	200	5
420	230	1250°C	1150°F	1500	300	68	4000	170	12.5
425	230	1350°C	1050°F	1500	300	68	4000	39.8	12.5
426	380	1150°C	1250°F	1000	300	68	4000	240	10.0
428	380	1150°	1250°F	1000	300	68	500	200	7.0
429	380	1250°C	1150°	1000	300	68	500	130	12.0
431	380	1250°C	1150°F	1000	300	68	4000	96.0	13.0
432	380	1350°C	1050°F	1000	300	68	500	31.0	17.0
434	380	1350°	1050°F	1000	300	68	4000	53.0	21.0
436	480	1150°C	1250°F	1000	300	68	500	216.0	6.0
438	480	1150°C	1250°F	1000	300	68	4000	462.0	10.0
439	480	1250°C	1150°F	1000	300	68	500	181.0	13.0
441	480	1250°C	1150°F	1000	300	68	4000	48.0	26.0
442	480	1350°C	1050°F	1000	300	68	500	204.5	28.0

TABLE III

1 of 2 Pages

TABLE III DEPOSITION CONDITIONS ON WIRES, PHASE II EXPERIMENTS

Run #	Pressure (Torr)	Part T	Gas: T	N ₂ (ccs/min)	SiHCl ₃ * (ccs/min)	C ₃ H ₈ (ccs/min)	H ₂ (ccs/min)	T.R.S. (ksi)	Rate (mils/hr)
469	380	1250°C	1180°F	1100	275	68	2200	157	25
470	380	1250°C	1150°F	1100	275	68	1500	393 100	25
471	230	1250°C	1120°F	1100	275	68	1500	218	23
472	230	1150°C	1130°F	1100	275	68	1500	394	20
473	230	1350°C	1150°F	1100	275	68	500	101	29

*Note change in Si bearing species from SiCl₄ to SiHCl₃

TABLE IV Deposition Conditions on Graphite Bend Bars, Phase II Experiments

Sample (Run) #	Substrate Temp (°C)	Hydrogen Flow (cm ³ /min)	MTS Flow (cm ³ /min)	SiHCl ₃ Flow (cm ³ /min)	TRS 3 pt. Bend (MPa/psi)	Vickers Hardness (kg/mm ²)	Fracture Toughness (MPa√m) load in gm-subscript	wt/o C1	wt/o Si
745	1230	3000	750	-	-	3530 3490	5.2) 6.5) 500	0.4	70.6
746	1210	2000	750	-	-	3130 3030	5.6) 5.5) 500	0.0	70.0
747	1225	1000	750	-	-	3192 3250	6.5) 7.2) 300	0.1	71.4
748	1225	500	750	-	-	3320 2930	4.4) 4.0) 500	0.3	68.6
749	1225	250	750	-	-	2930 3490	5.6) 5.6) 500	0.1	69.6
750	1230	125	750	-	-	3620 3100	4.7) 5.5) 500	0.00	67.9
751	1235	75	750	-	365/52,900	3990	13.2 2000	1.2	56.2
752	1235	50	750	-	641/92,890	3130 2570	11.3) 8.8) 2000	1.7	54.2
753	1235	25	750	-	347/50,350	2430 2455	7.67 2000 one indent-no cracks	1.6	53.1
754	1240	100	750	-	319,46,280	3400	4.8 500	1.8	56.4
755	1235	50	750	50	-	2600	microcracks No F.T.	2.2	53.8
756	1235	50	750	100 to 350*	630/91,400	2900	no cracks at 2000gm	0.9	58.8
757	1240	50	750	150	-	3250	4.9 500	0.2	67.7

*Flow Changed during run due to valve malfunction.

TABLE IV Deposition Conditions on Graphite Bend Bars, Phase II Experiments

Sample (Run)*	Substrate Temp (°C)	Hydrogen Flow (cm ³ /min)	MTS Flow (cm ³ /min)	SiHCl ₃ Flow (cm ³ /min)	TRS 3 pt. Bend (MPa/psi)	Vickers Hardness (kg/mm ²)	Fracture Toughness (MPa√m) load in gm-subscript	wt/o Cl	wt/o Si
758	1240	75	750	75	-	3580	5.0 2000	0.1	69.8
761	1240	400	500	350	-	3425	7.3 500	0.00	69.2
762	1230	750	500	350	-	3320	6.2 500	0.00	69.1
763	1240	50	500	500	-	3100	8.3 500	0.00	68.4
764	1180	50	500	500	475/68,870	3320	5.9 500	0.00	69.4
765	1170	50	500	400	-	3305	3.9 500	0.00	70.0
766	1170	25	500	250	-	3130	5.3 500	0.00	69.8

TABLE V HEAT TREATMENT STUDIES PHASE II Experiments

RUN NO.	H.T.* TEMP.	H.T. TIME	Cl% B.H.T.#	Cl% A.H.T.**	Si% B.H.T.	Si% A.H.T.	Hardness + Hardness†				F.T.# F.T. A.H.T.
							V.H.N. B.H.T.	V.H.N. A.H.T.	V.H.N. B.H.T.	V.H.N. A.H.T.	
753	1550°C	3 hrs	1.6%	1.5%	53.1%	56.5%	2442	2070	7.67	16.4	one indent no cracks
756	1550°C	3 hrs	0.9%	0.7%	58.8%	59.1%	2960	1735	no F.T.***	9.65	no cracks
745	1550°C	1 Hr	0.4%	0.01%	70.6%	70.0%	3510	2800	5.8	4.4	no cracks
755	1400°C	2½ hrs	2.2%	1.8%	53.8%	57.1%	2600	2910	Very brittle	8.2	no cracks
									No F.T. possible		
696	1400°C	1 hr	2.13%	2.1%	52.7%	51.4%	2900	2570	15.0	6.9	
757	1400°C	1 hr	0.2%	0.9%	67.7%	65.4%	3250	3060	4.9	7.25	

* H.T. = Heat Treatment

B.H.T. = Before Heat Treatment

**A.H.T. = After Heat Treatment

F.T. = Fracture toughness $\text{MPa}\sqrt{\text{m}}$

*** F.T. = No cracked indents observed in this sample therefore, No F.T. could be calculated.

† = All hardness values kg/mm^2 using 500 gm load

TABLE VI
CNTD SiC DISCS, 2.54 cm Diameter

Run#	Pressure (torr)	Part T	Gas T	Argon (cc/min)	MTS* (cc/min)	H ₂ (cc/min)	Thickness (mils)	Vickers Hardness** (kg/mm ²)
797	280	1200°C	875°F	1000	750	100	~ 20- 25	3525
798	254	1200°C	860°F	1000	750	1000	~ 20- 25	3360
799	260	1200°C	875°F	1000	500	100	~ 25	2895
802	272	1200°C	1190°F	2000	500	-	~ 20- 25	2270
803	267	1200°C	1190°F	2000	500	-	~ 20- 25	2150
804	267	1210°C	1255°F	2750	500	-	~ 20- 25	2995

*MTS: Methyltrichlorosilane

** 500 gm load