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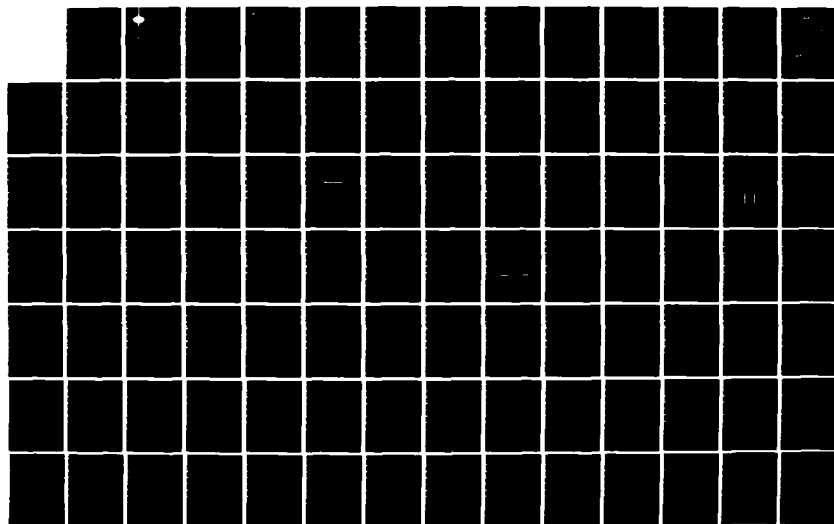
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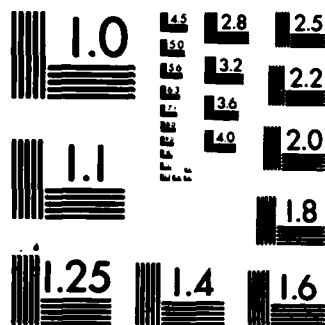
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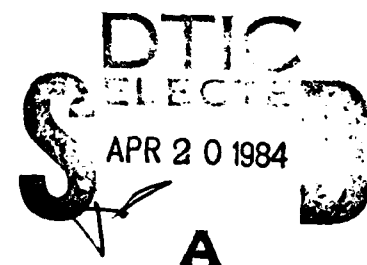
SYSTEM PLANNING CORPORATION

**SYNTHESIS OF REFRACTORY
COMPOUNDS WITH GASLESS
COMBUSTION REACTIONS**

SPC 931

September 1983

William L. Frankhouser
Keith W. Brendley
Michael C. Kieszek
Stephen T. Sullivan



Advanced Materials Technology Program
at Defense Advanced Research Projects Agency (DoD)
Currently monitored by: Capt. S. G. Wax

(Prepared under Contract 6819401 with
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ABSTRACT

System Planning Corporation (SPC) has participated with the Materials Science Division of the Defense Advanced Research Projects Agency (DARPA) and the Lawrence Livermore National Laboratory (LLNL) in development of advanced technologies for fabrication of refractory materials. This document is a final task report of SPC's study of gasless combustion synthesis of refractory compounds. The task objective has been to increase knowledge of chemical reaction and gasless combustion mechanisms in synthesis processes. The SPC approach has been to consider the technological nature of gasless combustion processing and the reaction phenomenology in regard to materials synthesis, to analyze research programs in the U.S.S.R. where this technology has been under intensive development for more than a decade, to develop appropriate analytical models of synthesis reactions and combustion mechanisms, and to suggest new directions for research in the United States.

Gasless combustion synthesis normally involves reactions among elemental constituents in condensed phases to form refractory compounds (which are often ceramic compositions). However, oxides and reducing agents sometimes are included in a modified reaction form that is similar to the classic thermite reactions. The appeal of gasless combustion vis-a-vis more conventional powder-compaction technology is its potential ability to use the exothermic heat of the synthesis reaction in forming densified product shapes of ceramic compounds in a single-step operation, to the point of excluding the need of conventional processing for externally supplied process heat. Process advantages claimed are low fabrication and capital investment costs, extremely high processing temperatures, relatively abrupt heatup and cooldown sequences, rapid processing, and product purification.

This last factor can be capitalized on to significantly lower fabrication costs, since relatively impure commercial grades of starting constituents may be employed.

Soviet researchers have patented various gasless combustion techniques for materials synthesis in at least four countries. The initial research phase (through about 1977) resulted in commercial applications of the technology in production of refractory powders--notably titanium carbide. The current Soviet research phase is concentrated on process modifications to produce densified solid shapes of ceramic, intermetallic, and cermet compounds. The major thrusts in the current research phase are on integrating the gasless combustion reaction with pressure (to facilitate full product densification) and on casting products (a thermite-like process modification). Considerable emphasis also is placed now on nitride compositions, which are reacted in pressurized nitrogen gas, and on direct formation of undressed cutting tools (probably cemented carbides).

The major constraint to commercial use of gasless combustion synthesis technology is the low level of knowledge about the interaction of process variables with combustion mechanisms. In plainer language, the process is difficult to control, and process controls vary among specific synthesis reactions. SPC has developed simple analytical models to aid in selecting favorable synthesis reactions, to predict reaction temperatures and phase changes, to analyze transient temperature and product concentration profiles, and to predict speed of combustion. These models have been used in studying combustion synthesis of the three ceramic compounds (aluminum nitride, titanium carbide, and titanium diboride) that are being synthesized in the laboratory at LLNL. With further development, these models can be extended by introducing heat loss terms to predict reaction behavior for specific geometric configurations and to study potential gasless combustion applications in surface coating.

Interest in gasless combustion synthesis has been growing in the United States since 1981, particularly within the defense community. SPC, therefore, has included some suggestions for future U.S. laboratory development programs to aid in focusing on specific synthesis product objectives

where the greatest potential advantages are foreseen and where unique opportunities to move beyond Soviet achievements are anticipated. The seven specific items included for consideration are:

- Synthesis of ceramic matrix composites
- Synthesis of complex (fracture tough) ceramic compounds
- Synthesis of nonoxide nuclear fuels
- Synthesis of compositionally gradated lightweight armors
- Combination of the synthesis reactions with isostatic pressing
- Combination of the synthesis reactions with electric arc technology in hard surfacing operations
- Casting composite materials in a zero-gravity environment.

I. INTRODUCTION

The objective of this System Planning Corporation (SPC) study is to increase knowledge of reaction mechanisms in gasless combustion as used in development of new processes for synthesis of refractory materials. The materials under study normally are classified within the categories of structural materials as ceramics, cermets, or intermetallic compounds. Many are somewhat difficult to fabricate and usually costly in comparison to conventional metallic structurals.

Gasless combustion synthesis has recently received considerable attention as an alternative to conventional ceramic or powder metallurgy processing technology because of the unique process simplicity. Potential advantages of gasless combustion include low processing cost, conservation of energy (in production), low capital investment (for equipment), and high purity of product. With self-generation of intense thermal energy in synthesis reactions, the need for external process heating is minimized or eliminated completely. This characteristic has led to distinctive process descriptions, such as exothermic, self-propagating [Ref. 1], and self-sustaining [Ref. 2].

An understanding of the fundamental reaction mechanisms involved in gasless combustion is important in determining compositions and physical conditions that are compatible for synthesis of refractory products and properties. A reliable predictive capability will provide a control for selection of products and for optimizing processing variables and should eventually have an impact on achieving lower costs in industrial applications. Although a detailed molecular-scale description of the combustion mechanism may be useful, it is not a necessary precursor to successful commercial scale-up of gasless combustion processes. For example, laboratory data obtained from more macroscopic variables, such as particle size and density, can be used effectively in controlling reactions.

This report considers both theory and practice in gasless combustion synthesis. It begins with observations on the nature of the combustion process and continues with synthesis process adaptations and products. Much of the information provided for those discussions has been obtained from the Soviet literature, since materials synthesis by gasless combustion processing has been under intensive development in the Soviet Union for more than a decade. Lastly, combustion reaction phenomenology and analytical modeling of reaction mechanics are described. Analytical modeling of the combustion process will be useful as a quantitative predictive tool to support future laboratory research and development (R&D) in the United States.

II. THE NATURE OF GASLESS COMBUSTION

A. A SIMPLE PROCESS FORM

A simple processing concept for gasless combustion synthesis of a refractory material is demonstrated in Figure 1. Precursor metallic and nonmetallic reactants are first mixed and lightly pressed together. After ignition with a short burst of electrical energy, the thermochemical reaction between the constituent materials (Ti and C) becomes self-sustaining, and a combustion wave propagates through the pressed mass to form the product (TiC). Ideally, this product form would be fully densified and in a readily usable shape. In that situation, the obvious advantages, when compared to more conventional processing methods, would be elimination of the need for either external heating or sophisticated processing equipment. As shown in Table 1, such process attributes are especially important when considering gasless combustion synthesis for potential industrial applications.

Another desirable attribute of gasless combustion synthesis is the extremely high reaction temperatures that can be generated. These high temperatures contribute to shorter reaction periods and completeness of reactions. High temperatures become even more significant when elimination of external heating is also possible. In fact, one investigator [Ref. 3] avers that gasless combustion synthesis can provide higher temperatures than any other industrial combustion process. His data, reproduced in part in Table 2, amply demonstrate this point, since most of the temperature range for gasless combustion synthesis and the maximum temperature exceed the other temperatures listed.

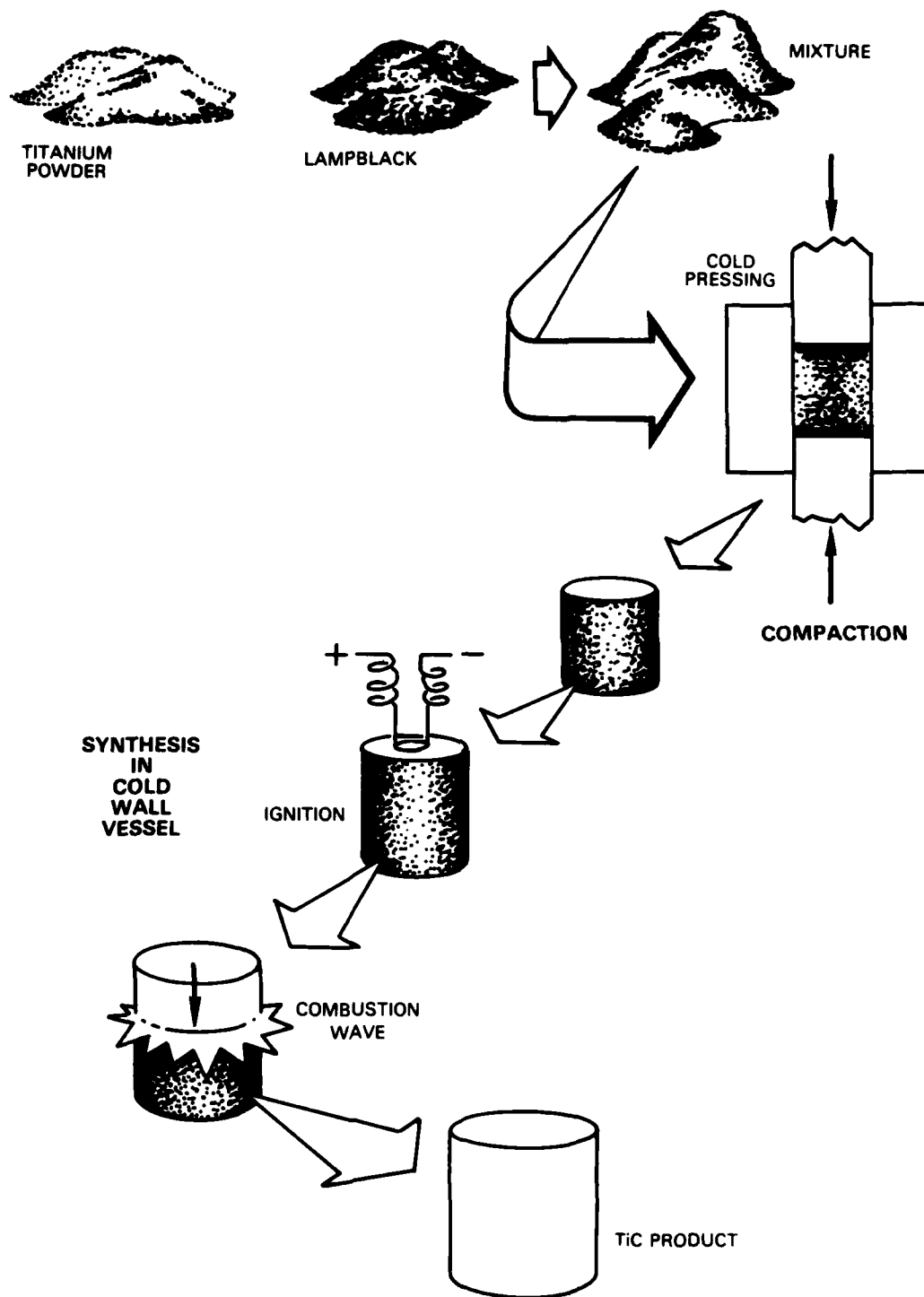


FIGURE 1.
GASLESS COMBUSTION SYNTHESIS IN SIMPLEST FORM

TABLE 1.
COMPARISON OF PROCESS ALTERNATIVES

<u>Process Step</u>	<u>Equipment</u>	
	<u>Conventional Powder Consolidation Technology</u>	<u>Gasless Combustion Synthesis</u>
1. Powder preparation	Powder attrition, sizing blending, etc.	Same
2. Cold compaction	Low-pressure press or cold-wall vessel	Same
3. Product reaction, conditioning, shaping, etc.		
• Pressure equipment	High-pressure press or hot-wall, high-pressure vessel	Reaction vessel with vacuum or modest pressure capability
• Thermal equipment	Thermal adaptation to high-pressure press, high-temperature furnace, or both	High-temperature furnace, only if post-reaction thermal conditioning required

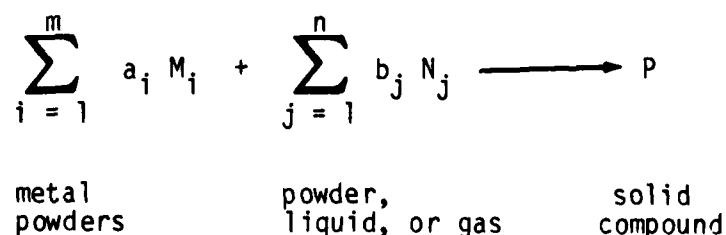
TABLE 2.
COMBUSTION TEMPERATURES FOR INDUSTRIAL PROCESSES

<u>Process</u>	<u>Products</u>	<u>Combustion Temperatures (°C)</u>
Combustion of hydrocarbons	Unsaturated hydrocarbons, industrial gas, carbon black	1,300-1,700
Gas-flame synthesis	Oxides	1,000-2,500
Oxidation treatment	Oxides	600-900
Blast furnace processing	Pig iron	1,600-1,900
Metallothermic processing	Ferroalloys and other master alloys	2,000-3,000
Gasless combustion synthesis	Refractory compounds	2,500-4,000

Another unique attribute of gasless combustion synthesis, when compared to more conventional processes, is localization of the combustion zone. With processes where external heating is required, heatups and cool-downs are considerably slower than with gasless combustion. Potential advantages attributable to short-time exposures in reacting, heating up, and cooling down are improved control over microstructures and properties and lessened extraneous contamination from both ambient atmospheres and containment materials. For example, Soviet researchers in gasless combustion synthesis claim that gasless combustion products are more pure chemically than starting materials, which is opposite to expectations for most conventional synthesis processes.

A final outstanding attribute of gasless combustion reactions is the potential versatility for synthesizing a variety of materials with distinctly different properties and in different forms with one basic process technology. For example, researchers already have synthesized many ceramic and intermetallic compounds and cermet materials, and the technology base undoubtedly can be extended to synthesis of composites and to materials with gradated compositions. To date, a number of materials have been synthesized in both massive and powder forms. Another possibility readily visualized for extending gasless combustion applications is to combine synthesis and bonding (e.g., ceramic-to-ceramic or metal-to-ceramic bonds) in one-step operations. Continuous production applications of the technology also can be surmised, for example, where a ceramic compound might be produced in powder form in a fluidized-bed reactor.

This versatility for production of a number of different compounds is demonstrated by the following generic form of a synthesis reaction between metallic (M) and nonmetallic (N) constituents:



Typically, the M elements in early Soviet research were transition metals from the A Groups in the periodic table, and the number of M and N elements was initially one [Ref. 3] (e.g., where titanium and carbon react to form titanium carbide). Later, reactions with one M and two N elements were examined by Soviet researchers (e.g. where titanium reacts with carbon and nitrogen to form a carbonitride), and other mixtures with two M and one N elements have been reacted (e.g. where titanium and chromium react with boron to form a diboride). More recently, Soviet researchers also have examined more complex compounds (e.g., where two M and N elements react, as exemplified by a reaction in which niobium and zirconium form a carbonitride).

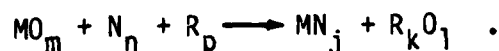
This capability to produce complex compositions of ceramic compounds is especially intriguing, since some of these compounds may exhibit high-temperature superplasticity and unexpected fracture toughness at ambient temperatures [Ref. 4]. Gasless combustion synthesis of complex, fracture-tough compounds is of interest for two reasons. First, it is simple and fast (implying low production costs). Second, the relatively high rates of heatup and cooldown are supportive in maintaining the small grain sizes and discrete duplex phase combinations that may be one requirement for improving fracture toughness.

Other types of reactions also have been reported in which gasless combustion synthesis is combined with metallothermic (oxidation-reduction) reactions [Refs. 5 and 6]. A typical reaction might be:



In this case, an oxide compound (MO_m) is reacted with an elemental oxidizer-reducer (X) to form a desired refractory product (MX_n) and a by product (X_kO_l). A specific example would be the reaction of molybdenum oxide with boron to form molybdenum boride (the product) and a slag that contains boron in the oxide form.

In other combined processes, a nonmetallic reactant (N) and reducer (R) might be introduced as separate elements, e.g.:



The number of individual compounds already synthesized by Soviet researchers with gasless combustion processes is reported to be more than 100. Most of these have been intermetallic and ceramic compositions, and most of the latter type have been borides, carbides, nitrides, and silicides. In addition, they have synthesized complex combinations of these compounds and have produced some cermet materials. Other ceramic compounds synthesized include germanides, hydrides, phosphides, selenides, and sulfides. Aluminide and nickelide compounds also have been produced.

The Soviet view on potential applications for various compounds synthesized by gasless combustion reactions, which is illustrated in Table 3, demonstrates the broad range of potential industrial utilization that is anticipated. It also reveals considerable variation in types of materials, since both relatively hard and refractory compounds (like borides) and soft materials (like chalcogenides) are included; in addition, some have a high degree of chemical stability (like carbides), while others are characterized with much lesser stability (like some hydrides).

Now that the favorable attributes of gasless combustion synthesis and its potential versatility for industrial applications have been reviewed, a logical question is why it has not already been fully exploited. This probably can be attributed to the belief that combustion processes are difficult to control. Thus, when techniques were developed for synthesis of new materials, emphasis was placed on technologies that were better understood and considered to be more controllable. Interest in gasless combustion (solid-state) reactions for synthesis arose only after development of solid fuels as rocket propellants [Refs. 7 and 8]. As a result of that combustion R&D, the potential for gasless combustion in materials synthesis was recognized, and development has since proceeded to varying degrees in at least four countries for the last 17 years. Much of this development effort concentrated on understanding the basic combustion mechanisms and the underlying thermochemical properties of the materials used in the combustion process.

TABLE 3.
A SOVIET VIEW ON SOME APPLICATIONS FOR GASLESS COMBUSTION SYNTHESIS
OF REFRACTORY COMPOUNDS^a

Compounds	Applications						
	Hard Alloys ^b	High Temperature Structural	Superhard Abrasives	Protective Coatings	Electrical and Electronic	Lubricants	Nuclear Energy
Borides	X	X	X	X	X		X
Carbides	X	X	X	X	X		X
Chalcogenides		X			X	X	
Hydrides							X
Intermetallic Compounds		X		X			
Nitrides	X	X	X	X	X	X	
Silicides		X		X	X		

^aSource: Reference 3

^aCemented carbide and related tool industry products

Soviet R&D in gasless combustion synthesis is considered to be the most advanced on a national basis. The Soviet investigative approach has been to predict the thermodynamic reaction potential for materials of interest, to explore reaction mechanics of several distinct combustion modes, and to apply that information in development of processes for synthesis of specific refractory compounds. Since the thermochemical properties of refractory and other materials vary widely, process controls have been developed by Soviet researchers to fit each unique product composition.

B. SOVIET EXPERIENCE WITH DIFFERENT COMBUSTION MODES

Several distinct modes of combustion wave propagation have been observed by Soviet researchers. These combustion modes may be divided into two general categories: steady-state and unstable combustion. In steady-state combustion, the combustion wave moves from the ignition surface at a fairly constant velocity through the reactant mass to the opposite surface where the reaction is completed. The unstable forms of combustion are varied and have not been studied widely because they are generally undesirable in synthesis processes. Unstable combustion often results in incomplete reactions with heterogeneous compositions and density. For the most part, Soviet researchers describe four modes of unstable combustion: spin, oscillating, repeated, and surface combustions [Refs. 9-11]. These unstable modes generally occur near the ignition limit for the system and represent marginal conditions for achievement of adiabatic combustion reactions. The conditions that lead to unstable modes of combustion need to be more thoroughly understood if they are to be avoided in synthesis processes.

1. Steady-State Combustion

One of the characteristics that separates gasless combustion from gaseous forms of combustion (see forms listed in Table 2) is the near absence of mass transfer in the direction of the combustion wave. The propagation of the wave is controlled primarily by diffusion in the plane of

the wave rather than in its direction of propagation. This leads to a comparatively broad, slow-moving combustion wave. Steady-state combustion has been modeled as a one-dimensional wave moving at constant velocity from the point of ignition at a propagation speed that is usually in the range of 0.1-15 cm/sec. This rate is affected by numerous parameters, such as compact diameter, physical characteristics of the initial mixture, combustion enthalpy, etc.; these are discussed in considerable detail in Chapter III.

2. Oscillating Combustion

Oscillating combustion, an often reported unstable mode, is a pulsating planar combustion wave that has a definable frequency and a constant mean wave speed. The average wave speed is normally less than 1 cm/sec with a frequency of less than 10/sec. The oscillations are of the saw-tooth type when recorded photographically and have been predicted theoretically in mathematical models. The burning rate and frequency may be increased or decreased by variations in the degree of dilution (when the initial mixtures have inert additives), the initial compaction density, and compact diameter, and may be influenced by mechanical compression during the combustion reaction. Theory indicates that the transition from steady-state to oscillating combustion is governed by the following parameter [Ref. 11]:

$$\alpha = 9.1 \times \frac{\overline{C_p}}{Q} \times \frac{RT_c^2}{E} \left(1 - 0.27 \frac{Q}{RT_c}\right)$$

where

C_p = the average specific heat

Q = the amount of heat generated per unit mass

R = the ideal gas constant

T_c = the adiabatic combustion temperature

E = the activation energy.

When α is < 1 , the reaction proceeds in the oscillating combustion mode; when α is > 1 , the reaction proceeds in the steady-state mode. The product usually has a layered structure that gives the appearance of separately sintered wafers. These layers are usually easily separated, and their thickness is dependent on the pulsation frequency.

3. Spin Combustion

The spin combustion mode is fairly common in gaseous combustion, and has been experienced in gasless combustion of condensed substances. Upon ignition of the compact, a small luminous spot appears on the outer cylindrical surface of the specimen; this spot moves along the outer surface of the unburned part of the specimen from the original site in a helical motion, leaving behind a bright track that gradually merges with the corresponding track from the preceding turn of the helix. This motion continues to the end of the combustion reactions usually at a rate of ~ 1 cm/sec.

Several spots may make a traverse simultaneously in the same or different direction, each leaving a faint spiral track. The thickness of the surface layer encompassed by spin combustion is at most 2 mm. It has been postulated that the focal point can move in a stable manner only along the heated layer formed by the preceding turn. Any breaking away from this layer track would lead to extinguishment due to increased losses of heat.

4. Repeated Combustion

Repeated combustion consists of the passage of a second combustion wave through the already burned substance, following the propagation of the first combustion wave on the fresh material. Two types of repeated combustion have been reported: normal and fast.

Fast repeated combustion occurs primarily in condensed systems in which the time of combustion is much less than the time of the reagent diffusion. Only a small portion of the reagents react with the passage of the first wave. The second wave often may appear as a volumetric reaction,

since the combustion zone is much broader and the combustion speed slower than in the first wave.

Normal repeated combustion is similar, but the disparity in wave speeds is not as large as in fast combustion, and it usually occurs in metal-gas systems. For example, the combustion of hafnium in a nitrogen-argon atmosphere ($P_{N_2} = 60$ atm, $P_{Ar} = 1$ atm) produced a first wave front speed of 0.7 cm/sec, with a following wave speed of 0.4 cm/sec.

The phenomena of repeated combustion also have been observed in samples ignited simultaneously at the upper and lower ends. The two primary wave fronts moved toward each other at equal rates. At the site of collision, two diverging secondary fronts originated and passed through the already burning material at reduced rates.

The phenomena of repeated combustion are influenced by the atmospheric pressure, specimen density, and particle size of the metallic reactant.

5. Surface Combustion

Surface combustion occurs in metal-gas systems with combustion only along the exterior surface. Inner parts of the sample either do not react or react only after the surface combustion front has passed. The limiting parameter that causes surface combustion is the filtration of gas to the inner surfaces. A pressure difference arises between the reaction zone and the resisting atmosphere due to the consumption of the gas. In surface combustion, the atmosphere cannot break through to the inner parts fast enough to allow the inner reaction to occur at the same rate as the surface reaction.

III. SOVIET PROCESS ADAPTATIONS

Soviet researchers in most instances have not been able to adapt gasless combustion in the simplest form, described in Figure 1, to synthesis of commercial refractory products. A series of precursor bench-scale experiments usually have been performed to establish a specific set of process conditions for each potential product form and composition. Some Soviet approaches to process adaptations are reviewed in this chapter. In general, they all can be related to the following two combustion controls:

- Combustion Intensification (or activation)--In this instance, the objectives generally have been to increase the reaction temperature, to lower the ignition temperature, to change from an unstable to steady-state combustion mode, or to increase the rate of combustion.
- Combustion Braking--In this case, the objectives generally have been to lower the reaction temperature, reduce the rate of combustion, or prevent dissociation of product compositions that otherwise would be unstable.

A. PROCESS VARIABLES IN SYNTHESIS OF SILICIDES

A major Soviet study [Ref. 12] in synthesis of silicides relates many process variables to the controls listed above. These process adaptations result in changes in combustion temperature, rate, modes, etc. Silicides were selected specifically as the experimental subject because of two unique characteristics that make them desirable for studying gasless combustion processes. First, silicides generally exhibit fairly low adiabatic reaction temperatures (below 3,000°K)¹, which suggests that both steady-

¹In contrast, almost all metal-carbon and metal-nitrogen systems and many metal-boron mixtures combust at higher temperatures (3,000 to 4,500°K).

state and unstable forms of combustion may be demonstrated in their synthesis. Second, silicides generally are not considered to be in the "interstitial" category² of compounds because of the large radius of the silicon atom; in this regard, the desirable characteristic for these experiments was that a relatively large number of (noninterstitial) silicide compounds could be formed over a wide range of stoichiometric ratios.

1. Stoichiometric Ratio

The impact of stoichiometry on the combustion process is summarized in Table 4 for silicides formed with three metals. In Item 1, a relationship is demonstrated between position of the elemental metallic reactant in the periodic list of elements (atomic mass) and combustion parameters. As reported previously in Reference 2, combustion tends to intensify (as measured by $Q \div T_{ad}$) as gram molecular weights of product compounds decrease. In some instances, products decompose when combustion intensifies greatly; conversely, adiabatic combustion reactions are not possible at low extremes of combustion intensity. For low-side intensity limits, Soviet researchers report (Table 5) the maximum stoichiometric values for achieving adiabatic combustion in three silicide systems. For higher mass metallic reactants, the maximum amount of metal is less.

As indicated by Items 2 and 3 in Table 4, changes in the metal-to-silicon stoichiometric ratio also can be related to combustion rate and stability. Steady-state combustion is achieved only with the titanium silicides. Maximum combustion rates varied from 0.7 cm/sec for the molybdenum compounds, to 1.2 cm/sec for zirconium compounds, to 3.5 cm/sec for titanium compounds. For example, a 5:1 rate relationship is predicted for Ti_5Si_3 and $MoSi$ compositions where the peak rates were measured in these two systems.

²The Hagge rule that interstitial phases have a ratio of metal to non-metal of ≤ 59 is not satisfied.

TABLE 4.
IMPACT OF STOICHIOMETRIC RATIO
ON COMBUSTION SYNTHESIS OF SILICIDES

1. The reaction temperature (T_{ad}) varies with changes in the stoichiometric ratio of metallic to nonmetallic constituents in silicides obtained with three metallic elements.
 - As Mo increases, T_{ad} decreases
 - As Ti increases, T_{ad} increases
 - As Zr increases, T_{ad} increases, peaks, and decreases.
2. As the level of each metallic constituent is progressively varied in relation to silicon, the combustion rate increases, peaks, and decreases. The stoichiometric ratios (metal: silicon) for the peaks are approximately 1.7 for Ti and Zr, and 1.0 for Mo.
3. Most of the titanium silicides were formed with a steady-state mode of combustion, while the pulsating combustion mode was observed in all reactions of silicon with molybdenum and zirconium.

TABLE 5.
ADIABATIC REACTION LIMITS
IN TERMS OF STOICHIOMETRIC RATIOS

<u>Silicide System</u>	<u>Ratios</u>
Mo-Si	1
Zr-Si	2.4 (12:5)
Ti-Si	3

2. Reactant Preform Diameter

A relationship between diameter of the reacting mass and attainment of adiabatic combustion was established for Mo mixed with 1.4 Si, 2 Si, and 2.4 Si. In all three instances, the minimum diameter threshold for adiabatic combustion was ~20 mm. Another experiment was designed to establish the relationship between diameter of reactant masses and combustion stability for Ti + 0.6Si, Zr + 2Si, and Mo + 2Si, all of which form single-phase products. In each case, combustion is unstable at diameters below a

threshold value, and combustion rates increase as diameters are increased in approaching the threshold value (see Table 6). At these threshold levels, unstable combustion modes change to steady-state combustion and combustion rates eventually become asymptotic. In addition to unstable combustion below the threshold values, the product reactions are incomplete.

TABLE 6.
THRESHOLD VALUES FOR STEADY-STATE COMBUSTION

<u>Threshold Values</u>	<u>Reactant Mixtures^(a)</u>		
	<u>Mo + 2Si</u>	<u>Zr + 2Si</u>	<u>Ti + 0.6Si</u>
Combustion Rate (cm/sec)	0.7	1	3.5
Diameter of Reactant Mass (mm)	20	20	15

(a) In all cases, pressed density of the reactant preforms was 60 to 65 percent of theoretical, and the product compositions were single-phase.

3. Reactant Preform Density

The Soviet researchers reported analogous relationships for these last three combustion systems when density of the reactant preform was changed and diameter was held constant at 20 mm. Although specific data are not reported, a threshold density level presumably exists below which combustion is not stable or does not occur. Data reported in other Soviet experiments indicate that these threshold values probably will range between 40 and 65 percent of theoretical density.

4. Reactant Powder Particle Size

Particle size of the metallic reactant has a considerable impact on the combustion process.³ Soviet researchers report that coarser particles and those with a broad fractional distribution of sizes result in reductions in the combustion rate and incomplete reactions. For silicide compounds, particle sizes less than 80 microns are recommended. In forming borides and carbides, coarser metallic particles probably could be used for many reactions.

5. Control of Combustion Temperature

A method widely used by Soviet researchers to reduce combustion temperature is dilution of the reactant mass with product material. This slows or "brakes" the reaction rate and often aids in obtaining a dense, fully reacted product. In an experiment with Ti_5Si_3 , dilution levels were increased from 0 to 45 percent of the reactant mass. This caused a gradual decrease in combustion rates from 4 to 0.7 cm/sec. Above 30 percent dilution, the normal steady-state combustion condition reverted to unstable combustion, which would be expected in undiluted mixtures of reactants with considerably lower adiabatic reaction temperatures.

Conversely, combustion temperatures are increased by preheating the starting reactant preform between 200 and 600°C. In these experiments, single-phase $TiSi_2$ ($T_{ad} = 1,800^\circ K$) was produced successfully by a gasless combustion reaction, after preheating to 300-400°C.

6. Purification During Gasless Combustion

An often repeated claim by Soviet researchers is that gasless combustion synthesis purifies the reactant materials. For example, in synthesizing Ti_5Si_3 , a metallic impurity content of 0.7 percent (6,978 ppm) in the charge was reduced to 0.05 percent (452 ppm) in the product--a reduction ratio of ~15:1.

³The nonmetallic powder is usually quite fine--in the low-micron and submicron range.

7. Silicon Products

Soviet researchers successfully synthesized MoSi_2 , Ti_5Si_3 , and TiSi_2 (aided by preheating), which are reported to be used in commercial applications as high-temperature furnace elements in the U.S.S.R. Among the zirconium silicides, only ZrSi_2 was synthesized successfully. Other silicides in this system destabilized during combustion, and charge dilution would be required for synthesizing them.

B. PHYSICAL VARIABLES

The impact of three physical factors (preform diameter and density and reactant particle size) on the combustion process were addressed in the foregoing discussion of synthesis of silicides. Similar relationships between physical factors and combustion mechanics also have been reported in the Soviet articles listed in Table 7. Although specific details may vary somewhat, the agreement is apparent on the following relationships between physical characteristics and combustion mechanics:

- Density
 - Increases in preform density tend to reduce levels of unreacted material in the product and increase adiabatic reaction temperature.
 - In one instance [Ref. 13], combustion rate increases were reported as preform density was increased to ~55 to 60 percent (relative); above this peak density range, the opposite relationship was observed.
- Diameter (in effect, reaction mass)
 - Increases in preform diameter tend to increase reaction rate and decrease amount of unreacted material in the product.
- Particle Size of Metallic Powder Reactant
 - Coarsening of metallic particle size tends to reduce reaction rate, increase amount of unreacted material, and decrease adiabatic reaction temperature.
- Particle Size Distribution of Metallic Powder Reactant
 - Wider fraction powder distributions tend to increase the amount of unreacted material.

- Post-reaction Cooling

-- Cooling slowdown tends to decrease amount of unreacted material.

TABLE 7.
SOME SOVIET EXPERIMENTS INVOLVING PHYSICAL
FACTORS THAT IMPACT ON GASLESS COMBUSTION SYNTHESIS

<u>Product Compounds</u>	<u>Physical Factors Investigated</u>	<u>References</u>
Hf, Mo, Nb, Ta, Ti, and Zr borides	● Preform diameter ● Preform density ● Reactant particle size (metal) ● Cooling rate	14
TiC	● Preform diameter ● Preform density ● Reactant particle size (metal) ● Reactant particle distribution	15
TaC and Ta ₂ C	● Preform diameter ● Preform density ● Cooling rate	16
TiC	● Surface area of non-metallic reactant ● Particle size of non-metallic reactant ● Microstructure characteristics of nonmetallic reactant	17
TiSi, TiSi ₂ , and Ti ₅ Si ₃	● Reactant particle size (metal)	18
Nb-Al and Nb-Ge	● Reactant particle size (metal) ● Preform density	13

In addition to the above cited relationships, most physical properties influence the mode of combustion. Changes in physical factors that speed up combustion or raise the reaction temperature generally tend to support steady-state combustion. In some cases, threshold values in various physical properties are reported for the transition from steady-state to the unstable modes of combustion. In Reference 14, a threshold combustion rate is related to physical factors. During synthesis of ZrB_2 , with a preform density of 60 percent (relative), the threshold combustion rate was reported to be 0.65 of that observed in a fully adiabatic regime.

When unstable combustion is encountered, physical properties have been related to the pulsing or vibrational frequency of the combustion. In essentially all instances when the combustion mode is not steady-state, incomplete reactions and product layering (variable-density regions) are to be expected.

In Reference 17 (the fourth listing in Table 7), characteristics of the nonmetallic reactant material, rather than the metallic particles, were related to combustion variables:

- Smaller lampblack particle sizes are effective in increasing both reaction rate and completeness. This relationship results from additional breakdown of the molecular "carbon chains" with additional comminution of the material.
- Larger lampblack surface areas had little influence on combustion rate.
- Absorbed gases on the lampblack particles cause an expansion of the product preform during synthesis. As a result, the rate of combustion is reduced and the amount of unreacted material is increased.
- Calcining of the carbon or graphitization are counterproductive to intensifying the synthesis reaction.

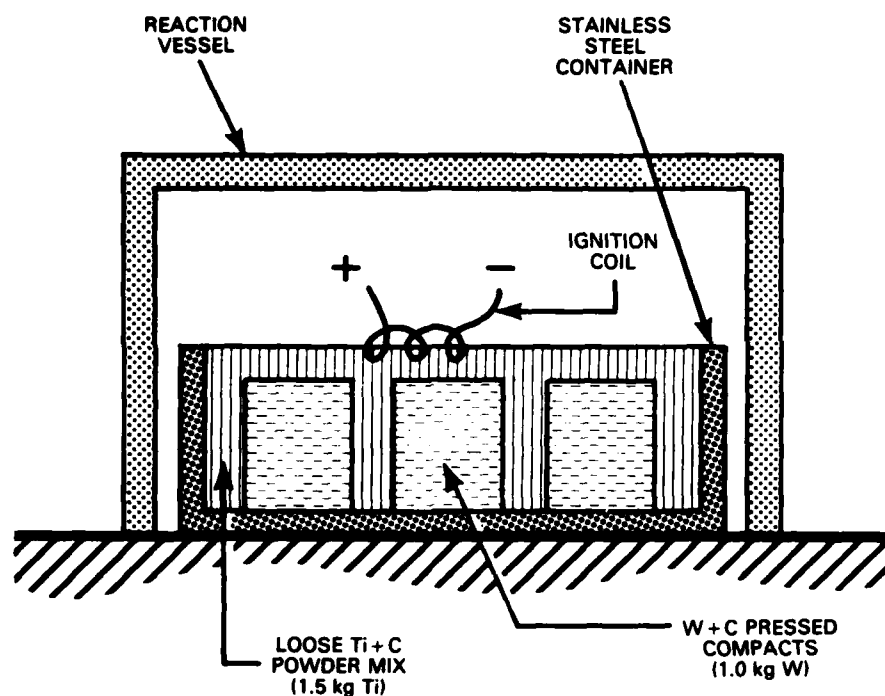
C. THE CHEMICAL FURNACE

Another process innovation that Soviet researchers use to attain higher reaction temperatures has been identified as a "chemical furnace." This furnace is simply a thermal blanket that is placed around reactant preforms that have inherently low adiabatic reaction temperatures. It is

designated as a chemical furnace because the thermal blanket is provided by another gasless combustion reaction that proceeds at a higher temperature than the desired product reaction. Normally, the "blanket" is a powder mixture and the "product" is the standard lightly pressed preform. For example, if a loose mixture of titanium and lampblack were packed around a group of preforms containing a mixture of tungsten and lampblack, as shown in Figure 2, upon ignition of the powder, the heat of reaction generated in forming TiC both ignites and provides a thermal boost to the less intense reaction that occurs between tungsten and carbon in forming WC. Although slow cooling over a period of 1-1/2 hours is recommended in this case, reciprocal contamination between the two materials has not been experienced. The crumbly TiC that results can be separated by hand pressure from the relatively dense product material.

A Soviet patent [Ref. 19] has been awarded to Soviet researchers in which the claim is made that the following products can be formed by this technique: MoB_2 , WB, WB_2 , Al_4C_3 , B_4C , Mo_2C , NbC, SiC, VC, and WC. The blankets usually are comprised of a mixture of Ti or Zr with boron or lampblack. Mass ratios between the blanket and product mixtures are required to be between 1:4 and 4:1.

Other references to the chemical furnace process adaptation are listed in Table 8, where the products include aluminides, carbides, and a germanide and silicide. In making tantalum carbide, the slower cooling rate obtained with the chemical furnace was cited as an advantage in achieving completeness of reaction. For niobium compounds, the chemical furnace materials (Ni and Al) reacted at about the same temperatures as the product materials. In this case, the "furnace" was used in the form of a large annular pellet that surrounded the product preform. In effect, it was also used to lengthen the post-reaction cooling of the product material, and it was effective in providing complete reactions and single-phase products. For copper aluminide products, titanium and boride material were used more as ignition tablets on flat planar ends of product preforms than as an encapsulating blanket.



Process:

- Make W + C compacts (50-60% density)
- Load in container
- Fill container with Ti + C powder
- Pre-evacuate (10^{-2} mm Hg pressure)
- React at 1-2 atm. (Ar)

Product:

- Dense WC shapes
- Crumbly TiC powder

FIGURE 2.
SCHEMATIC REPRESENTATION OF SOVIET "CHEMICAL FURNACE" SYNTHESIS

TABLE 8.
OTHER SOVIET USES OF A CHEMICAL FURNACE

<u>Product Compound</u>	<u>Blanket Reaction</u>	<u>References</u>
Mo_3Si	$\text{Ti} + 0.6 \text{ Si}$	12
TaC and Ta_2C	$\text{Ti} + \text{C}$	20
Nb_3Al and Nb_3Ge	$\text{Ni} + \text{Al}$ (pelletized)	13
CuAl and Cu_2Al	$\text{Ti} + 2\text{B}$	21

D. THE THERMAL EXPLOSION

Supplementary heating is a process innovation often identified in the Soviet literature as the "thermal explosion" process adaptation. Usually this term refers to preheating of the product material in order to obtain higher reaction temperatures or melting during the reactions. Per Reference 22, melting of product materials (TiC and AlNi) was achieved by preheating the reaction preforms in programmed steps that eventually reached self-ignition temperatures. Heating was achieved through an electrical current that passed between electrodes placed at both ends of the preform. In synthesis of silicides, per Reference 12, increased reaction temperatures were obtained by preheating preforms between 200 and 600°C. In producing tantalum carbide [Ref. 20], the amount of unreacted material was reduced from 12 to 2 percent by preheating preforms to 400°C. In synthesis of intermetallic aluminides, per Reference 13, preheating was required for gasless combustion of CrAl₃, MoAl₂, and TiAl but not for CoAl and NiAl. In synthesizing copper aluminides [Ref. 13], relationships among preform diameter, preform density, and preheating temperature were established for steady-state combustion conditions. In general, preheating on the order of 450 to 540°C was considered to be necessary. An important conclusion and commercial implication in this reference was that the copper aluminides formed by this synthesis technique could be used directly as electrodes in electric arc remelting operations.

E. CHEMICAL ACTIVATING AGENTS

In other instances, Soviet researchers have reported the use of chemical activating agents to control gasless combustion reactions. In one instance [Ref. 23], a method was patented to synthesize borides (GeB, MoB₂, and Mo₂B) in which activators (CaCl₂, KMnO₄, NaF, and NH₄ClO₄) were employed in levels of 0.0005 to 0.003 moles/gm-atom of boron. The additives increased the purity of product compounds. A special boronizing agent (magnesium polyboride, 12% Mg and 88% B) also was employed [Ref. 24] in synthesizing titanium-chromium and zirconium-chromium borides. The activating material reduced combustion rates and extended the compositional

regions of the homogeneous solid solution that were obtained in synthesis. Other uses of activating agents are discussed in Section B of Chapter IV in regard to synthesis of powder products.

F. REACTION BRAKING BY DILUTION

In cases where Soviet researchers desire to reduce intensity or to "brake" the gasless combustion reaction, elemental reactants often are mixed with some product material. Specific cases in Reference 25 demonstrate that reaction braking reduces the high adiabatic reaction temperatures experienced in synthesis of MoB, NbB₂, TaB₂, and ZrB₂. In these instances, product additives between 10 and 67 percent of the various reaction mixtures resulted in reductions of adiabatic reaction temperatures of about 50 to 1,000°C. Discussions in References 12 and 14 demonstrate the effects of product dilution on reducing the combustion rate and on the combustion mode. As product dilutions are increased in synthesis of silicides (Ti₅Si₃) and of borides (HfB₂, NbB₂, TiB₂, and ZrB₂), the combustion rate decreases progressively; at some point, the combustion mode changes from steady state to an unstable form of combustion (auto-oscillatory or autovibrational). In the case of Ti₅Si₃, this transition in combustion mode occurs at 30 percent dilution of the reactant mixture with the product. In synthesis of tantalum carbide [Ref. 20], the effects of product dilution are reduction of the adiabatic reaction temperature and increase of reaction completeness. Similarly, in another experimental synthesis of tantalum carbide [Ref. 16], product dilutions of the reactant mixture resulted in decreases in combustion rate, increases in unreacted material, and decreases in the oscillation frequency in auto-oscillatory combustion. In another dilution experiment [Ref. 18], requirements for particle sizes were cited in synthesis of Ti₅Si₃. For titanium and silicon elemental powders, sizes were ≤ 45 microns, and for the product diluent the required size was ≤ 63 microns. In this case, as the weight percentage of dilution was increased up to 20 percent, the measured reaction temperature dropped in a linear relationship, from 2,400 to 1,850°C, and the combustion rate dropped in a similar relationship from 3 to 0.5 cm/sec.

G. REACTIVE DENSIFICATION

One of the major problems faced in development of the various gasless combustion processes for synthesis of refractory compounds is lack of full densification of the product. If process conditions are not customized in each case, the product is often a porous, low-density mass. An obvious solution to this problem is to combine pressure with the simple form of gasless combustion to provide the desired additional densification, and Soviet researchers have performed a number of experiments with this objective in mind. Use of pressure applications in synthesis of compounds from elemental reactants is reviewed in this section. Another discussion (Section C of Chapter IV), deals separately with use of pressure in thermite-like reactions that include an oxide among the reactants and produce cast products.

Most of the investigations in densification of products during gasless combustion synthesis involve the manipulation of atmospheric pressure, mechanical pressure, or both, during the reaction period. Although high atmospheric pressures were used effectively in production of nitrides and hydrides from gaseous nitrogen or hydrogen, Soviet researchers also discovered that increasing the pressure of an inert atmosphere during gasless combustion of other compositions increased reaction speeds while decreasing porosity. Promising results also have been noted in Australian studies of mechanical compression combined with gasless combustion synthesis reactions [Refs. 26 and 27].

For conventional sintering, the precursor green compact normally has a relative density in the range of 55 to 70 percent. This compact shrinks to form a denser product during the subsequent heating, which is usually conducted at atmospheric pressure and without mechanical compression. This is analogous to gasless combustion in that one begins with a precursor green compact that subsequently gets heated; however, the reaction kinetics involved in gasless combustion often cause the final product to become larger and more porous than the initial compact [Refs. 28 and 29]. Two phenomena have been postulated as the reason for this size increase:

- Byproduct gases and the efflux of volatile components that expand within closed pores [Ref. 16]
- Diffusion of one component across a boundary into another component that results in porosity and an enlarged skeletal structure [Refs. 30 and 31].

The mechanism of enlargement can be explained by imagining a stationary control volume that is traversed by a combustion wave. The initial compact is not fully densified, and the elemental components probably contain both adsorbed and absorbed gases, oxides, and other contaminants. This control volume is initially at room temperature in an inert atmosphere at atmospheric pressure. Enlargement begins as the prereaction zone traverses the control volume, and the more volatile contaminants begin to boil off. Since the path for release of the gases to the compact exterior is through a chain of minute pores, local pressure gradients are created and an overall pressure gradient probably exists between the inner sites of boil-off and the compact surface. These effects become reinforced as the temperature rises and expands the gas. As the combustion wave continues to pass through the control volume, diffusion effects become more important. For simplicity, assume that one of the two reactants melts in the prereaction zone and that interfacial diffusion drives the molten component to the surface of the more refractory component. The molten component then begins to diffuse into the particle surface and, if the temperature is sufficiently high, an exothermic reaction occurs on the surface--creating the condensed product. The molten element continues to diffuse through the product layer until equilibrium is achieved or reaction kinetics become unfavorable. The result of this process is a skeletal structure of product particles among the sites vacated by the molten component; hence, the product would be expected to be more porous than the initial green compact.

Although an inert atmosphere was assumed for this example, gasless combustion also has been conducted in reactive atmospheres for production of hydrides and nitrides [Refs. 32 and 33]. Typically, the nitride-forming process takes place in a nitrogen atmosphere at 50 to 100 atm. The gas pressure affects not only the final porosity but also the product homogeneity and the completeness of reaction. Since variations in gas pressure

also would affect the mixing composition, the reaction effects directly attributable to pressure alone are not clearly understood for reactive atmospheres.

The pressure variation of an inert gas is far more elucidating. For example, several product properties have been related to inert gas pressure: porosity, combustion speed, and completeness of reaction. In a Soviet study of tantalum-carbon mixtures, the combustion rate and relative density increased proportionally with the gas pressure to a maximum value of 40 atm [Ref. 16]. A similar phenomena was observed in a study of titanium-boron mixtures [Ref. 34]. Here, the combustion velocity (u) was reported to vary with pressure (p) to a power (ν), where

$$u = p^{\nu} .$$

The power term is a function of the material properties and is determined empirically. For example, the combination of titanium particles of less than 40 microns and boron particles of less than 4 microns results in a value of $\nu = 0.2$. For this system, the combustion speed leveled out to a maximum at 10 atm. This maximum combustion speed is also a function of the physical properties of the materials.

In the study of tantalum-carbon mixtures, a test also was performed with ends of the compact clamped to prevent lengthening, which resulted in an overall increase in relative density and combustion velocity. In addition, the density and velocity remained constant as the atmospheric pressure was varied. This indicates that the combustion process itself becomes more intense as the interparticle distance decreases. Furthermore, since the values of density and combustion velocity are greater than at the gas pressure saturation value, a mechanism other than gas release must be responsible for product lengthening. One possible mechanism is the diffusion process mentioned previously.

In view of the low-density, porous product forms often obtained in gasless combustion synthesis and the combustion mechanisms that contribute to them, an obvious question is why mechanical pressure has not been used more extensively to achieve full densification. A partial answer to this

may be the difficulties involved in the design of adequate press equipment. As shown by the Australian researchers, a mechanically constrained synthesis specimen shrinks very rapidly when under load (2,500-4,000 psi) [Refs. 26 and 27]. This complicates the design of pressing equipment, as shown in Figure 3. Most of the Australian work was concentrated on two-phase solid solutions containing silicides, such as $\text{Al}_2\text{O}_3\text{:MoSi}_2$. Relative densities of 99.5 percent were achieved in silicide products and 95 percent was reported for borides. A Soviet approach [Ref. 22] was to hold the green compact (a Ti powder and lampblack mixture) between molybdenum electrodes, as shown in Figure 4. Presumably, both atmospheric and mechanical pressures and electrical transmission were used for product densification. TiC shapes were produced in the form of cutting tools at density levels of 96 percent of theoretical, and AlNi_3 also was reported as a product obtained with this process adaptation.

The primary counter mechanisms to specimen enlargement in densification under mechanical pressure are probably plastic flow and intergranular slip. If an external force above the minimum required for plastic flow is applied, the grains flow past each other. This reduces the intergranular spacing, which subsequently increases combustion speed and relative density. Intergranular slip occurs when neither component nor an intermediate phase melts. The ceramic grains slip if a large shear force can be generated within the structure. Small grain sizes greatly aid the slip mechanism. Some ceramic compounds, generally two-phase compounds with very small grains ($< 25 \mu\text{m}$), have exhibited superplastic behavior at gasless combustion temperatures [Refs. 35 and 36].

Combinations of mechanical and atmospheric pressure also may be beneficial for densification, but only limited published information has been found. Some researchers also have recommended reaction pressing a specimen in a vacuum to aid the removal of volatile impurities, but this may cause some reaction components to boil. Another method of removing gaseous efflux is gettering the specimen with aluminum flakes [Ref. 27]. Although such methods may render high-pressure combinations less practical, more study is required in this area to find optimal solutions.

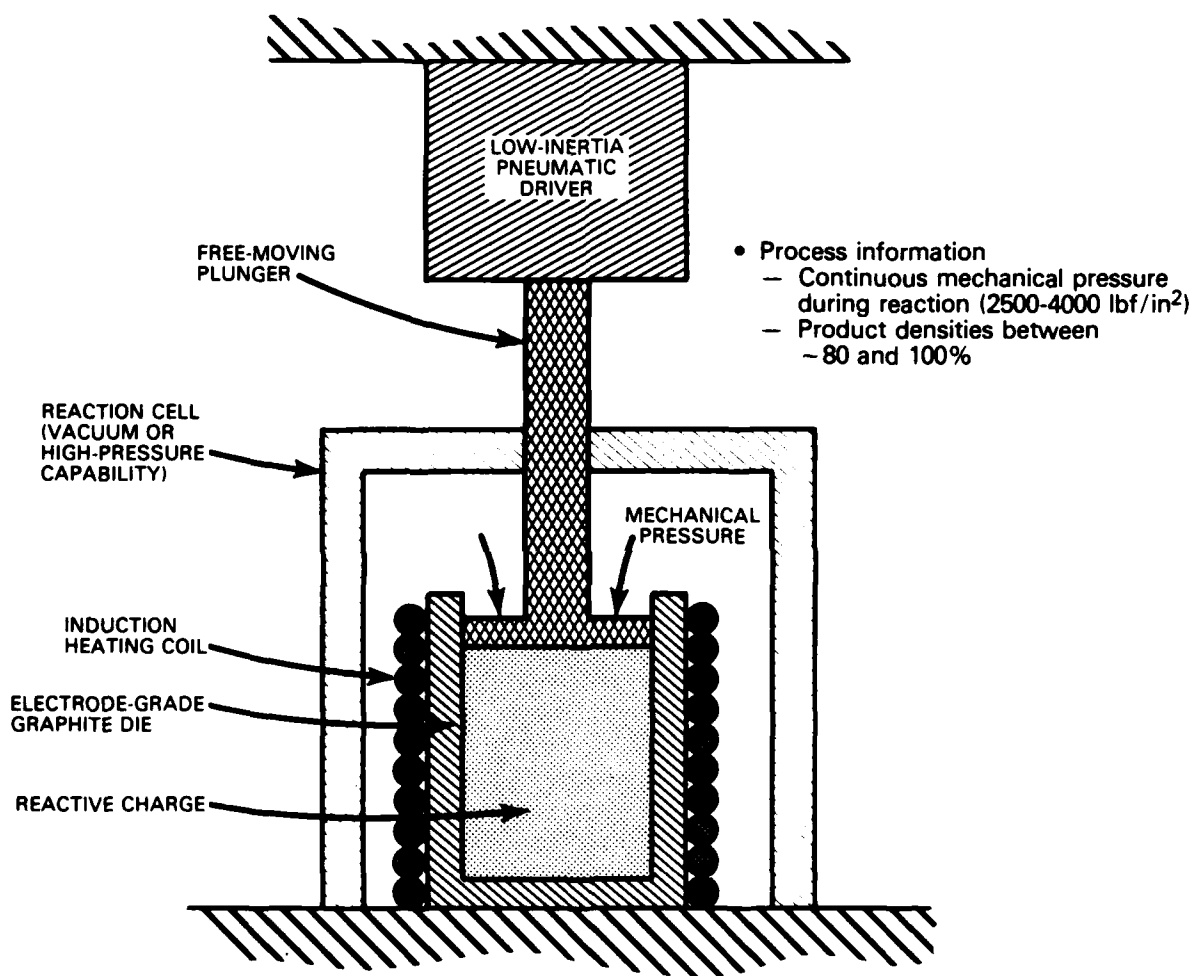
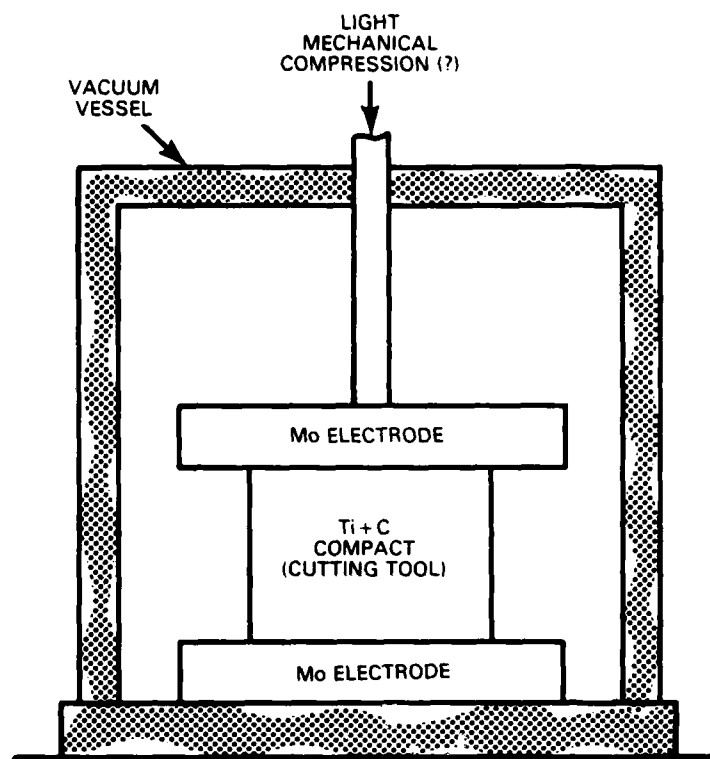


FIGURE 3.
SCHEMATIC REPRESENTATION OF AUSTRALIAN REACTION PRESSING



Process information:

- Electrical input to electrodes is step-programmed prior to ignition of combustion wave
- "Continuous compression (?)" of 0.5 to 5 atm

FIGURE 4.
SCHEMATIC REPRESENTATION OF SOVIET PRESSURE – AIDED DENSIFICATION

Mechanisms that explain the effects of atmospheric and mechanical pressures on gasless combustion are not thoroughly understood. The products resulting from the application of pressure, especially mechanical pressure, have been analyzed in only the most rudimentary manner. The attempts at mathematical modeling pressure effects have been restricted to order-of-magnitude, one-dimensional type models and apply only to a specific specimen under study. In general, research on pressure applications for gasless combustion has been highly qualitative and empirical in nature. Further refinement and quantification of the basic mechanisms are needed to develop a sound theory and useful analytical models. As an example, the mechanisms responsible for the volume increase of a gasless combustion product have not been quantitatively examined. While it is generally accepted that gas release and diffusion result in product expansion, the fraction of expansion attributable to each mechanism has not been predicted for a given system.

The expansion phenomenon could be studied and measured through simple experiments. Two identical compacts of a given mixture, such as Ti and C, could be fabricated. The first compact could be reacted at atmospheric pressure and the second in a high-pressure atmosphere (~50 atm). The volume increase of the latter compact would be due primarily to diffusion processes since the effect of volatile gas release is minimized by the high pressure. A comparison of the two volume increases should indicate the relative comparative magnitudes of the expansion contributions for gas evolution and diffusion mechanisms. In addition, a comparison of pore structure would be of interest. The specimen combusted under pressure should have smaller and more evenly distributed pores.

Knowledge of the basic combustion mechanisms that contribute to product expansion would be beneficial in developing approaches to product densification. The current approach of exerting extreme mechanical compression through a fast-acting plunger may not be the optimal procedure. The development of more suitable procedures can be aided through a basic study of combustion kinetics and mechanisms.

IV. SOVIET GASLESS COMBUSTION PRODUCTS

In addition to Soviet claims that gasless combustion synthesis is capable of producing several compositional types of products for a number of diverse applications (Table 3), some diversity also has been noted in physical forms of products. Soviet processes that have been patented for synthesis of three product forms are described in this chapter. They include (1) the standard form, in which powder mixtures of elemental constituents are transformed in situ into product compounds (without basic shape changes), (2) a powder form, and (3) a cast form, in which both the product compound and a slag are formed and separated during the reaction.

A. PRODUCTS IN THE STANDARD FORM

Soviet researchers have obtained patents on gasless combustion synthesis in at least four countries. A basic synthesis process technology is patented both in the United States [Ref. 37] and U.S.S.R. [Ref. 32]. These patents emphasize reactions with the metallic transition elements in the periodic table to form many compositional categories⁴ of simple ceramic compounds. The process generally follows the operational sequence illustrated in Figure 1, except that special ignition compounds or nonsolid reactants sometimes are used. The ignition compounds are special powder mixtures that have low ignition temperatures. They are placed on the ignition surface and facilitate initiation of the combustion wave. The nonsolid reactants are nonmetallic elements. Gaseous hydrogen has been used in synthesizing hydride compounds, and gaseous or liquid nitrogen normally is used in synthesis of nitride compounds.

⁴For example, borides, carbides, chlorides, fluorides, nitrides, phosphides, silicides, and sulphides.

Other U.S.S.R. patents have been obtained or requested by Soviet researchers where each is limited to a unique process adaptation or to a single or relatively few product compositions. These patents are listed sequentially in Table 9 by patent number or application year. In each case, product material(s) and descriptive information also are provided with the identification listing in the table.

These patents include synthesis processes for producing borides, carbides, nitrides, intermetallics, and ferroalloys. Process adaptations, which were discussed in Chapter III, include prereaction heating (thermal explosion), use of chemical activating agents, the chemical furnace (thermal blanketing), and use of pressure in combination with the gasless combustion reaction.

During 1977 and 1978, patents were issued for production of master alloying compounds that are used in steelmaking. In the United States, those materials usually are produced in electric furnaces; Soviet researchers claim that gasless combustion synthesis is a lower-cost alternative.

From the industrial viewpoint, direct synthesis of dense TiC in the shape of a tool bit also may be of considerable significance [Ref. 22]. No other reference has been found in Soviet literature that claims success in direct synthesis of fully densified final shapes in the standard product form. This patent may well describe the process used to manufacture titanium ceramic cutting tools at the Dneprovskiy Hard Alloys Plant that has been the subject of a recent press release [Ref. 47].

The manufacture of MoSi_2 industrial heating elements using gasless combustion synthesis also has been announced in the Soviet press as a significant industrial accomplishment [Ref. 48], although no specific patent of an invention has been identified. Furthermore, no evidence has been found in the technical literature to determine whether these heating elements are synthesized directly as final shapes or converted by some other process from synthesized powder into final shapes.

TABLE 9.
SOME U.S.S.R. PATENT ACTIVITY
IN GASLESS COMBUSTION SYNTHESIS

<u>Number</u>	<u>Material Produced</u>	<u>Remarks</u>
264,365 [1970, Ref. 38]	Tantalum mononitride	Used liquid nitrogen
420,394 [1971, Ref. 39]	Aluminide intermetallics	Green compacts are pre-heated
1,834,577/23-26 [1974, Ref. 40]	(a)	(a)
465,544 [1975, Ref. 23]	Molybdenum diboride	Activating agents used in the reaction mix
556,110 [1977, Ref. 19]	Carbides and borides (mostly of heavy elements)	A blanket of Zr-C or Ti-C mixture is used as a chemical furnace
557,117 [1977, Ref. 41]	Nitrided ferroalloys	Process is low cost in comparison with alternatives
584,052 [1977, Ref. 22]	Fused TiC and AlNi ₃	Product density was increased by adding product diluent, preheating between Mo electrodes during combustion
2,130,084/2-02 [1977, Ref. 42]	(a)	(a)
2,382,703/26 [1978, Ref. 43]	(a)	(a)
2,386,649/23-26 [1978, Ref. 44]	(a)	(a)
589,276 [1978, Ref. 45]	Nitrogen-containing master alloy	Used in steel production
594,204 [1978, Ref. 46]	Nitrogen-containing master alloy	Used in steel production

(a) Have not been able to obtain this patent application document or to identify the corresponding patent.

Another Soviet press release on industrial uses of gasless combustion synthesis is production of titanium nickelide [Ref. 49]. This has been used as a "memory alloy" in applications where its thermal sensitivity is a useful property. Hundreds of kilograms have been produced in the form of wire, plate, and tubes [Ref. 50]. The products are now being used in Soviet aircraft, especially in fuel and air lines.

Some additional Soviet references to industrial application of gasless combustion synthesis are listed below:

- Large-area welding of graphite and molybdenum [Ref. 51]
- Bonding of double-layer pipe, to be used in handling corrosive media [Ref. 51]
- Gasless combustion electrodes with which the heat of reaction is used for surface repair of worn industrial equipment [Ref. 52]
- Surface coating of turbine blades with refractory ceramic layers [Ref. 53].

Proposed uses of gasless combustion technology for metal-nonmetal bonding are intriguing as industrial processes. When the proposed applications are extended to repair of worn industrial equipment, simple battlefield repairs of heavy equipment also can be visualized as a potential direct defense application.

The fact that gasless combustion technology has received considerable attention in recent Soviet press releases about industrial applications indicates that the R&D programs probably will continue to receive budgeting support. Thus, continued surveillance of the Soviet programs should be of special interest to R&D programs in the United States.

B. POWDER PRODUCTS

In view of the difficulty in achieving fully densified synthesis products, Soviet researchers probably were reminded of potential industrial uses for ceramic powders. At least their technical literature indicates that a number of compounds have been synthesized where the powder form is intended as an end product.

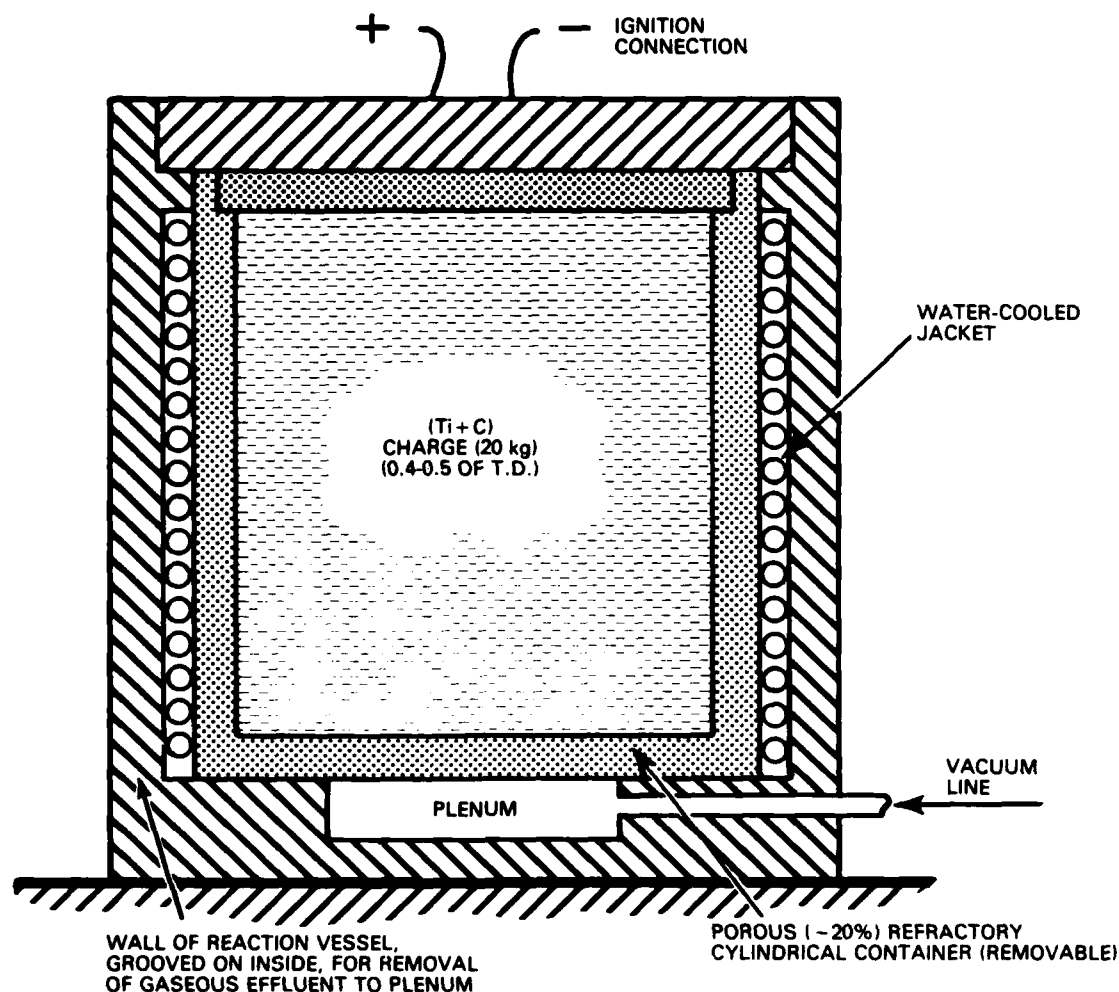
The powder product that has received the most attention in Soviet technical articles and press releases is titanium carbide. Both U.S.S.R. and U.S. patents have been issued for this synthesis process [Refs. 54 and 55]. The schematic illustration in Figure 5 indicates how 20-kg batches of powder are manufactured in reusable containers.

In another U.S.S.R. patent, a process is described for production of zirconium and titanium carbide powders [Ref. 56]. In this case, a hydride of the metallic reactant element is combined with the elemental metal and lampblack in the reactant mixture. The reported influences of the hydride ingredient are to control reaction temperature and to increase particle size of the carbide product, for which values were reported between 3 and 25 microns.

In various literature references, the favored industrial uses for the titanium carbide powder products were reported to be in grinding and polishing applications [Refs. 51, 52, 57-60]. Another press release indicated that a production source of these products was the new powder metallurgy pilot plant at Baku [Ref. 61]. Although production processes were not identified, other products reported for this facility are boron carbide, titanium carbonitride, and silicon nitride. Each of these compounds has been produced by gasless combustion synthesis in the U.S.S.R.

Other industrial uses of powder products formed by gasless combustion synthesis have been reported in Soviet literature:

- A patent has been issued for production of hydride powders (neodymium, samarium, scandium, titanium, and yttrium) [Ref. 62].
- Successful production of a number of hydrides, which were subsequently crushed into powder has been reported by the Academy of Sciences of the Armenian SSR [Refs. 63 and 64].
- Titanium diboride and disilicide powders that were produced by gasless combustion synthesis have been used to dispersion-harden extrusions of titanium structural alloys [Ref. 65].
- The production and use of sulfide and selenide powders as lubricants also has been reported [Refs. 9, 52, 66, and 67].



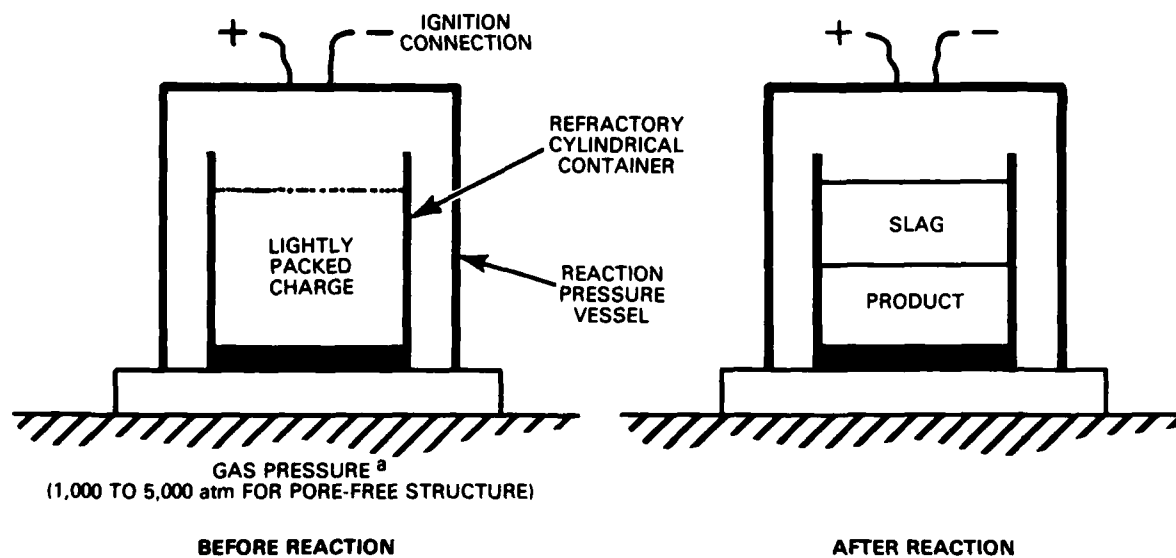
- Starting materials
 - Impure Ti powder (e.g., sponge fines) and lampblack
- Process yield
 - ~98%
- Product purity
 - Free C = 0.08%
 - Oxygen = 0.1%

FIGURE 5.
SCHEMATIC REPRESENTATION OF SOVIET SYNTHESIS
OF TITANIUM CARBIDE POWDER

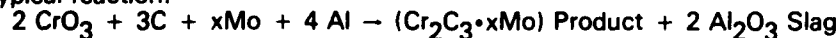
A patent has been awarded to a U.S. researcher for production of tungsten carbide powder [Ref. 68] that appears to have some process similarities to Soviet gasless combustion technology. In the U.S. process, 72 tons of tungsten (mixed with iron oxide, aluminum, and calcium carbide) are reacted over a period of 60 minutes to yield 22 tons of tungsten carbide.

C. CAST PRODUCTS

One of the approaches investigated by Soviet researchers to obtain dense products in gasless combustion synthesis is liquefaction. A reaction of the type used in metallothermic processes [Ref. 69] has been integrated with the standard form of synthesis, as illustrated in Figure 6. Generally, an elemental reactant, metal oxide, and reducing agent are combined and pressed to form a green compact.



A typical reaction:



^aAn alternative is to use a centrifuge with 100 to 1,500 g acceleration, which is under 1 to 100 atm gas pressure.

FIGURE 6.
SCHEMATIC REPRESENTATION OF CAST PRODUCTS FORMED WITH
MODIFIED GASLESS COMBUSTION SYNTHESIS

After ignition, a narrow reaction wave propagates through the charge and separated layers of cast product and slag result. Soviet process descriptions do not state specifically that an open, unlined reaction container is used as shown. Another possibility would be to enclose containment in the manner of a hot isostatic pressing (HIP) operation.

Apparently, the first public announcement of cast products produced by gasless combustion synthesis was at a national Soviet meeting on combustion processes [Ref. 70]. This announcement more or less coincided with issuance of patents to Soviet researchers for the process in the United Kingdom [Ref. 5] and the U.S.S.R. [Ref. 71], although an earlier patent had been obtained in France [Ref. 6]. It was followed by a description of the process in a technical overview by the Soviet leader of the gasless combustion synthesis program [Ref. 72], and by discussion of a potential application for producing titanium nickelide. The products include:

- Borides - MoB
- Carbides - Cr_3C_2 , Mo_2C , VC, WC
- Nitrides - VN
- Silicides - NbSi_2 , V_3Si
- Intermetallics - titanium nickelides
- Complex compounds or cermets - (MoB and Ni), (Cr_2C_3 and Mo), (Mo_2C with TiC and Ni), (TiC and Cr_2O_3 with Ni or Ni and Mg), (TiC and Mo_2C with Ni or Ni and Mo), (VC and Co), (VC and Ni), (WC and Co), (WC and Mn).

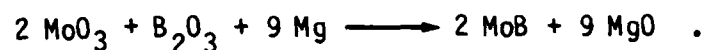
1. Thermodynamic Aspects

This process can be better understood through the examination of examples: one that uses Al as the reductant and another that uses Mg. Soviet researchers report the production of MoB with either Al or Mg as the reducing agent. With Al as the reductant, the stoichiometric equation is



Using the methods illustrated in the previous section on thermodynamics and a standard chemistry handbook, the excess enthalpy of this reaction is

calculated to be 267.3 kcal/mole. With Mg as the reductant, the stoichiometric equation for the production of MoB is,



This yields 315.8 kcal/mole of excess enthalpy. Although the enthalpy obtained with Mg as the reductant exceeds that of the Al reduction reaction, Al is the reductant selected for most reactions reported in Soviet literature.

A large reaction heat is essential to these metallothermic processes, since the reaction temperatures must be above the melting points of all the constituents, and sufficient energy must be available to initiate the reaction. It is essential that the actual reaction temperatures be 150 to 200°C above the fusion temperature of all components to compensate for heat losses, which vary from 8 to 30 percent during the course of the reaction [Ref. 71]. The methodology of calculating these quantities can become quite complex, and some metallothermic reactions may challenge current calculation techniques. The Soviet production of a TiC cermet (50 percent TiC + 40 percent Cr₃C₂ + 10 percent Ni), for example, involves five initial components and several intermediate phases. In addition, generation of a large amount of gas from volatile components is not uncommon, which not only complicates calculations but also could contribute to reaction explosions.

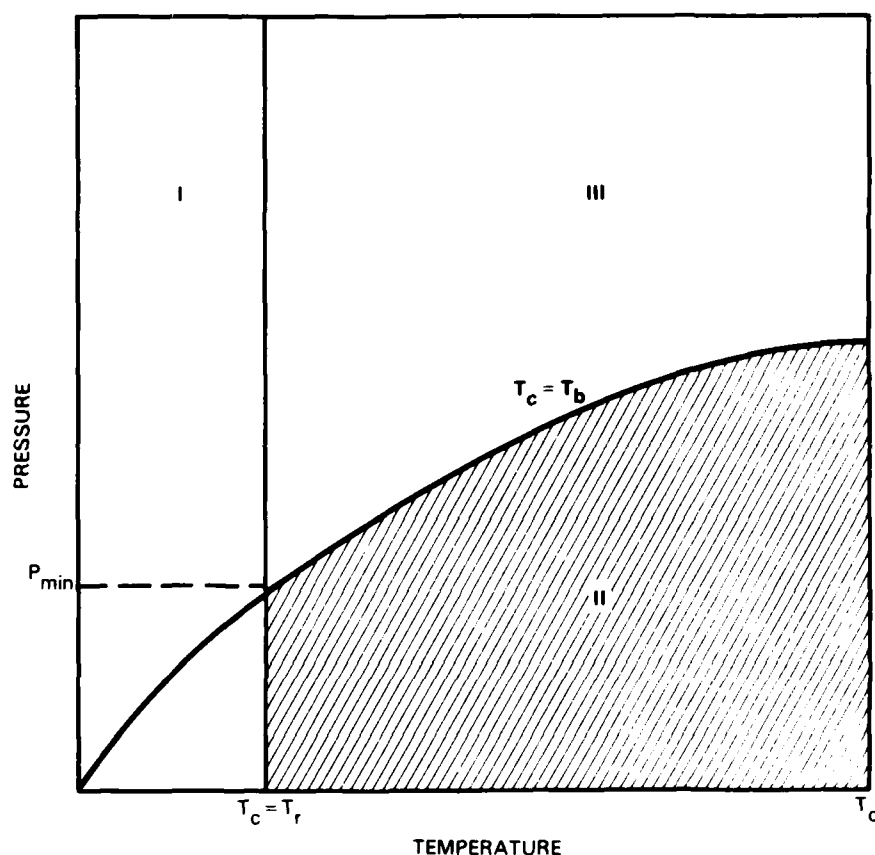
2. Reaction Kinetics

The kinetics of metallothermic reactions must be considered to predict the behavior of the reaction during the combustion separation and congelation phases and to predict characteristics of the final product. The following discussion presents Soviet views of reaction kinetics that are based upon experimental observations [Ref. 69, 72].

Metallothermic reactions may proceed in either steady-state or unstable modes. For a given system, the combustion mode is influenced by atmospheric pressure (P), combustion temperature (T_c), the melting temperature of the reducing agent (T_r), and the boiling point temperature of the

most volatile component (T_b). The most volatile component is usually the metal that is used as a reducing agent or, perhaps, B_2O_3 . In Figure 7, the Regions I, II, and III of this T, P diagram are defined by the following parameters:

- I $T_c < T_r$
- II $T_c > T_r$ and $T_c > T_b$
- III $T_c > T_r$ and $T_c < T_b$.



T_c = CRITICAL TEMPERATURE
 T_b = BOILING TEMPERATURE OF MOST VOLATILE COMPONENT
 T_r = MELTING TEMPERATURE OF REDUCING AGENT

FIGURE 7.
ZONES OF STEADY STATE AND UNSTABLE COMBUSTION
(Regions I and III, Steady State; Region II, Unstable)

Regions I and III define areas of steady-state combustion, while Region II is an area of unstable combustion. A reaction in this latter region might proceed with a strong scattering of products or even result in an explosion.

The combustion wave speed is also an important parameter since it is an indicator of reaction rate, combustion zone size, and the temperature at which the reaction occurs. For example, a slow combustion wave would indicate a relatively slow reaction rate and a broad combustion zone (with much of the reaction occurring at temperatures below the calculated combustion temperature). Another factor strongly affecting combustion kinetics is the effective thermal conductivity (λ). In general, for high-temperature reactions ($T_c > 2,000^\circ\text{C}$), an increase in λ increases the propagation speed of a steady-state wave. Conversely, low-temperature reactions tend to have a decreasing combustion wave speed with increasing λ . This indicates the existence of an optimal value of λ , for which a variation from this optimum decreases the combustion wave speed. One Soviet explanation attributes this phenomena to the constituent melt rates and the flow of the melted constituents.

If the reactants have different melting temperatures, preliminary mixing occurs through capillary spreading (migration) of the liquid substance along the surfaces of the grains. With aluminum granules (0.1-0.2 mm) at relatively low temperatures (1,000-1,400°C) the migration rate of aluminum reaches 1.11 to 1.85 cm/sec [Ref. 67]. This falls within the range of the combustion rates of high-temperature reactions. It may even be possible for the reaction to proceed faster than the migration rate if the melt rate (a strong function of thermal conductivity) is high enough. For the lower-reaction temperature species, the migration rate is faster than the reaction rate; this allows the migrating component to remove a large amount of heat from the reaction. Some chemical reduction then may occur at a lower temperature in the prereaction zone. An increase in thermal conductivity abets this phenomena and further decreases the reaction rate. It is even possible to quench a reaction in this manner.

The reaction rate, as well as the combustion temperature and ignition temperature, also may be significantly affected by the addition of catalysts or other additives. Such additives may be categorized into two basic groups: additives that increase combustion temperature and reaction rate, and those that decrease ignition temperature, combustion temperature, and reaction rate. Thermite compounds are included in the first group: NaNO_3 , KClO_3 , and BaO_2 . Compounds that increase λ , and therefore affect reaction rate as previously discussed, include fluorides, chloride salts, and lime. Compounds that decrease λ include fluoride salts (AlF_3 , MgF_2 , CaF_2 , NaF), alkali, and alkali-earth metals.

Another method employed to increase reaction rate entails maximizing the area of contact of the reactant particles. This has been accomplished by using fine grains of nearly equal sizes for all species. The g value has been increased with increased atmospheric pressure (100-5,000 atm); but, more importantly, a high atmospheric pressure also inhibits vaporization of volatile reaction components and absorbed contaminants. An excess amount of boil-off not only removes reactants but also interferes with the reaction and creates pores in the final product. High atmospheric pressures have been employed in Soviet synthesis casting processes with very positive results. High pressure tends to increase the yield of products and the reaction rate while decreasing the amount of boil-off and pores.

High centrifugal acceleration has been used to achieve similar results in regard to reduction of pores and cavities. Its use also would aid in separation of product and slag. As the combustion wave passes through a green compact, the product remains molten for some finite time period, T_m . If we define a process where ignition occurs at the top of the mold at $t_0 = 0$ sec, the reaction proceeds down the mold to completeness in a finite time period, T_c . For complete separation to occur, the product must coagulate and settle to the bottom; one may define the settling time for the topmost layer to be T_s . Therefore, for complete separation of the phases,

$$T_s \leq T_m + T_c \quad .$$

In actual practice, $T_c \ll T_m$, and the oxide phase must form a continuous medium through which drops of the refractory compound move.

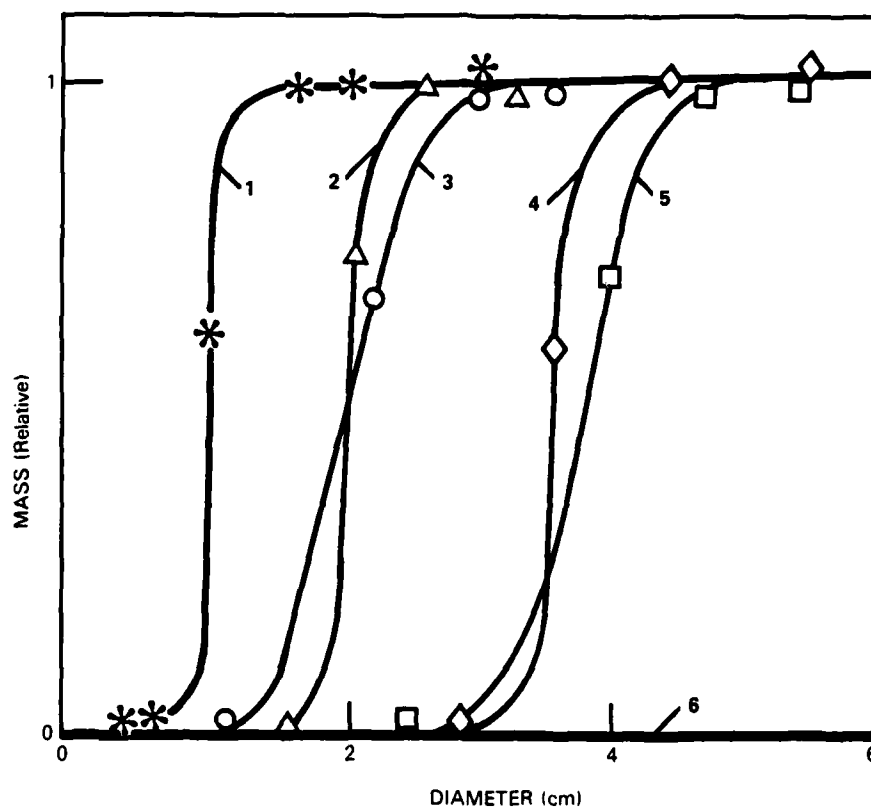
Centrifugal acceleration also has some unwanted side effects, the primary one being its tendency to decrease the yield of desired products. For this reason, centrifugal acceleration should be considered for only those metallothermic conditions where $T_s > T_m$.

In regard to phase separation, a critical vessel diameter (d_c) has been reported below which phase separation is difficult to achieve even at high centrifugal accelerations. With $d < d_c$, congelation is faster than phase separation, and the combustion product consists of a fused but unseparated mass. With $d > d_c$, phase separation is faster than congelation, and the product and slag separate cleanly into distinct layers. The magnitude of d_c decreases with increasing centrifugal acceleration and increasing initial temperature. The d_c for several systems is shown in Figure 8 by the pronounced S-shaped curves.

3. Development Status

The status of development of gasless combustion casting in the U.S.S.R. can be illustrated best by reviewing results reported in one of the Soviet patents [Ref. 5]. The data, listed in tabular form in Appendix A, demonstrate that a wide compositional range of products has been synthesized (col. 2) by using reactant oxides and an aluminum or magnesium reducing agent (col. 3). The most significant claim represented by the data is that the products are pore-free (col. 12) when either elevated atmospheric pressure (col. 4) or centrifugal acceleration (col. 5) is used. In other cases, correlations became difficult to understand in this table without additional data. For example, the density of a given product remains roughly constant despite the presence of pores, the boil-off of components, or the differences in completeness of reaction (col. 11).

Increased atmospheric pressure tends to be more supportive of reaction completeness than centrifugal acceleration, as shown in cols. 6-9. One reason for this could be the increased effectiveness of high atmospheric



($m_c = M/M_0$, where M_0 is the calculated mass of the ingot and M is the instantaneous mass of the ingot) as a function of the diameter of the reaction volume (d).

- 1) Mo_2C , $T_0 = 300 \text{ K}$, $a = 500 \text{ g}$
 - 2) $\text{WC} + \text{Co}$, $T_0 = 300 \text{ K}$, $a = 1000 \text{ g}$
 - 3) WC , $T_0 = 300 \text{ K}$, $a = 1000 \text{ g}$
 - 4) VC , $T_0 = 300 \text{ K}$, $a = 1000 \text{ g}$
 - 5) WC , $T_0 = 800 \text{ K}$, $a = 1g$
 - 6) WC , $T_0 = 300 \text{ K}$, $a = 1g$
- (g) is the acceleration of gravity)

SOURCE: Reference 69

FIGURE 8.
RELATIVE MASS OF CAST REFRACTORY COMPOUNDS

pressure over centrifugal acceleration in inhibiting the release of volatile gases. As discussed earlier, these gases apparently result from reactant boil-off and interfere with the reaction.

Another item of considerable interest in regard to this table is that both simple compounds (e.g., Mo_2C) and combinations (e.g., TiC and Mo_2C) have been synthesized. The production of hard alloys (cemented carbides, e.g.: WC, 90 percent, Mo, 10 percent; and Cr_3C_2 , 85 percent, Mo, 15 percent are reported as Items 94 and 75, respectively in Appendix A) and of an intermetallic compound [Ref. 73] could both be of considerable commercial significance.

Even though much theoretical work needs to be completed, the practical methods developed are significant. Production of dense products under high atmospheric pressures (1,000-5,000 atm) or moderate atmospheric pressures (100 atm) in a centrifuge (100-1,500 g) is impressive, but understanding of reaction mechanisms for these metallothermic processes is at a low level. The Soviet researchers identify the following areas for further research:

- Refinement of thermal and thermodynamic calculations
- Development of methodology to optimize the overall process
- Detailed study of the mechanism and kinetics of metallothermic reduction at various temperatures and pressures
- Study of the sources of gasification and of the composition of generated gases and sublimates
- Identification of processes that may lead to explosions.

V. GASLESS COMBUSTION REACTION PHENOMENOLOGY

A. INVESTIGATIVE OBJECTIVES AND PLANNING

This chapter analyzes reaction phenomena in gasless combustion synthesis. The objectives are to understand the scientific phenomena underlying reaction behavior and to develop a predictive capability for potential synthesis reactions. These predictive capabilities will be useful in controlling reaction variables (e.g., reaction rate, local reaction temperature, phase conversion) and for identifying and evaluating feasibility of self-sustaining adiabatic reactions.

The analysis begins with a review and discussion of relevant Soviet studies of synthesis reaction theory. It continues with an SPC extension of that reaction theory and concludes with a discussion of synthesis reactions for production of AlN, TiC, and TiB₂.

B. RELEVANT SOVIET RESEARCH

The initial Soviet study of gasless combustion in its pure form was basically academic; however, that study was soon extended to development of self-propagating high-temperature synthesis, which since has been used to produce ceramic products. Since fabrication techniques, experimental methodology, and the general characteristics of gasless combustion synthesis have been documented in previous chapters, only the theory is reviewed here. The theory is used to develop analytical models that define the character and movement of the combustion front, that determine physical states and investigate their stability, and perhaps most importantly, that predict certain thermophysical constants. A brief examination of Soviet theory and analytical modeling of gasless reactions follows.

System Planning Corporation has collected and reviewed more than 200 Soviet papers published within the past 20 years on the subject of gasless combustion. In addition, more than 200 Soviet researchers who have contributed to those papers have been identified. Among the most prominent of these scientists are A. G. Merzhanov, I. P. Borovinskaia, S. K. Dolukhanian, Yu. M. Maksimo, and V. M. Shkiro. Although experiments on gasless combustion processes have been performed at many laboratories, the overall program originated at and has been controlled from the Institute of Chemical Physics U.S.S.R. Academy of Sciences at Chernogolovka.

Soviet researchers have expended considerable effort in analytical modeling of gasless combustion synthesis reactions. Generally speaking, these models are characterized by process simplifications identified below [Ref. 74]:

- The field of temperatures in the combustion wave is one-dimensional, and temperature changes only in the direction of displacement of the combustion wave.
- Diffusion transfer of the combustion product in the direction of displacement of the combustion wave is absent.
- The velocity of heat release during combustion is defined by conventional laws for homogeneous reactions, and melting is not made evident in the zone of heat release.
- The physical parameters that characterize the system--density, coefficient of thermal diffusivity, and thermal heat capacity--do not change in the course of the combustion process.

A set of reaction conditions also are assumed for each model. Conservation of energy and heat diffusion equations are applied to a characteristic control volume for a given reaction. Numeric integration of partial differential equations results in expressions for the mass and temperature distributions within the reaction volume.

These Soviet models are severely limited in scope and applicability, as made evident in the course of this chapter. For example, almost all gasless synthesis reactions experience phase changes in the products, the reactants, or both. The production of either liquids or gases almost surely would initiate mass transfer in the traverse direction of the combustion wave. Obviously, in view of the substantial temperature range of

the reactions, most physical properties (i.e., thermal conductivity and specific heat) will vary widely. Additionally, the assumption of homogeneous behavior of a powder reaction seems dubious, and system heat loss, which is assumed to be nonexistent, is an important parameter that defines the shape or thickness limitations associated with the reactions. These issues are discussed at greater length in Chapter VI, where SPC models are presented.

Several dozen Soviet models that address a large number of specific phenomena were reviewed, and summaries are provided in Appendix B for a few selected from this group. For example, a zero-dimensional adiabatic thermodynamic model was reviewed that estimated the adiabatic reaction temperature for a given reaction system (Appendix B, pp. B-2 through B-4). Also, a classical one-dimensional model was presented for a nonsteady-state reaction of a metal sphere in a nonmetal fluid, as in reactions of pyrotechnic or incendiary materials (Appendix B, p. B-5). The subjects of other models that are summarized in Appendix B are:

- Formation of solid solutions, p. B-6.
- Steady-state combustion of powder, pp. B-7 and B-8.
- Combustion of powders, pp. B-9 and B-10.
- Combustion in heterogeneous solid media, pp. B-11 through B-13.

New models appear to be developed continuously to fit specific experimental data and certain qualitative considerations. Generally speaking, these new models have not been validated for other general uses. For example, in one investigation of the gasless combustion of nickel and aluminum [Ref. 83], the following statements appeared:

- The relationship of the combustion velocity (u), the concentration of diluent (v), and the initial temperature (T_i) is smooth over the whole range of values v and T_i .
- The relationship of u and the combustion temperature (T_c) is essentially unchanging, since the points for different values of v and T_i lie on a single curve.
- The T_c for nickel and aluminum reaction is equal to the melting temperature of NiAl.

A model was developed that fits these data, and from the model, certain thermodynamic parameters for the reaction were obtained. Significantly,

a conclusion was stated that this model could be extended to other systems where the combustion temperature is equal to the melting point of the product, but no evidence has been found of attempts to develop the generic model.

This review suggests that Soviet models are usable only for a specific set of assumptions concerning, for example, phase conditions, reaction geometry, thermal properties. A change in one or more of these assumptions can and generally does invalidate the applicability of the models, and a phase transformation of one of the constituents requires that a new or modified model be introduced. Before a model can be applied to a given reaction scheme, for example, the phenomena to be modeled must be known or hypothesized. This includes identification of the constituents and their phase conditions, the potential reactions they undergo, the potential reaction locations, and the local geometry of the system (depending on the nature of the model application).

Although Soviet researchers generally assume a physical reaction environment and model the mass and energy transport phenomena within this environment, they rarely describe explicitly how the system reaches the given state or when the given state is transformed into another state. This omission invalidates their models for a broad range of reaction systems. For example, a model of a reacting solid sphere submerged in a reactant fluid is adequate only while the sphere is solid. When the sphere melts, the model becomes invalid, and another model must be introduced. The choice of a model for a given reaction environment was influenced by the nature of the phases and phase interfaces present in the system, mass and energy transfer rates, the rates of various reactions, and other considerations.

As this understanding of the limitations of Soviet models emerged, it illuminated the need for a fairly rigorous physical description of the specific reaction system of interest, which further requires supporting physical and chemical data. Basic reaction parameters of combustion mechanisms were therefore identified and studied as the next step in SPC's combustion analysis. After consideration of those parameters, supporting

data were collected to study synthesis of the three compounds that have been designated as reference development products in the DARPA/LLNL Program--AlN, TiC, and TiB₂.

C. SOME ANALYTICAL REACTION PARAMETERS

1. Adiabatic Reaction Temperature

The adiabatic reaction temperature for self-sustaining high-temperature synthesis reactions is calculated by assuming that all of the heat released by the reaction ultimately is used to raise the temperature of the final contents of the reaction vessel (products and unreacted reactants). It provides a measure of the temperatures the reaction vessel must accommodate.

Expressed in terms of enthalpies, the calculation takes the form:

$$\Delta H_{\text{rxn}} = \sum_i^{\text{No. of Products}} n_i \int_{T_0}^{T_{\text{ad}}} C_{pi} dT - \sum_j^{\text{No. of Reactants}} n_j \int_{T_0}^{T_{\text{ad}}} C_{pj} dT ,$$

where ΔH_{rxn} is the enthalpy of reaction for the entire reaction; C_{pi} is the molar heat capacity of product species i ; C_{pj} is the molar heat capacity of the reactant species j ; n_i is the number of moles of product species i in the reaction volume; and n_j is the number of moles of reactant species. This equation assumes that the product undergoes no phase transformation over this temperature range.

If complete conversion is assumed, n_j for all reactants becomes zero, and n_i for all products becomes one. This provides an upper limit for the adiabatic reaction temperature (T_{ad}), since the reactions of interest are generally exothermal over the entire range of temperatures. Regardless, any heat lost to the surroundings is ignored.

Two difficulties encountered in applying these equations in the SPC reaction analyses are the lack and questionable reliability of heat capacity data over temperature ranges of interest and reconciliation of the value of the initial temperature (T_0) and T_{ad} with existing data. Energy put into the system during the initial preheat and ignition stage of the experiments also must be taken into account.

In addressing the first problem, heat capacity data were found for the reaction constituents of interest over the required temperature ranges. The reliability of these data is uncertain, but agreement among the various sources consulted generally has been good.

The second problem can be addressed by measuring or estimating the amount of thermal energy entering the system. One approach is to assume that no reaction occurs until the local temperature (temperature at the filament or external heat source) reaches a threshold reaction temperature, at which time the source of energy is assumed to be ceased and an adiabatic condition is imposed. This essentially involves modeling the thermal driving source. In SPC's approximations of T_{ad} , the approach used assumes that only an insignificant amount of external heat is added and that T_0 is 298°K. This might be the case, where a hot filament is suddenly brought into contact with a compact or where a very fast initiation reaction (e.g., thermite) occurs. In effect, the reaction occurs at the initial system temperature of 298°K and releases a quantity of thermal energy equivalent to the enthalpy of the reaction. The reaction vessel contents (100 percent product) are warmed until all of the available energy is absorbed. This methodology appears reasonable, since enthalpy is a state function and is, therefore, independent of path.

2. Equilibrium Conversion

Equilibrium conversion represents the fraction of a given mole of a particular reactant that is converted into a product. It occurs when the chemical potential of the product is in equilibrium with that of the reactants, taking into account the existence of phases. It is also a function of temperature and pressure (since chemical potential is a function of

these two variables in addition to composition) that is related to conversion by the heat of reaction. Equilibrium conversion is determined by calculating the conditions at which the change in chemical potential is zero--neither the forward nor the reverse reaction is spontaneous.

Reaction spontaneity, equilibrium conversion, and adiabatic reaction temperature are brought to bear in this study by using available thermodynamic data to describe the reaction phenomenon in conjunction with phase transformation data. A macroscopic, zero-dimensional analysis in which system spontaneity, adiabatic reaction temperature, equilibrium conversion, and other macroscopic quantities are estimated has been considered first.

3. Thermal Energy Transport

The local availability of thermal energy is a vital concern in gasless combustion processes. Phase and phase interface conditions, mass diffusivity, reaction spontaneity, equilibrium conversion, and kinetics are all temperature-dependent. Therefore, energy transport within the reaction system should be understood as well as is possible given the available information.

The driving force for thermal energy transport is a temperature gradient. This fundamental principle is expressed as a linear function by Fourier's law of heat conduction:

$$\bar{q} = -\nabla (kT) ,$$

where $\bar{q}$ is the thermal flux (a vector), T is the temperature, and k is the thermal conductivity (a proportionality constant).⁵ The thermal conductivity

⁵Thermal conductivity (k) is expressed in a different form by some authors who prefer thermal diffusivity (α) where:

$$\alpha = \frac{k}{\rho \bar{C}_p} , \text{ when}$$

ρ = density and $\bar{C}_p$ = specific heat at constant pressure.

of a substance is a function of its composition, phase, and temperature. Note that k generally is assumed to be an isotropic quantity (i.e., k is assumed to have the same value for all three spatial directions). This assumption is valid for fluids and for most homogeneous solids; however, some solids, including single noncubic crystals, and many heterogeneous systems are nonisotropic [Ref. 84].

For a given pure solid substance, thermal conductivity is a function of temperature and possibly the solid crystalline phase. If the solid is porous, thermal conductivity is also strongly dependent on void fraction, pore size, fluids adsorbed on pore walls or occupying the pores, and thermal radiation. Since these quantities are difficult to measure and predict with accuracy, thermal conductivity data are determined empirically. In some cases, thermal conductivity data for pure metals can be estimated from electrical conductivity data since, for pure metals, conduction electrons are the principal carriers of the thermal energy transferred.

4. Lewis Number

The Lewis number is defined as:

$$Le = \frac{\alpha}{D} = \frac{k}{\rho C_p D} ,$$

and represents the relative rates of thermal and mass diffusion [Ref. 85] (e.g., values greater than one indicate that thermal energy diffuses faster than mass). If Le is very large ($Le \gg 1$), thermal diffusion is essentially instantaneous relative to mass diffusion, and only the latter need be considered, since it is the limiting step. The converse is true for $Le \ll 1$.

Although thermal conductivity data are available over a broad range of temperatures, mass diffusivity is lacking and difficult to obtain. Some data have been found, and several correlations may be useful for estimating values over selected temperature ranges. Regardless, the availability of mass diffusivity data may be problematic.

D. PHYSICAL AND CHEMICAL SYNTHESIS DATA

Based on the review of Soviet reaction models and the subsequent SPC investigation, the following types of data are anticipated to be of importance in describing reaction phenomenology:

- Thermodynamic data
 - heat capacity
 - enthalpy
 - entropy
 - enthalpy of phase transformations
- Physical data
 - phase transformation temperatures
 - vapor pressure
 - solubility
- Chemical kinetic data
 - thermal diffusivity
 - mass diffusivity
 - rate of reaction.

The data search was not a full-scale literature review. It was concentrated on readily available handbooks and tabulations, found mostly in U.S. and U.S.S.R. technical literature. As anticipated, some data were not readily available for specific materials of interest in the reactions that were investigated.

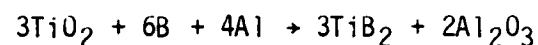
Of principal concern in collection of reaction data are the phase conditions, reaction zones, mass distributions, etc. These quantities dictate the form of applicable models, their boundary conditions, and their ranges of validity. Data were sought to help define these parameters over the temperature ranges of interest for the following five reactions:

- Aluminum Nitride
 $2\text{Al}_{(s)} + \text{N}_{2(g)} \rightarrow 2\text{AlN}_{(s)}$
- Titanium Carbide (elemental)
 $\text{Ti}_{(s)} + \text{C}_{(\text{graphite},s)} \rightarrow \text{TiC}_{(s)}$
- Titanium Carbide (oxide)
 $3\text{TiO}_{2(s)} + 3\text{C}_{(\text{graphite},s)} + 4\text{Al}_{(s)} \rightarrow 3\text{TiC}_{(s)} + 2\text{Al}_2\text{O}_{3(s)}$

- Titanium Diboride (elemental)



- Titanium Diboride (oxide)



In the first, second, and fourth reactions, products are formed from elemental metallic constituents. In the third and fifth reactions, products are formed from oxides (in the manner described in IV.C regarding synthesis of cast products). In regard to the production of cast products from oxides, the synthesis processing may be more complex, but the raw materials costs are expected to be lower since elemental metallic powders often cost considerably more than the oxide forms.

To describe combustion mechanics for the reactions above, data are required for the following reaction constituents and products:

- | | | | |
|----------------------------------|---------------------------------|------------------|--------------------|
| • Al | • B | • C | • Ti |
| • AlN | • B ₂ O ₃ | • N ₂ | • TiB ₂ |
| • Al ₂ O ₃ | | | • TiC |
| | | | • TiO ₂ |

Generally, data were not available for the preferred forms of B and C. Although our preference was data on amorphous carbon or lampblack and amorphous boron, data were located readily only for graphite and crystalline boron. In addition, differences were encountered in data--especially in regard to AlN, B, and C--and evaluation of the relative quality of those sets of data was not possible. Purities of commercially available material also vary widely and will introduce uncertainty in analytical studies. In regard to that difficulty, the assumptions used in SPC investigations are presented later.

Sources for tabulations of chemical thermodynamic data were previously referenced in an SPC document [Ref. 2] and for that reason are not repeated in toto in the list of references at the end of this report. Many of the data used for the current investigation were obtained from a metals handbook [Ref. 86] and a group of thermochemical tables [Ref. 87], although other references also have been informative [Refs. 88 and 89]. Selected

data from Reference 86 that were useful in studies of specific synthesis reactions (Sections E through I of this chapter) are presented in Appendix C.

Since temperatures of the five reactions studied vary over a considerable range, phase changes and variations in specific heat of the reacting species must be considered in calculating adiabatic reaction temperatures, reaction energies, etc. Accordingly, some basic data have been calculated and plotted for the 11 reactants and products listed above. Results of these calculations are presented in Appendix D. Figures D-1 through D-11 represent graphs of specific heat (C_p) versus temperature (T) data that were taken originally from tables in Reference 87. Each figure contains the phases of the species, the modeled C_p versus T equations for each phase, and the curves that were generated from those equations.

Those specific heat equations, combined with latent heat data, also were used to develop equations for calculating enthalpy, entropy, and Gibbs free energy of the reacting and product species over broad ranges of temperature. The data calculated with those equations also are presented in Appendix D as Tables D-1 through D-11.

Each of the five reactions identified previously was analyzed using the calculated data to predict combustion behavior of the reaction systems. Thermodynamic analyses were conducted to determine reaction spontaneity, overall heat of reaction, adiabatic reaction temperatures, and phases for each reaction. Reaction phenomenology also was addressed to analyze phase conditions and the roles of diffusion, adsorption, etc., for each system as it is ignited and combusts.

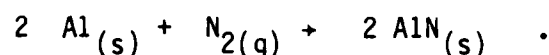
Approximate descriptions of the phases and phase interfaces that exist over the course of reactions were based on specific heat and latent heat data. Where available, solubility and kinetic reaction rate data have been analyzed to estimate mass distribution within the given system. From these estimates, gross indicators, such as mass diffusivity, thermal diffusivity, and Lewis number, have been addressed to determine at which stages and locations reaction is likely to occur.

The format used in presenting the succeeding discussions and findings for each reaction follows:

- General considerations; reactants, products, initial conditions.
- Thermodynamic analysis; spontaneous reaction temperature, adiabatic reaction temperature, heat of reaction, equilibrium conversion, phases.
- Reaction phenomenology; step-by-step analysis of the system environment, phase conditions, etc.

E. SYNTHESIS OF ALUMINUM NITRIDE

The first reaction considered involves the production of aluminum nitride from elemental aluminum metal and nitrogen gas as written below:



The initial charge for this reaction is assumed to be high-purity aluminum metal particles (powder) and pure nitrogen gas. Unless stringent measures are taken, the aluminum particles will have a chemisorbed oxide layer about 5 nm thick on all surfaces exposed to air; this may affect the reaction mechanics, for example, by limiting diffusion of aluminum or nitrogen or by impeding thermal transport. Aluminum nitride particles also may be included to dilute the reaction mixture and to provide nucleation sites for crystalline growth of product phase.

1. Thermodynamic Analysis

The Gibbs free energy or chemical potential data for the reaction are provided in Table 10. These data indicate that the forward reaction is thermodynamically favored even at low temperatures, but the reverse reaction is favored at temperatures above approximately 3,100°K. Since enthalpy ultimately decreases, and the Gibbs free energy monotonically increases as the temperature increases, these data suggest that this reaction becomes entropy dominated at temperatures above 3,100°K. Heat introduced externally or from adjacent zones of reaction enthalpy may

TABLE 10.
FREE ENERGY VALUES FOR
SYNTHESIS OF ALUMINUM NITRIDE

Adiabatic Reaction Temperature = 2,790°K
Aluminum Nitride Phase: 67% Solid, 33% Dissociated Gases

<u>T (°K)</u>	<u>Enthalpy^(a)</u>	<u>Gibbs^(b)</u>
300.00	-152000.00	-137100.00
400.00	-152400.00	-137200.00
500.00	-152700.00	-132100.00
600.00	-152900.00	-127000.00
700.00	-153000.00	-121800.00
800.00	-152500.00	-116800.00
900.00	-152500.00	-111700.00
1000.00	-157500.00	-106900.00
1100.00	-157500.00	-101200.00
1200.00	-157400.00	-95600.00
1300.00	-157300.00	-89980.00
1400.00	-157300.00	-84370.00
1500.00	-157200.00	-78760.00
1600.00	-157200.00	-73160.00
1700.00	-157100.00	-67550.00
1800.00	-157200.00	-61980.00
1900.00	-157200.00	-56370.00
2000.00	-157100.00	-50770.00
2100.00	-157100.00	-45170.00
2200.00	-157100.00	-39580.00
2300.00	-157000.00	-33980.00
2400.00	-157000.00	-28390.00
2500.00	-156900.00	-22790.00
2600.00	-156900.00	-17200.00
2700.00	-156900.00	-11610.00
2800.00	-165.40	-17.95
2900.00	-800.70	-23.44
3000.00	-1438.00	-6.61
3100.00	-2078.00	32.43
3200.00	-2721.00	92.54
3300.00	-3366.00	173.40
3400.00	-4013.00	274.50
3500.00	-4662.00	395.00

(a) Calories.

(b) Calories per °K.

increase the final product temperature but will not contribute to further conversion. Although these thermodynamics dictate spontaneity, nothing is implied about kinetics; therefore, the discussion of spontaneous reaction temperature is not conclusive.

Gibbs free energy at a constant temperature is given by the expression:

$$\Delta G = \Delta H - T\Delta S$$

Since ΔH is less than zero over the entire temperature range of interest, and temperature is always positive, the term ΔS must be less than zero for positive values of ΔG . Thus, the highly ordered solid-phase aluminum nitride product has lower entropy than the fluid-phase reactants--particularly nitrogen, which has a large entropy.

The adiabatic reaction temperature of 2,790°K may be calculated from the enthalpy of the constituents of this reaction (using data from Ref. 87) as described in Reference 76. The heat of reaction in this case is 1,850 cal/g.

2. Reaction Phenomenology

Phase data for the pure constituents of the reaction are shown in Figure 9 and Table 11. The first temperature range of interest extends from 298°K to 933°K. At 298°K, aluminum is a solid, and nitrogen is a gas. If any aluminum nitride is added to the initial charge, it will be in solid phase. Given this initial configuration, it is expected that aluminum will diffuse by solid-state molecular diffusion through any oxide layer, as shown in Figure 10. Similarly, nitrogen gas molecules will be expected to diffuse into the oxide layer. However, nitrogen gas first may be adsorbed to the oxide surface and subsequently diffuse inward, as the adsorbed surface concentration builds, enhancing the concentration gradient that serves as the driving force for diffusion. Depending on the relative rate and intensity of each of these processes and on the reactivity of aluminum and nitrogen under these conditions and this temperature range,

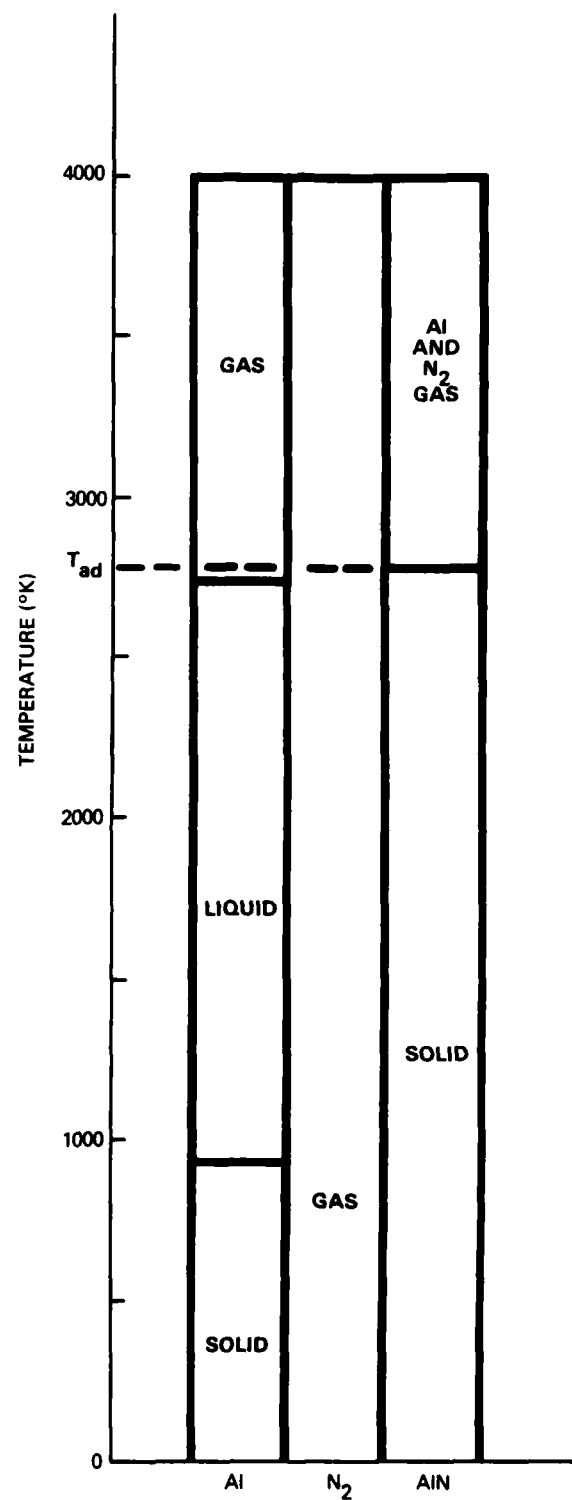
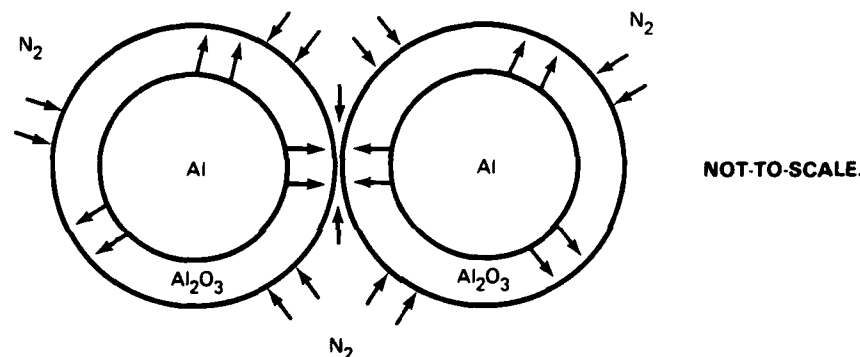


FIGURE 9.
PHASE DATA FOR ALUMINUM NITRIDE REACTION

TABLE 11.
PHASE DATA FOR PURE CONSTITUENTS
IN SYNTHESIS OF ALUMINUM NITRIDE

T (°K)	Al	N ₂	AlN	Al ₂ O ₃
298 < T < 933 T = 933	s s ~ l	g g	s s	s s
933 < T < 2,315 T = 2,315	l l	g g	s s	s s ~ l
2,315 < T < 2,790 T = 2,790	l l ~ g	g g	s decomposes	l l
2,793 < T < 3,253 T = 3,253	g g	g g	-- --	l decomposes



- Al DIFFUSES OUTWARD THROUGH Al₂O₃ LAYER
- N₂ ADSORBS TO Al₂O₃ SURFACE AND DIFFUSES INWARD

FIGURE 10.
DIFFUSION OF ALUMINUM AND NITROGEN

the reaction producing aluminum nitride can occur at a number of locations and points in time. If the aluminum is in a pure nitrogen gas environment, nitrogen gas will be adsorbed to the surfaces of the particles and will fill the pores in the particles. If the reaction does not take place in a pure nitrogen gas environment, nitrogen molecules will compete for adsorption sites with gaseous contaminants, as can be estimated by adsorption thermodynamics.

As nitrogen gas molecules encounter the aluminum or aluminum oxide surface, some will be adsorbed. A portion of these adsorbed nitrogen molecules may diffuse through the oxide layer to react with aluminum atoms and form solid aluminum nitride; the remainder will remain intact as adsorbed nitrogen molecules. The conversion will create a new adsorption site, but the substrate will be aluminum nitride rather than aluminum. Thus, newly adsorbed nitrogen must diffuse through an inert product layer in addition to the oxide layer before additional reaction can occur, unless adjacent sites of aluminum substrate are available.

As adsorption of gas molecules into the metallic particle surfaces takes place, a concentration gradient is established between the surface and the interior of the particle, which creates a driving force for mass diffusion into the particle. As gaseous constituents diffuse into the solid particle, a solid solution is formed (assuming no significant extraneous behavior is experienced, e.g., bond breaking), which alters the melting and vaporization temperatures. Therefore, the phase data shown in Figure 9 are only approximations of phase conditions in the reactions.

Where unreacted nitrogen is adsorbed to the aluminum substrate surface, and free nitrogen diffuses into the solid, new nitrogen gas molecules will be adsorbed in vacant sites, and gaseous nitrogen molecules from the bulk gas phase may diffuse into the adsorbed nitrogen film that exists on the surface.

The second temperature range of interest lies between 933°K and 2,315°K. At approximately 933°K, the aluminum particles melt. While the melting temperature of Al_2O_3 is 2,318°K (which suggests that the liquid aluminum contained in the Al_2O_3 shell might not be able to escape), the shell likely will break up into small Al_2O_3 particles because of defects in the shell layer, its shallow depth (about 5 nm), and the mechanical forces of thermal volume expansion as the temperature rises. The volume expansion of aluminum upon melting is 6.5 percent. Thus it is expected that free liquid aluminum will be present in the system.

Molten aluminum is relatively viscous near its melting temperature. (Viscosity of aluminum is between 1.0 and 1.2 centipoises (CP) from 973 to 1,023°K, that of water at 25°C is about 0.9 CP, and that of mercury at 25°C is about 1.6 CP.) Therefore, since nitrogen gas fills the interstices between the particles, some gas will be trapped as the particles liquefy. The gas bubbles thus entrapped in this viscous liquid metal will create surfaces at which reaction may occur. In addition, the gas-liquid interface at the bulk-gas/bulk-liquid phase interface will provide a reaction surface. At each of the liquid aluminum/nitrogen gas interfaces, nitrogen will diffuse into the liquid by molecular diffusion. The flow of nitrogen into the aluminum is dependent on the concentration of nitrogen in the gas phase and the mass diffusivity of nitrogen in liquid aluminum. Both of these quantities are dependent on temperature.

As the temperature is raised beyond the melting temperature of aluminum, the entrapped gas may expand and buoy to the bulk surface. The increased temperature will increase the volume of the entrapped gas, increasing its surface area and decreasing its density or concentration. Archimedes' principle may be used to obtain an approximation of the buoyant force of these entrapped nitrogen bubbles⁶. For nitrogen bubbles ranging in size from 1 to 10 microns, buoyant forces vary from a minimum of 10^{-9} dynes to a maximum of 10^{-6} . Since the Reynolds numbers for the bubbles are much less than 1, Stokes' law of creeping motion may be involved to calculate bubble velocities:

$$^6 \rho_{Al} = 2.646 - 0.28 \times 10^{-4}T \text{ gm/cm}^3 \quad T(^{\circ}\text{K}) \text{ [Ref. 86]}$$

$$\rho_{N_2} = P/RT = (1/82.05)T^{-1} \text{ gm/cm}^3 \quad T(^{\circ}\text{K})$$

$$\text{Force} = (\rho_{Al} - \rho_{N_2})gv$$

$$= [(2.646 - 0.28 \times 10^{-4}T) - (1.219 \times 10^{-2}T^{-1})] (980.7) [(4/3)\pi r^3]$$

For a 10-micron bubble at 1,000°K, $F = \sim 10^{-6}$ dynes.

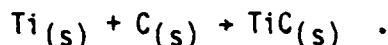
$$C_D = \frac{24}{Re_D} = \frac{F_D}{1/2 \rho U^2 A_p}, \text{ and}$$

$$Re_D = \frac{\rho U D}{\mu},$$

where combining these two equations yields velocities of 14.2 cm/s and 1.4 cm/s for the 10-micron and 1-micron bubbles, respectively. This suggests that the principal source of nitrogen reactant will be dissolved nitrogen, and the solubility of nitrogen in liquid aluminum merits consideration.

F. SYNTHESIS OF TITANIUM CARBIDE (ELEMENTAL)

The elemental reaction producing titanium carbide is presumed to be the following:



Lampblack has been used in Soviet experimental work associated with this study. Since physical data for lampblack were not found readily, data for graphite were substituted. The error introduced by this substitution is unknown, since the absence of lampblack data leaves no basis for comparison. The initial charge is presumed to be pure titanium powder and pure carbon powder.

1. Thermodynamic Analysis

The Gibbs free energy for the reaction is presented in Table 12. Based on available data, the forward reaction is spontaneous at and above the standard temperature for 1 atm of pressure. Thus kinetics will be of primary importance. Based on the heat capacity data [Refs. 76 and 87], the adiabatic reaction temperature is 3,290°K, which is also the melting temperature of titanium carbide. This is in agreement with Soviet estimates, which report that 33 percent of the TiC product is in liquid phase as compared to 24 percent as calculated in this study [Ref. 87]. Based on the same heat capacity data, the heat of reaction for this system is approximately 730 cal/g.

TABLE 12.

FREE ENERGY VALUES FOR SYNTHESIS OF
TITANIUM CARBIDE (FROM ELEMENTAL FORMS)

Adiabatic Reaction Temperature = 3,290°K
Titanium Carbide Phase = 76% Solid, 24% Liquid

<u>T (°K)</u>	<u>Enthalpy (a)</u>	<u>Gibbs (a)</u>
300.00	-44010.00	-43160.00
400.00	-44010.00	-42880.00
500.00	-43990.00	-42600.00
600.00	-43930.00	-42320.00
700.00	-43850.00	-42060.00
800.00	-43780.00	-41810.00
900.00	-43720.00	-41570.00
1000.00	-43700.00	-41330.00
1100.00	-43930.00	-41050.00
1200.00	-44960.00	-40710.00
1300.00	-44930.00	-40360.00
1400.00	-44900.00	-40010.00
1500.00	-44890.00	-39660.00
1600.00	-44880.00	-39320.00
1700.00	-44960.00	-39030.00
1800.00	-44960.00	-38680.00
1900.00	-44960.00	-38330.00
2000.00	-49360.00	-37860.00
2100.00	-49340.00	-37290.00
2200.00	-49290.00	-36710.00
2300.00	-49230.00	-36140.00
2400.00	-49140.00	-35580.00
2500.00	-49030.00	-35020.00
2600.00	-46900.00	-34460.00
2700.00	-48750.00	-33910.00
2800.00	-48570.00	-33360.00
2900.00	-48380.00	-32820.00
3000.00	-48170.00	-32290.00
3100.00	-47930.00	-31760.00
3200.00	-47670.00	-31240.00
3300.00	-30850.00	-30470.00
3400.00	-30810.00	-30460.00
3500.00	-30770.00	-30450.00

(a) Calories.

(b) Calories per °K.

2. Reaction Phenomenology

Gasless combustion theory appears to approximate the mechanics of the reaction fairly closely. Both reactants are solids over the range from 298°K to approximately 1,933°K, as shown in Table 13 and Figure 11 (right side of chart). All three constituents continue to be in condensed states through the adiabatic reaction temperature of 3,290°K; carbon as a solid, titanium as a liquid, and titanium carbide as a solid. Some minimal gas phase is expected to exist in equilibrium with the condensed phases, particularly at the temperatures considered here.

Over the temperature range from 298°K to 1,933°K, the cold reactant compact and regions of interstitial surfaces are presumably in contact with a low-density gas phase. The interstitial surfaces may contain adsorbed gases unless the reaction vessel is evacuated or maintained in an inert gas environment. Given this system, reaction may occur in one or more of the following zones:

- In the gas phase of the interstices
- At or near one of the solid-gas interfaces on an interstitial surface
- In the regions of solid-solid contact.

TABLE 13.
PHASE INFORMATION FOR SYNTHESIS OF
TITANIUM CARBIDE WITH ELEMENTAL FORMS

<u>T(°K)</u>	<u>Ti</u>	<u>C</u>	<u>TiC</u>
298 - 1,155	s _α	s	s
1,155	s _α ~ s _β	s	s
1,155 - 1,933	s _β	s	s
1,933	s _β ~ l	s	s
1,933 - 3,290	l	s	s
3,290	l	s	s ~ l
3,290 - 3,591	l	s	l
3,591	l ~ g	s	l

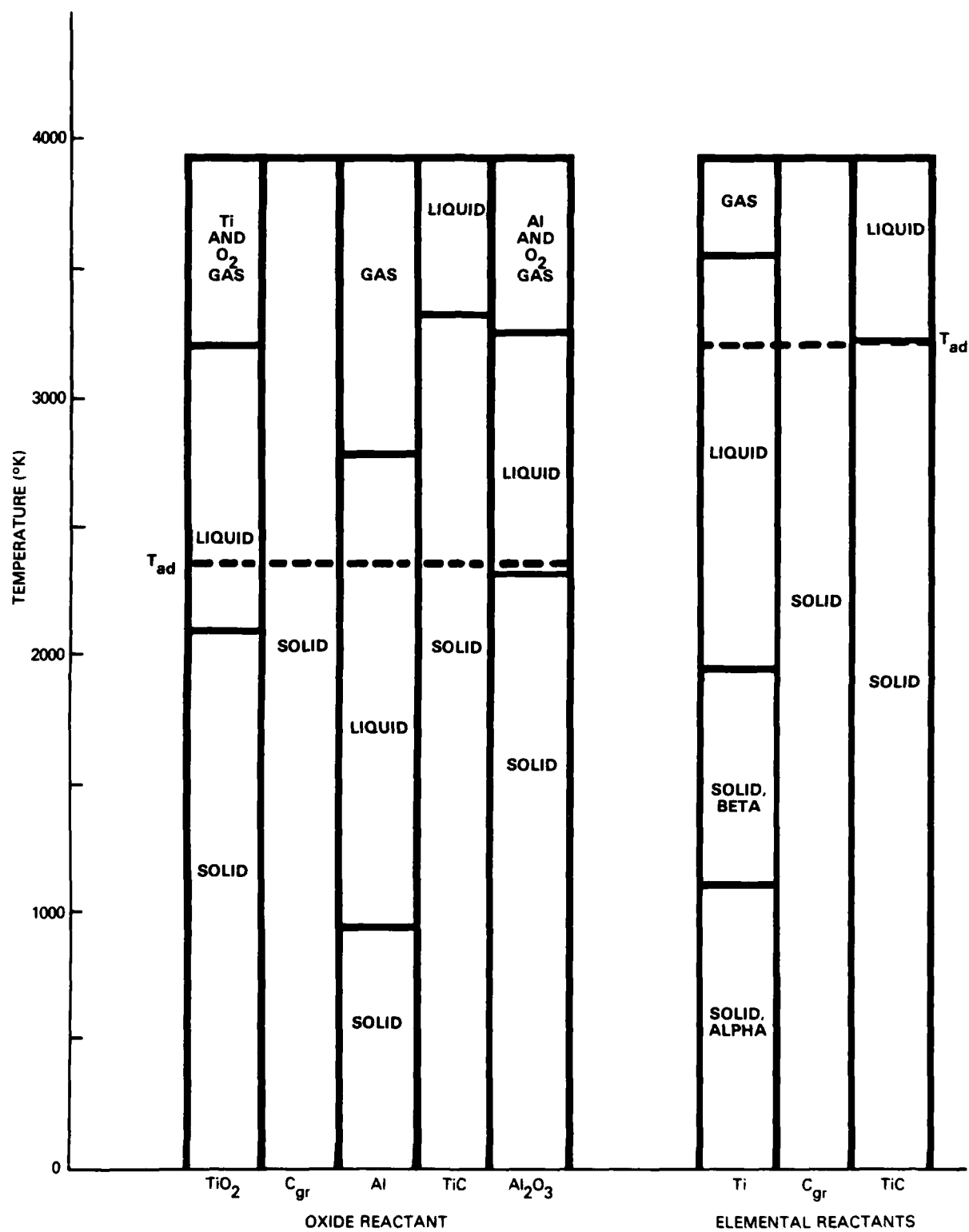


FIGURE 11.
PHASE DATA FOR TITANIUM CARBIDE REACTIONS

The transfer of mass and energy to, from, and through each of these zones must be considered in order to assess the likelihood of a significant reaction taking place there. This consideration can involve many factors, including:

- Vapor pressure, sublimation energy, surface tension
- Diffusivities of constituents in solid, liquid, and gas phases
- Adsorption data, surface energy.

Mass transport phenomena where the solid surfaces are not in contact or in close proximity are based on the need for the reactants to leave the bulk-solid phase and enter the gas phase. From there, they may diffuse to another solid reactant particle, adsorb to this reactant particle, and react at this adsorption site or diffuse into the particle until reaction occurs, or reaction may take place in the gas phase. In either case, these events are likely to be limited by the first step--reactant molecules from the bulk-solid phase converting into the gas phase. Indicators of the resistance of sublimation are provided by the equilibrium vapor pressure, sublimation energy, and surface tension.

Regardless of whether or not a gas phase is a dominant feature of the reaction, diffusion may be important at or near regions of solid-solid particle contact. On a microscopic scale, the surfaces of the solid reactants are far from smooth. However, points or surfaces of solid-solid contact will exist. At these points of contact, mass transfer of a Reactant A into a Mass B and B into Mass A will occur by solid-phase molecular diffusion. These diffusion rates will be controlled by the respective concentration gradients and diffusivities. If reaction occurs, molecular diffusion of each of the reactant molecules (metal atoms, in this case) through the product layer thus formed must be taken into account.

In regions of close proximity to contact regions, depletion of reactant molecules and decreases in density or concentration in the contact region, possibly brought about by temperature increases for exothermal reactions and interdiffusion of foreign product and reactant molecules, will cause molecules from the solid-bulk phase to migrate to the contact region. In addition, bulk-phase reactants in close proximity to contact

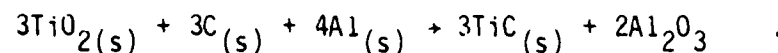
regions that enter the gas phase have only a short distance to diffuse through the gas phase before contacting the adjacent particle surface, where they may be adsorbed. If this distance is on the order of the mean free path of a gas-phase molecule, barriers to mass diffusion may be minimal and probably will be controlled by the rate of sublimation. The equilibrium vapor pressure of a condensed-phase constituent provides a measure of the concentration of gas-phase reactant that exists in dynamic equilibrium with it and represents a means to calculate the concentration of a constituent over a condensed-phase/gas-phase interface.

As temperature approaches the melting temperature of pure titanium, the titanium particles presumably will exist as solid solutions with titanium solvent and carbon solute, and vice versa. If other constituents are present (such as gases in an open or unevacuated system or adsorbed gases other than carbon), they also may exist in the particles as solutes in a multicomponent solution. The presence of solute molecules will alter the melting point of the titanium particles to some extent; however, data on melting point depression for titanium were not available for this study. So long as the titanium particles melt before substantial reaction occurs, this melting point alteration is unlikely to be of major importance. However, if reaction occurs largely during this transition, it may be important to know the temperature at which it occurs.

After the titanium particles have melted, the carbon particles will be surrounded by titanium liquid. From this point to the vaporization temperature of titanium (an interval of approximately 1,600K°), classical models for reacting spherical particles appear to be appropriate.

G. SYNTHESIS OF TITANIUM CARBIDE (OXIDE)

This reaction involves production of titanium carbide from the oxide form, as shown by the following empirical formula:



Aluminum powder is added as a reducing agent and appears in the reaction product as a liquid slag.

The initial charge is assumed to contain essentially pure titanium dioxide powder, carbon powder, and aluminum powder. The charge is well mixed before heating. As before, data on lampblack were unavailable for this study, and the solid carbon is assumed to be graphite. The uncertainty introduced by this substitution again is unknown.

1. Thermodynamic Analysis

Values for the change in Gibbs free energy for this reaction are provided in Table 14. These data indicate that the forward reaction is thermodynamically favored from room temperature to the adiabatic reaction temperature.

The adiabatic reaction temperature as calculated from heat capacity data from Reference 87 is 2,317°K. A value for T_{ad} from Soviet researchers in this area was not provided for this reaction [Ref.76]. The heat of reaction for the empirical equation given above is 665 cal/g.

2. Reaction Phenomenology

All three reactants are initially solid phase, as shown in Table 15 and Figure 11 (left side of chart). Upon heating to approximately 933°K, the aluminum particles melt. If stoichiometric amounts of reactants are used, liquid aluminum constitutes about 40 percent of the reaction volume at 933°K and about 43 percent at 2,100°K. Thus, the system will consist of solid particles of titanium dioxide and carbon surrounded by liquid aluminum over the temperature range from approximately 933°K to 2,100°K.

Several mechanisms of mass transfer and reaction are possible while the reaction system is in this temperature range:

- The surfaces of the particles may be such that they are not wetted by the liquid phase, and no diffusion or reaction occurs.
- Carbon may dissolve into the liquid phase and diffuse to the titanium dioxide particle surface.

TABLE 14.
FREE ENERGY VALUES FOR
SYNTHESIS OF TITANIUM CARBIDE (FROM AN OXIDE)

Adiabatic Reaction Temperature = 2,317°K

Titanium Carbide Phase: 100% Solid

Aluminum Oxide Phase: 100% Liquid

<u>T (°K)</u>	<u>Enthalpy(a)</u>	<u>Gibbs(b)</u>
300.00	-255500.00	-247900.00
400.00	-255900.00	-245300.00
500.00	-256100.00	-242600.00
600.00	-256500.00	-239900.00
700.00	-256500.00	-237100.00
800.00	-256500.00	-234300.00
900.00	-256600.00	-231500.00
1000.00	-266700.00	-228200.00
1100.00	-267500.00	-224200.00
1200.00	-267600.00	-220200.00
1300.00	-267700.00	-216300.00
1400.00	-267800.00	-212300.00
1500.00	-267900.00	-208400.00
1600.00	-266700.00	-205400.00
1700.00	-266800.00	-201600.00
1800.00	-266600.00	-198000.00
1900.00	-266400.00	-194200.00
2000.00	-266200.00	-190400.00
2100.00	-265900.00	-186600.00
2200.00	-314200.00	-180700.00
2300.00	-313900.00	-174700.00
2400.00	-258300.00	-170400.00
2500.00	-257800.00	-166700.00
2600.00	-257300.00	-163100.00
2700.00	-256700.00	-159500.00
2800.00	-533700.00	-152500.00
2900.00	-532000.00	-139000.00
3000.00	-530200.00	-125400.00
3100.00	-528300.00	-112000.00
3200.00	-526400.00	-98470.00
3300.00	-92700.00	189400.00
3400.00	-92410.00	198000.00
3500.00	-92160.00	206500.00

(a) Calories.

(b) Calories per °K.

- Titanium dioxide may dissolve into the liquid phase and diffuse to the carbon particle surface.
- Carbon and titanium dioxide may dissolve into the liquid phase and interdiffuse. They may react in the liquid phase, at one or both particle surfaces, or they may not react at all. Also, they may diffuse to the surface of a particle where they adsorb to the surface, diffuse in, and react internally.
- Titanium dioxide may undergo electrochemical reaction with the liquid aluminum solvent.

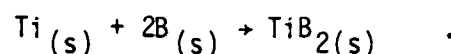
TABLE 15.
PHASE DATA FOR SYNTHESIS OF
TITANIUM CARBIDE WITH AN OXIDE

<u>T(°K)</u>	<u>TiO₂</u>	<u>C</u>	<u>Al</u>	<u>TiC</u>	<u>Al₂O₃</u>
298 - 933	s	s	s	s	s
933	s	s	s ↔ l	s	s
933 - 2,143	s	s	l	s	s
2,143	s ↔ l	s	l	s	s
2,143 - 2,315	l	s	l	s	s
2,315	l	s	l	s	s ↔ l
2,315 - 2,767	l	s	l	s	l
2,767	l	s	l ↔ g	s	l
2,767 - 3,200	l	s	g	s	l
3,200	decomposes	s	g	s	l
3,200 - 3,253	$\frac{\text{Ti(g)}}{\text{O}_2\text{(g)}}$	s	g	s	l
3,253	$\frac{\text{Ti(g)}}{\text{O}_2\text{(g)}}$	s	g	s	decomposes

The likelihood of the last mechanism above can be assessed by calculating the electrochemical potential for this reaction, while an indication of the likelihood of the other mechanisms could be investigated by estimating the solubility of carbon and titanium dioxide in liquid aluminum over the stated temperature range.

H. SYNTHESIS OF TITANIUM DIBORIDE (ELEMENTAL)

This is an elemental reaction producing titanium diboride, as shown by the formula below:



The initial charge consists of stoichiometric amounts of titanium and boron powders. Crystalline boron is assumed, since data are available for this form.

1. Thermodynamic Analysis

The change in Gibbs free energy as a function of temperature is shown in Table 16. These data indicate that the forward reaction is thermodynamically favored at room temperature and above.

The adiabatic reaction temperature, as calculated from available data, is 3,193°K [Ref. 87]. This value is in agreement with Soviet estimates [Ref. 76]. It occurs at the melting temperature of titanium diboride. The heat of reaction for the empirical formula is 960 cal/g.

2. Reaction Phenomenology

Both reactants are solid powders at 298°K and 1 atm of pressure, as indicated in Table 17 and Figure 12 (left side of chart). When the reactants are heated to the vicinity of 1,933°K, the titanium particles begin to melt. When completely melted, titanium will constitute 57 percent of the reaction volume at 1,950°K and 59 percent at 2,450°K.

The findings of this study are relatively uncertain for temperatures above about 2,450°K, primarily because of conflicting data for boron. Conflicting values have been found in reported data for crystalline boron, and no data were readily found for the preferred amorphous form. The U.S. National Bureau of Standards [Ref. 87] reports that boron melts at 2,450°K and vaporizes at 3,931°K, while in Reference 85, values are given for melting at

TABLE 16.

FREE ENERGY VALUES FOR SYNTHESIS OF
TITANIUM DIBORIDE (FROM ELEMENTAL FORMS)

Adiabatic Reaction Temperature = 3,193°K

Titanium Diboride Phase: 28% liquid, 72% solid

<u>T (°K)</u>	<u>Enthalphy^(a)</u>	<u>Gibbs^(b)</u>
300.00	-66880.00	-65060.00
400.00	-66870.00	-64460.00
500.00	-66950.00	-63850.00
600.00	-67080.00	-63220.00
700.00	-67230.00	-62570.00
800.00	-67390.00	-61890.00
900.00	-67560.00	-61190.00
1000.00	-67850.00	-62920.00
1100.00	-68020.00	-62420.00
1200.00	-69120.00	-61830.00
1300.00	-69140.00	-61230.00
1400.00	-69150.00	-60620.00
1500.00	-69150.00	-60010.00
1600.00	-69150.00	-59400.00
1700.00	-69150.00	-58790.00
1800.00	-69220.00	-58160.00
1900.00	-69220.00	-57540.00
2000.00	-73610.00	-56810.00
2100.00	-73580.00	-55970.00
2200.00	-73520.00	-55130.00
2300.00	-73460.00	-54300.00
2400.00	-73380.00	-53470.00
2500.00	-84080.00	-52430.00
2600.00	-83970.00	-51170.00
2700.00	-83850.00	-49910.00
2800.00	-83720.00	-48660.00
2900.00	-83580.00	-47410.00
3000.00	-83440.00	-46160.00
3100.00	-83310.00	-44920.00
3200.00	-58990.00	-45180.00
3300.00	-58700.00	-44760.00
3400.00	-58410.00	-44340.00
3500.00	-58120.00	-43930.00

(a) Calories.

(b) Calories per °K.

TABLE 17.
PHASE DATA FOR SYNTHESIS OF
TITANIUM DIBORIDE WITH ELEMENTAL FORMS

<u>T (°K)</u>	<u>Ti</u>	<u>B</u>	<u>TiB₂</u>
298 - 1,155	s _α ~ s _β	s	s
1,155 - 1,940	s _α ~ s _β	s	s
1,933	s _β ~ l	s	s
1,933 - 2,450	l	s	s
2,450	l	s ~ l	s
2,450 - 3,193	l	l	s
3,193	l	l	s ~ l
3,193 - 3,591	l	l	l
3,591	l ~ g	l	l
3,591 - 3,931	g	l	l
3,931	g	l ~ g	l
3,931 - 4,250	g	g	l
4,250	g	g	decomposes

2,573°K and vaporizing at 2,823°K.⁷ Values from Reference 89 have been used arbitrarily because heat capacity data are provided for high temperatures. Presumably, boron will melt between 2,450°K and 2,573°K. At this point, the miscibility or solubility of titanium and boron must be determined.

The vapor in equilibrium with this solution will be composed of titanium, boron, and any inert or other gases present in the system. Titanium diboride most likely will not be found in the gas phase since, even if it has been formed, it will exist as a solid precipitate. However, if it has been formed, this assumption may be tested by calculating the solubility of TiB₂ in the solution; if it is highly soluble in the liquid, it also may be present in the gas phase.

⁷Reference 86 is in agreement with Reference 85.

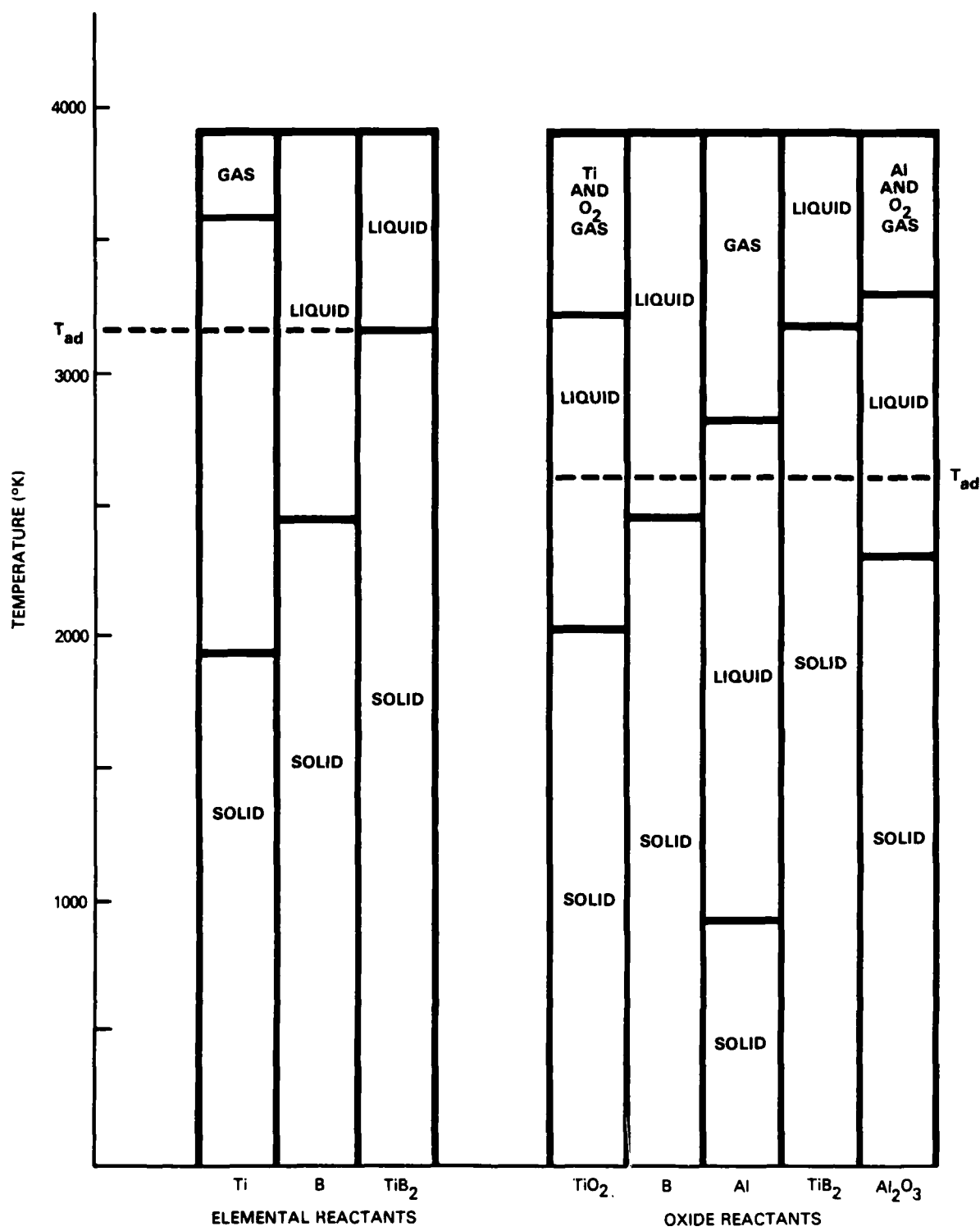


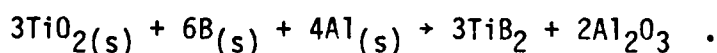
FIGURE 12.
PHASE DATA FOR TITANIUM DIBORIDE (TiB₂) REACTIONS

If appreciable conversion does not occur in the liquid solution, it may occur in the gas phase. This may be tested by analyzing yield at various pressures. If the reaction occurs in the gas phase, increasingly higher pressures will increase conversion, as suggested by the LeChatelier-Braun principle.

From the analysis presented above, the elemental reaction of titanium and boron to form titanium diboride appears to occur in the liquid state. Therefore, a homogeneous reaction model seems to be warranted.

I. SYNTHESIS OF TITANIUM DIBORIDE (OXIDE)

This reaction involves the production of titanium diboride from titanium dioxide, as shown in the empirical formula below:



As in the other TiB_2 -synthesis reaction, boron is assumed to be in a crystalline state. Since data for amorphous elemental boron over the temperature range of interest have not been found, the uncertainty introduced by this assumption is unknown.

For the purpose of analysis, the initial charge is assumed to be stoichiometric amounts of titanium dioxide crystalline powder and crystalline boron powder. These powders also are assumed to be well mixed.

1. Thermodynamic Analysis

The change in Gibb's free energy as a function of temperature is shown in Table 18. These data indicate that the forward reaction is thermodynamically favored from room temperature to the adiabatic reaction temperature. The calculated adiabatic temperature, using data from Ref. 87, is 2,527°K. It occurs with aluminum oxide in the liquid phase and titanium diboride in the solid phase, as shown in Figure 12. The heat of reaction at the adiabatic reaction temperature is 785 cal/gl.

TABLE 18.

FREE ENERGY VALUES FOR SYNTHESIS OF
TITANIUM DIBORIDE FROM AN OXIDE

Adiabatic Reaction Temperature = 2,527°K

Titanium Diboride Phase: 100% Solid

Aluminum Oxide Phase: 100% Liquid

<u>T (°K)</u>	<u>Enthalpy(a)</u>	<u>Gibbs(a)</u>
300.00	-324100.00	-13600.00
400.00	-324500.00	10000.00
500.00	-324900.00	-306400.00
600.00	-325900.00	-302600.00
700.00	-326600.00	-298600.00
800.00	-327400.00	-294600.00
900.00	-328100.00	-290400.00
1000.00	-339200.00	-292900.00
1100.00	-339700.00	-288300.00
1200.00	-340100.00	-283600.00
1300.00	-340400.00	-278900.00
1400.00	-340600.00	-274100.00
1500.00	-340700.00	-269400.00
1600.00	-339500.00	-265700.00
1700.00	-339300.00	-261100.00
1800.00	-339300.00	-256400.00
1900.00	-339100.00	-251600.00
2000.00	-338900.00	-247200.00
2100.00	-338600.00	-242700.00
2200.00	-386900.00	-236000.00
2300.00	-386600.00	-229100.00
2400.00	-331000.00	-224100.00
2500.00	-363000.00	-219000.00
2600.00	-362500.00	-213200.00
2700.00	-362000.00	-207500.00
2800.00	-639100.00	-198400.00
2900.00	-637600.00	-182700.00
3000.00	-636000.00	-167100.00
3100.00	-634400.00	-151500.00
3200.00	-560300.00	-140300.00
3300.00	-176300.00	146600.00
3400.00	-175200.00	156300.00
3500.00	-174200.00	166100.00

(a) Calories.

(b) Calories per °K.

2. Reaction Phenomenology

All three reactants are solid powders at 298°K and 1 atmosphere of pressure, as indicated in Table 19 and Figure 12 (on the right side). The forward reaction is favorable at room temperature. At 933°K, aluminum melts. The system now consists of solid powders of boron and titanium dioxide surrounded by liquid aluminum over the temperature range from approximately 933°K to 2,143°K.

TABLE 19.
PHASE DATA FOR OXIDATION REDUCTION
SYNTHESIS OF TITANIUM DIBORIDE

<u>T(°K)</u>	<u>TiO₂</u>	<u>B</u>	<u>Al</u>	<u>TiB₂</u>	<u>Al₂O₃</u>
298-933	s	s	s	s	s
933	s	s	s + l	s	s
933-2,143	s	s	l	s	s
2,143	s + l	s	l	s	s
2,143-2,315	l	s	l	s	s
2,315	l	s	l	s	s + l
2,315-2,450	l	s	l	s	l
2,450	l	s + l	l	s	l
2,450-2,767	l	l	l	s	l
2,767	l	l	l + g	s	l
2,767-3,200	l	l	g	s	l
3,200	dissociate	l	g	s	l
3,200-3,253	--	l	g	s	l
3,253	--	l	g	s	dissociate
3,253-3,931	--	l	g	s	--
3,931	--	l + g	g	s	--
3,931-4,250	--	g	g	s	--
4,250	--	g	g	dissociate	--

At 2,143°K, titanium dioxide melts. The system then will consist of solid powders of boron surrounded by liquid aluminum and liquid titanium dioxide up to temperatures of about 2,450°K. Above 2,450°K, the findings are again uncertain due to the conflicting data for boron. Melting temperatures

for boron have been given as 2,400°K and 2,573°K. At high temperatures (above 3,200°K), titanium dioxide will have decomposed into Ti and O₂ gases. B will be in a liquid phase, and Al will be in a gaseous phase at the high temperature.

Titanium diboride will exist in the solid phase up to approximately 4,250°K. Titanium diboride most likely will not be found in the gaseous phase below this temperature; even if it has been formed, it will exist as a solid precipitate. Although aluminum melts at 933°K, Al₂O₃ does not melt until 2,318°K. This suggests that the liquid aluminum contained in the Al₂O₃ shell will not be able to escape. The shell likely will break up into small Al₂O₃ particles because of defects in the shell layer, its shallow depth (about 5 nm), and the mechanical forces of thermal volume expansion as the temperature rises. The volume expansion of aluminum upon melting is 6.5 percent. Thus, it is expected that free liquid aluminum will be present in the system. At the adiabatic temperature of 2,527°K, titanium diboride will exist 100 percent in the solid phase, and aluminum oxide will exist 100 percent in the liquid phase. At high temperatures (above 3,250°K), Al₂O₃ decomposes, while titanium diboride will exist as a liquid until 4,250°K, when it decomposes into titanium and boron gases.

VI. ANALYTICAL MODELING OF GASLESS COMBUSTION SYNTHESIS

A. MODELING OBJECTIVE AND APPROACH

The SPC objective in regard to modeling of gasless combustion synthesis reactions has been to integrate the foregoing background information on Soviet R&D and results of the phenomenology investigations into a numeric predictive capability. General models can be constructed to describe the behavior of specific combustion systems. The models are intended to be used for:

- Selection and evaluation of candidate reaction systems.
- Understanding of reaction mechanics and kinetics.
- Control of process variables to obtain products with desirable properties.
- Determination of data and phase relationships for process scale-up.

An ideal model would require minimal input, (e.g., molar reactant ratios, diluent quantities, compact shape, environmental boundary conditions). Output should include temperature as a function of time and spatial coordinate, combustion wave speed, and reaction rates.

Soviet models (see Chapter V and Appendix B) have predicted combustion behavior for specific types of systems, such as condensed phase or liquid-metal/solid-nonmetal systems. Although these models have been useful in predicting a limited scope of qualitative behavior, their output often does not correlate well with quantitative results. The assumptions and constraints imposed by Soviet researchers must be broadened to be more realistic. For example, heat loss, phase change, and non-Arrhenius heat generation terms should be included.

The SPC approach to modeling has followed two paths:

- Studying and recreating Soviet models (Appendix B)
- Expanding those initial ideas to include additional and more realistic constraints.

Toward this goal, SPC has created three separate software packages in FORTRAN 77 (THERMLIST, COMBUST, and THERM), which are described in Sections B through D, following.

B. DESCRIPTION OF THERMLIST

An overall sense of the ideal thermodynamic behavior of a reaction system may be realized through a zero-dimensional heat and energy balance. THERMLIST performs such a balance on any reacting system. As mentioned in Chapter V, specific heats are modeled as functions of temperature per a standard reference. The resulting equations then are integrated with latent heat and entropy data as boundary conditions to produce enthalpy and entropy equations.

The inputs to the model are simply the balanced molar quantities of reactants and products at a given initial temperature, the maximum temperature, and temperature intervals. The tables in Appendix D have been generated as output.

Reactant product and state functions are listed at various temperatures along with reaction properties, such as enthalpy, entropy, free energy. The adiabatic reaction temperature is calculated, and the product phases existing at that temperature are listed.

THERMLIST is a highly modular program. It currently is capable of producing results containing any combination of these species: Ti, TiB_2 , TiC , and TiO_2 . Additional features include adding one subroutine, adding two input files. The approach is similar to that of the other programs in Appendix D.

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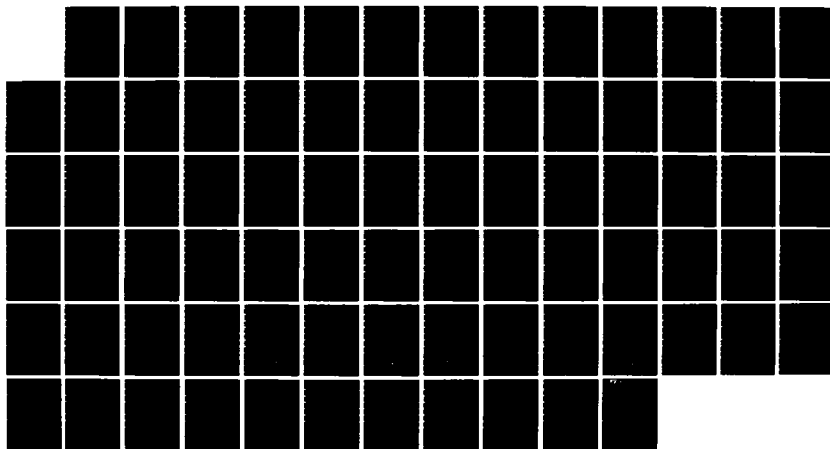
SYNTHESIS OF REFRACTORY COMPOUNDS WITH GASLESS
COMBUSTION REACTIONS(U) LAWRENCE LIVERMORE NATIONAL LAB
CA W L FRANKHOUSER ET AL. SEP 83

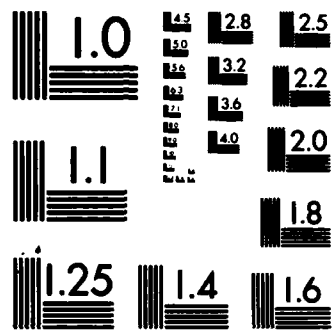
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C. DESCRIPTION OF COMBUST

The most frequently cited Soviet model to date seems to be the one-dimensional, transient model described in Appendix B (pp. B-2 through B-4). From that model, a criterion is established for the transition from a steady to a nonsteady mode of combustion. The Soviet equations as outlined in Appendix B are reproduced in COMBUST.

An explicit, iterative solution scheme was chosen since the model is most useful when small time and spatial steps are employed. The central difference form of the one-dimensional, transient heat diffusion equation with an Arrhenius heat generation term is shown below:

$$\frac{\overline{c_p} (T_i^{m+1} - T_i^m)}{\Delta t} = \frac{\overline{\lambda} (T_{i+1}^m + T_{i-1}^m - 2T_i^m)}{\Delta x^2} + Q_p \phi(T, \eta)$$

$$\phi(T, \eta) = k_0 e^{-E/RT_i^m} (1 - \eta)^n ,$$

where m indicates the present time step and i the present spatial step.

For this one-dimensional model, one boundary exists at each end of the cylinder. Adiabatic boundary conditions were imposed at each of these ends. A uniform initial temperature is specified, and the first node is subsequently and instantaneously raised to the ignition temperature. Since the model is incapable of negotiating the kinetics of ignition, the ignition temperature is an input, and it is artificially imposed on the calculations. The degree of reaction completeness, η , is constrained to be a linear function of the present, initial, and adiabatic temperatures, with $\eta = 0$ at the initial temperature and $\eta = 1$ at adiabatic temperature.

The inputs to the model are the length of the compact, the number of spatial nodes, the total combustion time, the number of time steps, the

ignition, initial, and adiabatic temperatures, the heat generation per unit mole, and the average material properties. From these data, the temperature and the degree of reaction completeness (η) of each node are output at each time step as shown in Table 20.

D. DESCRIPTION OF THERM

Since it could prove beneficial to expand COMBUST to two dimensions or to study the interaction of a reacting system with the environment, SPC has developed a two-dimensional, transient heat diffusion model called THERM, capable of mapping nodal temperatures for an arbitrarily shaped object given any arbitrary combination of temperature, heat, convection, and radiation along the edge nodes. It also is capable of modeling laminated materials.

A Crank-Nicolson iterative solution scheme is employed. The inputs to the model are a file containing the nodal structure, the initial temperature, the overall time, the number of time steps, the nodal size, the maximum allowable temperature error, the materials properties, and the boundary conditions. The temperature distribution at the final time, arbitrary selected boundary conditions, and other input data are output as shown in Table 21.

The input parameters and the overall energy change are listed first in the table, followed sequentially by the nodal temperature listing and the boundary conditions. In this case, the shape selected for the diffusion mass is a 45° wedge with a horizontal 1m base, a 1m vertical side, and a 1m depth. In addition, an adiabatic boundary condition has been arbitrarily imposed upon the hypotenuse. The right half of the base has been arbitrarily cooled by a 300°K fluid with a film coefficient of $15 \text{ W/M}^2\text{-}^\circ\text{K}$, while the left half has a heat influx of 5000 W/M^2 . Two arbitrary thermal parameters also have been imposed on the vertical side. The top half is radiating to a large black body of 300°K, and the lower half has a heat influx of 5000 W/M^2 .

TABLE 20.
DEMONSTRATION OF PARTIAL DATA
OUTPUT FROM SPC COMBUST MODEL

COMPACT LENGTH (CM)=	5.000
NUMBER OF NODES =	5
COMBUSTION TIME (SEC)=	10.000
NUMBER OF TIME STEPS =	25
INITIAL TEMPERATURE (K)=	300.000
IGNITION TEMPERATURE (K)=	1000.000
COMBUSTION TEMPERATURE (K)=	2100.000
THERMAL CONDUCTIVITY (W/M ² -K)=	15.000
SPECIFIC HEAT (J/KG-K)=	300.000
DENSITY (KG/M ³)=	2000.000
HEAT GENERATION (W/M ³)=	.900E+06
REACTION ORDER =	2
ACTIVATION ENERGY (N-M)=	.200E+03
IDEAL GAS CONSTANT (N-M/K)=	2.000
ALPHA (M ² /S)=	.250E-04

TIME:	.00 SEC
1	T = 1000.00 NU = .00
2	T = 300.00 NU = .00
3	T = 300.00 NU = .00
4	T = 300.00 NU = .00
5	T = 300.00 NU = .00
TIME:	.40 SEC
1	T = 2130.00 NU = .40
2	T = 370.00 NU = .00
3	T = 300.00 NU = .00
4	T = 300.00 NU = .00
5	T = 300.00 NU = .00
TIME:	.80 SEC
1	T = 2386.00 NU = .54
2	T = 539.00 NU = .00
3	T = 307.00 NU = .00
4	T = 300.00 NU = .00
5	T = 300.00 NU = .00

INTERMEDIATE DATA ARE NOT SHOWN

TIME:	9.20 SEC
1	T = 2176.57 NU = .91
2	T = 2054.39 NU = .89
3	T = 1778.83 NU = .83
4	T = 1474.45 NU = .54
5	T = 637.45 NU = .00
TIME:	9.60 SEC
1	T = 2175.58 NU = .91
2	T = 2053.43 NU = .90
3	T = 1811.50 NU = .84
4	T = 1670.71 NU = .63
5	T = 721.15 NU = .00
TIME:	10.00 SEC
1	T = 2172.13 NU = .92
2	T = 2054.43 NU = .90
3	T = 1852.43 NU = .85
4	T = 1756.63 NU = .68
5	T = 816.10 NU = .00

[illegible][illegible]

BOUNDARY QSUM										
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
5000.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
5000.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
5000.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
5000.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
10000.000	5000.000	5000.000	5000.000	5000.000	.000	.000	.000	.000	.000	.000

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The nodal temperatures within the wedge, shown within the second section of Table 21, vary from approximately 310°K to 318°K. The boundary conditions are printed sequentially in the third, fourth, and fifth sections of the table for temperature (TSum), heat input (QSum), and film factors (HSum). In this case, no temperature boundary condition was imposed. The heat inputs are recorded as described above. The radiative boundary conditions had been linearized and recorded as film factors in units of $W/M^2-^{\circ}K$.

E. FUTURE MODELING EFFORT SUGGESTIONS

The most intriguing model of the foregoing discussion is COMBUST. A model that could accurately predict quantitative synthesis reaction results would reduce research costs and provide a basis for future experimentation.

There are four readily definable flaws in the current COMBUST model:

- It assumes an adiabatic, one-dimensional reaction.
- It assumes constant materials properties.
- It assumes no phase changes.
- It assumes Arrhenius-type heat production.

The discussion in Chapter V shows the last two assumptions to be clearly invalid for most gasless combustion synthesis reactions. The simple fact that reactants are being converted to products and the presence of a very large temperature increase in reaction indicate the second assumption to be highly doubtful. The first assumption also appears dubious when one considers the large temperature gradient between the reaction and the ambient temperatures.

A more realistic, non-Arrhenius heat generation routine that accounts for phase changes could be incorporated by combining parts of the COMBUST and THERMLIST models. THERMLIST contains the basic subroutines needed to replace the $Q_p \phi(T, \eta)$ term of the heat diffusion equation with a more realistic heat generation term, as calculated from the changes in system enthalpy. In addition, since the completeness of reaction is a direct function of the change in enthalpy, the η value for order-of-reaction need

not be known, and the relation of reaction completeness and heat release need not be assumed.

The change in the overall material properties is a function of the reaction completeness and temperature distributions along the reaction path. The reaction completeness can be calculated, and the temperature-dependent material property deviations can be curve fitted and inserted discretely. This would be similar to the method of modeling specific heats for calculations in THERMLIST.

To account for heat losses to the environment, the COMBUST model could be expanded to two dimensions, or heat loss terms could be included in the one-dimensional mode. (This would be similar to the numeric method normally employed in heat transfer calculations for fin designs.) Since a two-dimensional model would allow greater flexibility, it probably would be the better option. A model such as THERM could be integrated with COMBUST to create a reaction model for arbitrarily shaped two-dimensional geometries.

Other models could be designed as research needs are more clearly defined. For example, a model that examines the thermal characteristics of reaction bonding of ceramics to metal appears feasible. However, development of models of such esoteric applications should be withheld until the accuracy of the simpler reaction models has been verified.

VII. CONSIDERATION OF FUTURE GASLESS COMBUSTION SYNTHESIS

The objective of this discussion is to provide planning guidance on gasless combustion synthesis for extended basic R&D and for technology transfer into applied development phases. Deductive reasoning is used to accomplish this objective by reflecting on prior Soviet and U.S. accomplishments in the field, the current status of those programs, and their apparent strengths and weaknesses. The results of these reflections take the form of suggestions for follow-on activities and direction in the domestic program.

A. HISTORICAL ASPECTS

Soviet work in gasless combustion synthesis is recognizable as a specific R&D program over the period since the late 1960s, as revealed in the extensive file of publications that has been established at SPC [Ref. 91]. The director of the national Soviet council that ultimately was established to administer that program recently has written a concise history of his program [Ref. 92]. The director, Dr. Merzhanov, characterizes two program phases. The first was the "powder" phase, which extended through circa 1977. The second is the "advanced" phase, in which dense solid-form products have been emphasized. Merzhanov claims that the powder phase has been quite successful in finding applications for his products (see IV.B) and that the total program development costs have been more than recovered by the savings to the national economy that resulted from introduction of only one of his products--the titanium carbide powder that is now used in abrasives, polishing pastes, and tools. An important factor in the success of this phase is attributed to construction of a pilot-scale powder production facility at his laboratory. This action enabled him to supply powder

rather than "technology" to potential users. As a result, much of the bureaucratic entanglement that normally would be associated with technology transfer in his country was circumvented.

Although Merzhanov concluded that the gasless combustion process could be employed effectively in fabricating dense solids, he decided that a different administrative approach should be used during the current advanced phase, because the technological problems were more varied and much more complex. He apparently feels that each dense product form merits a process development program that is somewhat unique unto itself; whereas in powder production, a considerably greater degree of cross-transfer of technology among different product materials was possible. He also realizes that equipment required for the advanced phase of his program will be more varied in form and expensive than for powder production. He emphasizes an integration of pressing with gasless combustion synthesis reactions and direct casting of product materials following the reactions. He also apparently is emphasizing three product groups: ceramic and cermet cutting tools (undressed) that are reacted in a press die, nitrides that are formed by reaction in pressurized nitrogen gas, and castings (including bilayer pipes).

He is trying to facilitate technology transfer through the Soviet bureaucratic system by obtaining help from the Ministry of Higher Education and by finding a major industrial user who will be a technology sponsor. The Ministry of Higher Education is training potential users of the technology in basic principles and concepts. The industrial user, the Ministry of Tank Production, is initially producing and evaluating the tool products, because many of their programs require extensive machining facilities.

In contrast to the matured R&D program and the industrial offshoots in the U.S.S.R., a recognizable U.S. R&D program is relatively new (since circa 1981) and industrial offshoots are not evident. However, interest in gasless combustion synthesis has been building rapidly in the United States as evidenced at reviews of the DARPA/LLNL program in which SPC has participated and by interest expressed in a technical session on this subject held

recently at a national meeting of the American Ceramic Society [Ref. 93]. Five papers were delivered at that session by representatives from national government laboratories, a defense center, a university, and commercial industry. Another obvious difference between the U.S. and Soviet programs is the greater diffuseness in objectives among the early participants within the U.S. program. Although this diffuseness probably has been advantageous heretofore, increased focus on some applications and product groups soon may be warranted.

Some reflections on what gasless combustion synthesis offers as a technology today and what may be needed to implement it industrially also may help in providing guidance for the future. The process offers an inexpensive source of process heat, extremely high processing temperatures, opportunities for rapid process heatup and cooldown, and inherent chemical purification. Each of these attributes is considered to be desirable for most materials-processing applications. The basic constraint to rapid and effective industrial implementation of the technology is the lack of knowledge in regard to process control. Industrial processes must be controllable to be reliable.

The initial planning approach in the Soviet program was to study the combustion technology aspects and, simultaneously, to produce a simple product form (powder). With that background, the Soviet planning approach for developing processes to produce dense solids as the product form has been drastically revised. Planning for the next phase of the U.S. program can benefit from both the Soviet background and the early domestic R&D activities.

B. SUGGESTIONS FOR THE FUTURE

The technical and economic issues that will decide the value and utility of gasless combustion synthesis as an industrial process in the United States ultimately must be resolved by industry. Since the basic combustion concepts of the process are now understood and have been verified in the laboratory, industry briefings appear to be appropriate. Furthermore, the briefings could be organized to serve two purposes:

- To provide a technology background to industry on gasless combustion synthesis theory and on U.S. and Soviet accomplishments.
- To encourage feedback from industry on prior relevant experiences and on future R&D directions.

An industry briefing on potential uses of gasless combustion in production of refractory powder materials is an example of a subject that is already timely. This briefing could stress, on one hand, the laboratory research at LLNL and the tendency to form aggregate and skeletal products in the absence of pressure, and on the other hand, the Soviet claims in regard to industrial use of powder products that have been synthesized. If production of titanium carbide were to be emphasized in the briefing, for example, the industrial participants logically could include producers of titanium sponge, titanium powder, and carbide powders. The feedback requested of those industrial participants would be expressions of commercial interest in regard to processing capability and economic appeal.

Another briefing that also is considered to be appropriate for the near term is the combination of pressing and gasless combustion synthesis to produce dense solid shapes of refractory compounds. The briefing could include details of the laboratory work at LLNL and discussion of Soviet experience and other experiments performed in Australia [Refs. 26 and 27]. These applications probably would be more specialized than powder production. With the Soviet planning approach, an individually styled R&D program probably would be pursued for each product. Industrial participants, therefore, typically might include cemented carbide tool producers (synthesis of cermets), those interested in producing ceramic components for engines, and those involved in development of titanium diboride inserts for melting electrodes used in refining aluminum.

Specific suggestions in regard to potential applications of gasless combustion synthesis follow. These suggestions are intended to be subjects for consideration in follow-on R&D rather than for near-term industrial briefings. Since most have not been reported in the Soviet gasless combustion synthesis program, opportunities are presented for rapid U.S. advances beyond current Soviet achievements. The suggestions also are intended to

capitalize on potentially unique capabilities of gasless combustion technology to synthesize compounds and perform processing operations that otherwise are considered to be difficult and expensive.

- Synthesis of Ceramic Matrix Composites. The compositional possibilities are almost unlimited. A suggestion for initial experiments is to mix commercially available graphite fibers (chopped or continuous) with transition metal and lampblack powders. With carefully selected stoichiometric proportions, potential products are fiber-reinforced carbides, carbide-carbon eutectic combinations, and carbides with carbon inclusions (in all cases, with compatible thermal expansion properties among the product constituents). Another suggestion is to react silicon powder, mixed with silicon carbide fibers, in nitrogen gas (presumably under pressure, to counteract dissociation tendencies and vaporization). The expected product would be some type of fiber-reinforced silicon nitride, although variations in phase structures can be envisioned with variations in composition.
- Synthesis of Complex Ceramic Compounds. Soviet claims about unique properties achieved with ternary ceramic compositions and with duplex microstructures of two binary phases [Ref. 94] should not be overlooked in planning future R&D in gasless combustion synthesis. The unique capability for rapid heatup and cooldown with this type of processing is well suited for synthesis of complex compositions. Suggestions for initial synthesis experiments include transition metal carborides and carbonitrides⁹ and cemented carbides (e.g., chromium carbide with a nickel binder or titanium carbide with a molybdenum or titanium binder).
- Unique combination of synthesis reactions and pressure. Although most researchers in gasless combustion synthesis agree that a pressure assist is required to produce dense solid shapes [Refs. 27, 91, and 95], most efforts have been concentrated on providing the pressure through standard powder press equipment or in a centrifuge. Only Soviet researchers have used gas pressure, which apparently was used in an open vessel to produce castings by a modified thermite process [Refs. 5, 6, and 71]. Isostatic pressing may be a more effective means for combining the pressure assist with the gasless combustion synthesis reaction. In effect, a hot isostatic pressing is thereby achieved in a cold wall vessel. The suggested experimental approach is to encapsulate the highly compacted mass within a thin metallic sheath and react it under pressure in a cold isostatic pressure vessel. The enclosure sheath would have to be prevented from melting by insulating it from the exterior of the reactant mass. Although this insulation might be accomplished in a number of ways, a direct

⁹Already produced in laboratory experiments at LLNL [Ref. 95].

and simple approach would be to fill an appropriate interim space between the sheath and reactant mass with powdered product material.

- Synthesis of nuclear power reactor fuels. With the recent emphasis on nuclear power for space missions, higher-temperature and higher-burnup fuels will be needed. Whereas fuels previously used for central station power reactors have been oxides of uranium and plutonium, carbide, nitride, and cermet compositions will be most favored in satisfying the more severe operating requirements. Gasless combustion synthesis is a potentially low-cost process for fabrication of either powders or finished fuel shapes of the desired compositions.
- Synthesis of laminated and gradated lightweight armor. With the emphasis on lightweight materials in armor, the use of ceramic compounds will increase. Also, laminations of ceramic layers or ceramics and metals will be employed. Ultimately, compositions will be gradated to provide, within a monolithic section, the advantages of laminated layers that have different properties. Gasless combustion synthesis is capable of bonding laminations simultaneously with the synthesis reaction and is especially adaptable to synthesis of gradated compositions. Appropriate experiments can be readily planned to produce materials already being tested in the lightweight armor programs and to add radiation protection as a dual-purpose armor.
- Hard surfacing of metallic and ceramic materials. Surface wear is a major factor contributing to obsolescence of equipment. Ceramic surface coatings are an obvious solution. The chronic problems in regard to effective use of such coatings are difficulty in application and tendency for poor adherence after coating. The extreme reaction temperatures available with gasless combustion synthesis and the adaptability to synthesis of gradated compositions are features that offer promise for placement of hard wear surfaces on metallic and ceramic substrates. A suggestion for a development project is to combine gasless combustion synthesis reactions with arc welding technology. Powder reactant materials (e.g., titanium, iron, lampblack) could be placed in the core of a metallic (e.g., steel) welding wire or rod. The exothermic release from the synthesis reaction would be added to the heat of the arc in placing the ceramic compound (e.g., titanium-iron carbide) on the substrate surface (e.g., steel). Furthermore, the compositional mix of reactants could be varied in a continuum in order to make the necessary adjustments in composition that emphasize adherence on the inner (substrate) side of the coating and hardness (wear resistance) on the outer side of the coating.
- Synthesis of a cast composite in zero gravity. A number of Soviet documents, including three patents [Refs. 5, 6, and 7], demonstrate that gasless combustion synthesis reactions, when modified by use of a reducing agent (e.g., aluminum, or magne-

sium) and oxide reactants, can be used to produce castings of ceramic, cermet, and intermetallic compositions. A problem created by this process modification is the formation of an oxide slag, which has been separated from the product material. Since the gasless synthesis reaction involves movement of a thin combustion wave through the reacting mass, separation of product and slag throughout the entire mass (even with the gravity assist that results from the density differential between oxide and product) creates an operational problem. Soviet researchers apparently have solved this problem by using centrifugal pressure.

A suggestion is made to consider using the slag to produce a reinforced composite ceramic material rather than separate it from the product form. For example, titanium carbide with a dispersed or continuous aluminum oxide phase might have some extremely interesting properties. One way to investigate such possibilities would be to experiment with a reaction in zero gravity (e.g., in the space shuttle laboratory). The dispersed oxide phase could be achieved by using aluminum powder in the reactant mix. The continuous (three-dimensional) oxide phase could be achieved by putting fine aluminum wire in the reactant mix.

In all instances, laboratory R&D should be combined with analytical process modeling. As indicated in Chapter VI, simple reaction models, once verified, can be extended into more sophisticated forms to predict behavior in the types of process application proposed above.

Appendix A
PROCESSING AND PRODUCT CHARACTERISTICS
IN GASLESS COMBUSTION CASTING

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)				Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b			
1	2	3	4	5	6	7	8	9	10	11	12
1	Mo ₂ C	288gMoO ₃ , +12gC + 108g Al	1	-	75	-	-	-	Mo ₂ C; Mo	9.1	yes
2			100	-	95	-	-	-	Mo ₂ C	8.8	no
3			200	-	99.5	-	-	-	Mo ₂ C	8.8	no
4			1	1,000g	78	-	-	-	Mo ₂ C; Mo	9.0	no
5			100	100g	80	-	-	-	Mo ₂ C; Mo	8.9	no
6			100	300g	83	-	-	-	Mo ₂ C; Mo	8.9	no
7			100	1,000g	96.5	-	-	-	Mo ₂ C	8.9	no
8			100	1,500g	97	-	-	-	Mo ₂ C	8.9	no
9	VC	552gV ₂ O ₅ , +72gC + 270g Al	1	-	43	-	-	-	VC, V ₂ C, V	5.2	yes
10			100	-	85	-	-	-	VC, V ₂ C, V	5.2	yes
11			2,000	-	94	-	-	-	VC, V ₂ C	5.1	no
12			1	1,000g	50	-	-	-	VC, V ₂ C, V	5.2	no
13			100	100g	78	-	-	-	VC, V ₂ C, V	5.1	no
14			100	1,500g	88.5	-	-	-	VC, V ₂ C	5.1	no
15	Cr ₃ C ₂	300gCr ₂ O ₃ + 24gC +162g Al	1	-	20	-	-	-	Cr ₃ C ₂ , Cr ₄ C, Cr	7.0	yes
16			100	-	78	-	-	-	Cr ₃ C ₂ , Cr ₄ C, Cr	6.9	yes

Example No.	End r	Starting xture position	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)				X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b			
1	2	3	4	5	6	7	8	9	10	11	12
17			2,000	-	97.6	-	-	-	Cr ₃ C ₂	6.8	no
18			1	1,000g	50	-	-	-	Cr ₃ C ₂ , Cr ₄ C, Cr	6.9	no
19			100	100g	76	-	-	-	Cr ₃ C ₂ , Cr ₄ C	6.8	no
20			100	1,500g	82	-	-	-	Cr ₃ C ₂ , Cr ₄ C	6.8	no
21	WC	232gMoO ₃ + 12gC + 54gAl	5	-	60	-	-	-	WC, W ₂ C	14.5	no
22			100	-	70	-	-	-	WC, W ₂ C	15.2	no
23			2,000	-	80	-	-	-	WC, W ₂ C	15.3	no
24	MoB	288gMoO ₃ + 70gB ₂ O ₃ + 162gAl	1	-	-	74	-	-	MoB, Mo ₂ B, Mo	8.4	yes
25			100	-	-	94	-	-	MoB, Mo ₂ B	8.2	yes
26			2,000	-	-	99.6	-	-	MoB	8.1	no
27			1	1,000g	-	78	-	-	MoB, Mo ₂ B, Mo	8.4	no
28			100	100g	-	82	-	-	MoB, Mo ₂ B	8.1	no
29			100	1,000g	-	96	-	-	MoB	8.1	no
30	MoB	288gMoO ₃ + 70gB ₂ O ₃ + 219gMg	1	-	-	80	-	-	MoB, Mo ₂ B	8.2	yes
31			100	-	-	90	-	-	MoB, Mo ₂ B	8.2	no

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)					Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b				
1	2	3	4	5	6	7	8	9	10	11	12	
32	VN	552g V ₂ O ₅ + 270g Al	100	-	-	-	-	60	VN, V ₃ N, V	5.8	no	
33			2,000	-	-	-	-	78	VN ₁ V ₃ N, V	5.9	no	
34	30 wt% TiC + 60 wt% MoO ₂ + 10 wt% Ni	87g MoO ₂ + 40g TiO ₂ + 11gC + 10.5g NiO + 36g Al	1	-	95	-	-	-	TiC, Mo ₂ C, Ti, Mo	8.2	yes	
35			100	-	97	-	-	-	TiC, Mo ₂ C, NiMo	8.1	yes	
36			5,000	-	99	-	-	-	TiC, Mo ₂ C, Ni	8.2	no	
37			1	1,000g	96	-	-	-	TiC, Mo ₂ C, Ni	8.2	no	
38			100	100g	97	-	-	-	TiC, Mo ₂ C, Ni	8.4	no	
39			100	1,000g	98	-	-	-	TiC, Mo ₂ C, Ni	8.2	no	
40	95wt%MC, + 5wt%Co	232gMo ₃ + 12gC + 11gCo + 54g Al	5	-	62	-	-	-	MC, W ₂ C, Co	13.7		
41			100	-	75	-	-	-	MC, W ₂ C, Co	13.7	no	
42			2,000	-	82	-	-	-	MC, W ₂ C, Co	13.7	no	

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)					Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b				
1	2	3	4	5	6	7	8	9	10	11	12	
43	90wt%WC + 10wt%Co	232gMo ₃ + 12gC + 28gCoO + 60gAl	5	-	60	-	-	-	-	WC, W ₂ C, W, Co	14.1	no
44		100		-	76	-	-	-	-	WC, W ₂ C, Co	13.8	no
45		2,000		-	80	-	-	-	-	WC, W ₂ C, Co	13.7	no
46	80wt%WC + 20wt%Co	232gMo ₃ + 12gC + 64gCoO + 69g Al	5	-	67	-	-	-	-	WC, W ₂ C, Al, Co	14.0	no
47		100		-	70	-	-	-	-	WC, W ₂ C, Al, Co	14.1	no
48		2,000		-	82	-	-	-	-	WC, W ₂ C, Co	14.1	no
49	50wt%TiC + 40wt%Cr ₃ C ₂ + 10wt%Ni	240g TiO ₂ + 240gCr ₂ O ₃ + 57gNi + 56gC + 250g Al	1	-	65	-	-	-	-	TiC, Cr ₃ C ₂ , Ti, Cr		yes
50		100		-	78	-	-	-	-	TiC, Cr ₃ C ₂ , Cr, Ni	5.7	yes
51		2,000		-	98	-	-	-	-	TiC, Cr ₃ C ₂ , Ni	5.7	no
52	90wt%WC + 10wt%Co	440g V ₂ O ₅ + 46gCoO + 58gC + 277g Al	1	-	50	-	-	-	-	VC, V ₂ C, V	5.5	yes
53		100		-	80	-	-	-	-	VC, V ₂ C, Co	5.4	no
54		2,000		-	97	-	-	-	-	VC, V ₂ C, Co	5.4	no

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)								Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b	9	10	11	12			
1	2	3	4	5	6	7	8	9	10	11	12				
55	90wt%MoB + 10wt%Ni	288gMoO ₂ + 70gB ₂ O ₃ + 29.5gNiO + 175g Al	1	-	-	25	-	-	-	MoB, Mo ₂ B, Mo	8.6	yes			
56			100	-	-	67	-	-	-	MoB, Mo ₂ B, Ni	8.5	no			
57			2,000	-	-	98	-	-	-	MoB, Ni	8.5	no			
58	85wt%VC + 10wt%Ni + 5wt%Mn	552gV ₂ O ₅ + 72gC + 59gNiO + 286g Al + 22.5gMn	1	-	57	-	-	-	-	VC, V ₂ C, V	5.6	yes			
59			100	-	75	-	-	-	-	VC, V ₂ C, Ni, Mn	5.5	no			
60			2,000	-	98	-	-	-	-	VC, V ₂ C, Ni, Mn	5.4	no			
61	85wt%VC + 14wt% Ni + 1wt%Mn	552gV ₂ O ₅ + 72g C + 62gNi + 4 gMn	1	-	52	-	-	-	-	VC, V ₂ C, V	5.7	yes			
62			100	-	79	-	-	-	-	VC, V ₂ C, V, Ni	5.6	no			
63			2,000	-	96	-	-	-	-	VC, V ₂ C, Ni, Mn	5.6	no			
64	45wt%TiC + 40wt%Cr ₃ C ₂ + 10wt%Ni + 5wt%Mg	180g TiO ₂ + 260gCr ₂ O ₃ + 52gNiO + 20gMg + 57gC + 258gAl	1	-	67	-	-	-	-	TiC, Cr ₃ C ₂ , Ti, Cr	5.2	yes			

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)				Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b			
1	2	3	4	5	6	7	8	9	10	11	12
65		100		-	71	-	-	-	TiC, Cr ₃ C ₂ , Ti, Ni	5.1	no
66		2,000			96	-	-	-	TiC, Cr ₃ C ₂ , Ni, Mg	5.1	no
67	45wt%TiC + 44wt%Cr ₃ C ₂ + 10wt%Ni + 1wt%Mg	(same as examples 64-66)	2,000	-	96	-	-	-	TiC, Cr ₃ C ₂ , Ni, Mg	5.2	no
68	W ₂ B	93gW ₂ O ₃ + 7gB ₂ O ₃ + 27gAl	1	100g	-	53	-	-	W ₂ B, W	12.6	yes
69		1	1	300g	-	60	-	-	W ₂ B, W	12.6	yes
70		1	1	1,500g	-	60	-	-	W ₂ B, W	12.3	no
71		100		1,500g	-	72	-	-	W ₂ B, W	12.4	no
72	90wt%WC + 10wt%Mn	232gW ₂ O ₃ + 12gC + 23gMn + 54gAl	1	-	62	-	-	-	WC, W ₂ C, W	14.5	yes
73		100		-	78	-	-	-	WC, W ₂ C, Mn	14.3	no
74		2,000		-	83	-	-	-	WC, W ₂ C, Mn	14.3	no

Example No.	End product	2	3	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)				Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
							C	B	Si	b			
1					4	5	6	7	8	9	10	11	12
75	85wt%Cr ₃ C ₂ + 15wt%Mo			300gCrO ₃ + 24gC + 28gMo + 162gAl	1	-	24	-	-	-	Cr ₃ C ₂ , C ₄ C, Cr	7.1	yes
76				100	100	-	75	-	-	-	Cr ₃ C ₂ , Cr ₄ C, Mo	7.0	yes
77				2,000	2,000	-	96	-	-	-	Cr ₃ C ₂ , Mo	7.0	no
78	NbSi ₂			80gNb ₂ O ₅ + 72gSiO ₂ + 70.2gAl	1	1,000g	-	-	76	-	NbSi ₂ , Nb	6.0	no
79				100	100	100g	-	-	82	-	NbSi ₂ , Nb	5.7	no
80				100	100	1,000g	-	-	86	-	NbSi ₂ , Nb	5.7	no
81	V ₃ Si			166gV ₂ O ₃ + 36gSiO ₂ + 103gAl	1	1,000g	-	-	78	-	V ₃ Si, V	5.2	no
82				100	100	100g	-	-	80	-	V ₃ Si, V	5.1	no
83				100	100	1,000g	-	-	83	-	V ₃ Si, V, Al	5.3	no
84	WSi ₂			70gW ₂ O ₃ + 36gSiO ₂ + 37.8gAl	1	1,000g	-	-	77	-	WSi ₂ , W ₁₀ Si ₇	10.0	no
85				100	100	100g	-	-	79	-	WSi ₂ , W ₁₀ Si ₇	9.6	no
86				100	100	1,000g	-	-	81	-	WSi ₂ , W ₁₀ Si ₇	9.6	no

Example No.	End product	Starting mixture composition	Gas pressure (atm)	Centrifugal acceleration (g)	Product chemical analysis (% of theory, bound)				Product X-ray phase analysis	Product density (g/cm ³)	Product pores and cavities
					C	B	Si	b			
1	2	3	4	5	6	7	8	9	10	11	12
87	MoSi ₂	43.2gMoO ₃ + 36gSiO ₂ + 38gAl	1	1,000g	-	-	88.5	-	MoSi ₂ , Mo ₃ Si	6.0	no
88	30 wt% TiC + 70 wt% Mo ₂ C	40gTiO ₂ + 101gMoO ₃ + 12gC + 58gAl	1	1,500g	90	-	-	-	TiC, Mo ₂ C, Mo	8.1	no
89			100	1,500g	95	-	-	-	TiC, Mo ₂ C	7.8	no
90	50wt%TiSi ₂ + 50wt%MoSi ₂	320gTiO ₂ + 402gMoO ₃ + 800gSiO ₂ + 750gAl	1	1,500g	-	-	78	-	TiSi ₂ , MoSi ₂ , Ti, Mo	5.0	no
91			100	1,500g	-	-	82	-	TiSi ₂ , MoSi ₂	5.1	no
92	50wt%Mo ₂ + 50wt%TiB ₂	288gMoO ₃ + 240gTiO ₂ + 280gB ₂ O ₃ + 430gAl	1	1,500g	-	86	-	-	Mo ₂ B, TiB ₂ , Mo ₂ S	5.6	no
93			100	1,500g	-	91	-	-	Mo ₂ B, TiB ₂ , Mo ₂ S	5.5	no
94	90wt%WC + 10wt%Mo	232gMoO ₃ + 12gC + 38gMoO ₃ + 56gAl	2,000	-	84	-	-	-	WC, W ₂ C, Mo	14.3	?

Appendix B
SUMMARIES OF SELECTED SOVIET
MODELS ON GASLESS COMBUSTION REACTIONS

TITLE: Theory of Gasless Combustion [Ref. 74]

SPC CONTROL NUMBER: 23

AUTHOR: A. G. Merzhanov

ABSTRACT: This paper provides a general review of the theory of gasless combustion and presents the standard adiabatic thermodynamic model and a one-dimensional energy balance model. This one-dimensional model is used to investigate the threshold of steady- to nonsteady-state reaction kinetics. The paper also discusses and presents results for a two-dimensional steady-state mass and energy balance model, which is presented in Reference 75. It also presents experimental results of pressure, reaction rate, and non-steady state kinetics.

MODELS:

Thermodynamic Model (p. 9)

The thermodynamic model briefly described in this paper is the same as one that the Soviets published (Novikov, et al.) in a 1975 paper [Ref. 76]. It assumes that the enthalpy of the system after the reaction is equal to the enthalpy of the system before the reaction, i.e., the system is perfectly adiabatic. This model will not be presented here since it is reviewed in the paper cited above.

One Dimensional Non-Steady State Model (p. 11)

1. Model

This model is a one-dimensional energy balance containing only accumulation, diffusion, and generation terms. The x-axis is assumed throughout the discussion to represent the longitudinal distance down a cylindrical reaction vessel of infinitely small radius (see Figure 3, p. 12):

$$(\text{accumulation}) = (\text{net diffusion in}) + (\text{generation})$$

$$\bar{c}_p \frac{dT}{dt} = \bar{\lambda} \frac{\partial^2 T}{\partial x^2} + Q_p \phi(T, n) \quad .$$

If the rate is constant (steady-state), a moving reference frame can be employed by introducing

$$u = \frac{dx}{dt} \quad .$$

2. Assumptions

- The reaction volume is one-dimensional, i.e., a cylinder of infinitely small radius.
- The specific heat $\bar{C}_p$ and thermal diffusivity λ are independent of temperature over the range of interest, and are therefore "effective" or averaged values. The paper states that the temperature dependencies of these two parameters has been "hardly investigated." This implicitly suggests that the reaction is essentially homogeneous.
- The reaction product does not diffuse during or after the reaction.
- The reaction kinetics follow a form of the Arrhenius equation

$$\phi(T, n) = k_0 e^{-E/RT} (1 - n)^n .$$

3. Initial and Boundary Conditions

4. Conclusions

- An important result of the investigation is the discovery of two basically different established combustion states--the stationary and the oscillatory.
- Stationary combustion $\equiv$ all points of the temperature and concentration profiles move along the substance with similar velocity equal to the combustion rate.
- Oscillatory state $\equiv$ the instantaneous combustion rate is variable in time with steady-state oscillations around a central mean velocity, $\bar{u}$. The instantaneous combustion rate is defined as

$$U_{inst} = \frac{d\phi_{max}}{dt}$$

where

$$\phi_{max} = \phi(X_{max}) .$$

- "The boundary between the stationary and oscillatory states is clearly defined by the magnitude of criterion α ."

$$\alpha = 9.1 \frac{\bar{c}}{Q} \frac{RT_c^2}{E} \left(1 - 0.27 \frac{Q}{\bar{c} T_c} \right) .$$

"When $\alpha \rightarrow 1$, steady-state combustion exists; when $\alpha < 1$, oscillatory." This equation is mentioned in the paper as coming from "the calculations;" the conditions for oscillatory behavior (excess enthalpy greater than a critical value, i.e., $T > T_0$ and $n \approx 0$) are inserted into the solution to the model.

TITLE: Theory of the Ignition of Metal Particles. II. Ignition of Metal Particles with the Simultaneous Formation of a Product Film and a Solid Solution [Ref. 77]

SPC CONTROL NUMBER: 121

AUTHORS: A. B. Arutyunyan, S. L. Kharatyan, and A. G. Merzhanov

ABSTRACT: A two-dimensional reaction model involving a moving boundary in a spherical particle was constructed in an earlier paper [Ref. 78]. A distinction is drawn between a two-component phase in which reactants are free to interdiffuse (solubility is important here) and a product phase in which rigid bands form the product phase through which reactants may interdiffuse. This paper presents results of applying the model to reaction systems with varying solubilities of reactants and kinetics, i.e., varying boundary conditions for the moving boundary. This model is oriented toward diffusion of a non-metal into a solid metal spherical particle.

MODEL:

One-Dimensional NonSteady State (Radius, Time)

1. Model

Mass and energy balances are made on a spherical metal particle. Since there is a discontinuity of concentration at the phase boundary between the outer product phase and the inner metal reactant phase, a separate balance is required for each phase.

2. Assumptions

- Perfectly spherical solid metal particle. The center is $r = 0$.
- Nonmetal reactant diffuses in $(-r)$ through the product layer to the phase boundary where it either reacts to form the product instantaneously or diffuses into the metal reactant phase until the reaction (phase) boundary reaches it.
- Concentrations of the diffusing nonmetal reactant on either side of the phase boundary are independent of time and can be determined from the phase diagram of the appropriate system.

TITLE: Formation of Solid Solutions Under Combustion Conditions [Ref. 79]

SPC CONTROL NUMBER: 77-47

AUTHORS: A. G. Merzhanov and E. N. Rumanov

ABSTRACT: This paper discusses and models the diffusion of a nonreacting solute gas into a porous solid solvent. Example of such systems are TiO, TiN, ZrN, and several other nitrides. Chemical reaction is assumed to occur when substantial changes in the banding structure of the reactants occurs (particularly the solvent phase, which is a solid here) and stoichiometric ratios of solute to solvent molecules conform to the product phase. A solid solution, described by solubility principles, occurs when one reaction (a solute) diffuses through a solvent reactant phase without major bonding structure changes. The latter category is considered in this paper. Diffusion of a solute fluid (a gas) is assumed to occur in a porous pressed metal powder solvent phase. The thermal effects of mixing (entropy dominated) are considered.

MODEL:

Diffusivity of Solute in Solvent

$$\frac{\partial a}{\partial t} = \text{divergence } (D \nabla a)$$

$$D = k_0 \exp \left(\frac{-E}{RT} \right)$$

with E/R usually on the order of 10^5 .

TITLE: The Theory of Steady-State Combustion in Powders [Ref. 80]

SPC CONTROL NUMBER: 0a

AUTHORS: A. G. Merzhanov and F. I. Dubovitskii

ABSTRACT: A simple one-dimensional steady-state energy balance model $T = T(x, u)$ where T is temperature, x is position, and u is combustion front velocity is presented. It is used to predict the dimensions of the reaction zone. The assumptions in this model are quite restrictive and should be reviewed carefully before using the results.

MODEL:

One-Dimensional Energy Balance

1. Model

The reference frame used in this model has an origin that moves with the combustion front (Lagrangian). Note that

$$u = \frac{dx}{dt}$$

and by the chain rule

$$u \frac{dT}{dx} = \frac{dT}{dt} ,$$

which is an accumulation term.

$$u \frac{dT}{dx} = \alpha \frac{d^2T}{dx^2} + \frac{Q}{\rho c_p} k_0 \exp\left(\frac{-E}{RT}\right)$$

accumulation	=	net energy	+	thermal generation,
		in, by		by reaction
		conjunction		

2. Assumptions

- The reaction geometry is one-dimensional, e.g., a cylinder with infinitely small radius.
 - The reaction is exothermic.
 - The reaction rate is given by

$$w = k_0 \exp \left(\frac{-E}{RT} \right) .$$

- The reaction occurs in a homogeneous phase and is rate-rather than diffusion-limited, i.e., the presence of a reaction is determined solely by the availability of a sufficient amount of energy and not by the availability of reactants at the reaction time.

TITLE: The Mechanism of the Combustion of Powders [Ref. 81]

SPC CONTROL NUMBER: Ob

AUTHORS: G. B. Manelis, A. G. Merzhanov, and F. I. Dubovitskii

ABSTRACT: This paper does not involve gasless combustion. It concerns the combustion reaction in which a solid-phase powder becomes a gas-phase product with the presence of a flame (radiant emission of energy). The phenomenon described is the mechanism of the solid-phase atoms being removed from the bulk solid phase and ultimately becoming gas-phase products by reacting at some stage with an oxidizer. The authors assume that the powder is dispersed into particles from the bulk solid phase, is carried by a gas stream, and either decompose into solid atoms somewhere between the bulk solid-phase surface and the hot flame zone, or are carried as particles to the flame zone and react there. Using a formula developed in one of the authors' earlier works [Ref. 80] that describes the dispersion of a particle as a function of the surface temperature of the bulk solid phase, expressions are obtained for the lifetime of the particle and the distance the particle is carried by the gas stream during this lifetime.

MODEL:

Thermal Decomposition of a Solid Particle in a Flowing Gas Stream

1. Model

$$u^2 = \frac{1}{1 - d} a k_0 e^{\frac{-E}{RT_s}} \left[\frac{\frac{RT_s^2}{E}}{T_s - T_0 - \frac{1}{2} Q (1 - \eta_d)/c} \right]$$

(From Ref. 80.)

2. Observations

According to the authors, "an exact solution of the problem of the thermal decomposition of dispersed particles in space and time can be obtained from a knowledge of the laws governing the movement of particles and the laws of heat exchange between particles and a surrounding gas." Yet the formula given contains only one term related to the mass transfer aspect of the diffusion of solid particles from the decomposing particle surface into the gas phase (the degree of dispersion, η_d). It would be enlightening to see derivation of this "exact" solution in Ref. 80.

2. Conclusions

The authors find that, under the assumptions embodied in the model [from Ref. 80] and the mechanism described, the particles decompose into atoms near the bulk solid-phase surface, releasing 300 cal/gm or more of thermal energy before being carried into the flame zone by the gas stream where they react with oxidizer to form products.

TITLE: Towards a Theory of Combustion Processes in Heterogeneous Condensed Media [Ref. 82]

SPC CONTROL NUMBER: 30i

AUTHOR: B. I. Khaikin

ABSTRACT: This paper presents a two-dimensional model and reviews the work of the author, A.G. Merzharov, and four other coworkers, all of whom are supporting the SHS experimental laboratory work with theoretical analyses. It is based on gasless combustion. The model presented in this paper describes a linear interface (phase boundary) between a layer of reactant A and reactant B (see Assumptions). As the combustion front (a point) progresses along the interface, the product is formed. Before the product can be formed on either side of this interface, now containing the product, reactant A must diffuse through this product layer to reach fresh reactant B, and vice versa.

MODEL:

Two-Dimensional Steady-State Mass and Energy Balance

1. Model

The two-dimensional model is a one-dimensional phase boundary separating a pure homogeneous phase of reactant A from a pure homogeneous phase of reactant B. This model describes a vertical cross-sectional view of a flat horizontal system with layers of solid reactants. It also could be used to describe the boundary between two grains of solid reactants, one of A and one of B.

A mass balance is made over an infinitesimal volume element to determine the concentration distribution as a function of time. The model basically takes the form

$$\begin{array}{ccccc} \text{accumulation} & = & \text{net diffusion in} & & \\ \text{uc, } \frac{dy_1}{dx} & = & D \frac{y_C}{y_Y} & - & D \frac{y_C}{y_X} \frac{y_Y}{y_X} \\ \text{mass flux at} & & \text{net molecular} & & \text{net molecular} \\ \text{moving interface} & & \text{diffusion in} & & \text{diffusion in} \\ & & \text{the y-direction} & & \text{the x-direction} \end{array}$$

The model is made steady-state by adopting a Lagrangian reference frame that lets the origin move with the combustion front. This is done by assuming that the velocity (U) is constant and modifying the accumulation term:

$$\text{accumulation} = \frac{\gamma C_i}{\gamma t} = \frac{dx}{dt} \frac{\gamma C}{\gamma x} = u \frac{\gamma C}{\gamma t} .$$

The mass flux (mass/L²t) at the moving interface is provided by molecular diffusion of A through the product phase (AB) in the y-direction less the A that is introduced into the product phase but that does not contribute to the flux of A at the interface (y₁) because it diffuses in the -x-direction. An A molecule diffusing in the -x-direction will encounter more A molecules, and one moving in the +x-direction will encounter more A molecules whereas one moving in the +x direction will encounter the interface and B.

A similar balance is performed for energy. A balance is generally made on enthalpy. If solid phases are considered with no phase transformations, dH = C_pdT. The entire balance equation can be divided by C_p to get dT rather than dH:

$$\text{accumulation} = \frac{\gamma T}{\gamma t} = \frac{dx}{dt} \frac{\gamma T}{\gamma x} = u \frac{\gamma T}{\gamma x}$$

$$\text{net diffusion in} = \frac{-\gamma}{\gamma x} \left(\alpha \frac{\gamma T}{\gamma x} \right) - \frac{\gamma}{\gamma y} \left(\alpha \frac{\gamma T}{\gamma y} \right) .$$

2. Assumptions

The reaction is diffusion limited as a general rule.

The kinetics are assumed to be instantaneous upon contact of reactants. The heat release occurs instantaneously upon reaction.

Several statements are made about the dispersion of the heat released by reaction:

- The reaction heat separates locally in the product layer rather than evenly along the reaction zone.
- The assumed mechanism of interaction corresponds to maximally localized heat release (on the surface of the separation of phases).

3. Boundary Conditions

$$\text{At } y = y_1(x)$$

i.e., the reaction boundary at x between reactant B and the product layer

$$(-l_1 < y_1 < 0)$$

defined to lie between the longitudinal center axis and the far side of reactant layer B

$$C = C_1$$

the concentration of A at the AB/B interface but in the AB phase at any point in time is C_1 .

These boundary conditions are apparently based on the assumption that for a given length cross section in the y-direction, an equal number of reactant molecules are contained whether they are A or B molecules. Therefore, if $\ell_1 = 1/2 \ell_2$, the B molecules in ℓ_1 and one half of the A molecules in ℓ_2 will ultimately combine to form AB, leaving half of the A molecules unreacted.

Appendix C

THERMOCHEMICAL MATERIALS PROPERTIES OF RELEVANCE TO SYNTHESIS OF AlN , TiB_2 , and TiC

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TABLE C-1
SOME THERMODYNAMIC PHASE TRANSITION DATA

Legend:

• T_b , T_m , T_s , and T_t in $^{\circ}\text{K}$

• L_m , L_s , L_t , and L_v in $\frac{\text{kJ}}{\text{gmol}}$

• $\Delta V_m = \frac{V_{\text{liquid}} - V_{\text{solid}}}{V_{\text{solid}}}$

<u>No.</u>	<u>Compound</u>	<u>Data</u>
1	Aluminum	$T_m = 660.1$ $T_b = 2,520$ $L_m = 10.47$ $L_s = 324.1$ $L_v = 291.4$ $\Delta V_m = 6.5\%$
2	Boron	$T_m = 2,300$ $T_b = 2,550$ $L_s = 577.8$
3	Carbon (Graphite)	$T_m = 5,000$ $T_s = 5,000$ $L_s = 712$ $L_t, \text{Diamond} \rightarrow \text{Graphite} = 1.90$
4	Nitrogen (N_2)	$T_m = -210.0$ $T_b = -195.8$ $L_m = .72$ $L_b = 5.581$ $\Delta V_m = 7.3\%$
5	Titanium	$T_m = 1,667$ $T_b = 3,285$ $T_t, \alpha + \beta = 882$ $L_m = 18.8$ $L_s = 469.3$ $L_b = 425.8$ $L_t, \alpha + \beta = 3.43$
6	Titanium Oxide (TiO_2)	$T_t, \alpha + \beta = 991$ $L_t, \alpha + \beta = 3.43$

TABLE C-2
SOME THERMODYNAMIC DATA ON STATE FUNCTIONS

Substance	Properties at 20°C		Gibb's Free Energy, $-\Delta G$ (kJ/gmol)				
	$-\Delta H$ (kJ/gmol)	s (J/gmol $^{\circ}K$)	300K	500K	1,000K	1,500K	2,000K
Al	0	28.34	8.5	--	--	--	--
AlN	320.3	87.0	294.3	275.9	--	--	--
Al ₂ O ₃	1,674.7	51.1	1,580.5	1,517.3	1,359.9	1,143.4	--
B (crystalline)	0	5.9	1.8	--	--	--	--
B ₂ O ₃	1,281.6	54.0	1,201.0	1,148.9	--	--	--
C (graphite)	0	5.69	1.7	--	--	--	--
N ₂	0	191.63	57.5	--	--	--	--
O ₂	0	205.24	61.6	--	--	--	--
Ti	0	30.31	9.1	--	--	--	--
TiC	183.8	24.3	180.0	177.9	172.9	167.1	160.4
TiO	518.7	34.8	485.3	467.7	422.9	378.5	333.7
TiO ₂	944.1	50.2	862.1	827.3	739.5	652.7	564.8
Ti ₂ O ₃	1,519.4	78.7	1,424.3	1,373.3	1,243.9	1,115.4	986.9
Ti ₃ O ₅	2,457.2	129.4	2,309.4	2,224.4	2,010.1	1,797.0	1,581.8

TABLE C-3
SOME DATA ON SPECIFIC HEAT CONSTANTS

$$C_p = 4.1868 [a + 10^{-3}bT + 10^5 cT^{-2}] \text{ (j/kmol)}$$

Substance	State	a	b	c	Temperature Range (°K)
Al	Solid	4.94	2.96	--	298 - T_m
Al	Liquid	7.0	--	--	T_m - 1,273
AlN	--	5.47	7.80	--	298 - 900
Al ₂ O ₃	--	25.48	4.25	-6.82	298 - T_m
B	Amorphous	3.835	2.39	-1.50	298 - 1,240
B	Crystalline	4.013	2.165	-1.79	298 - 1,100
B ₂ O ₃	Crystalline	13.63	17.45	-3.36	298 - 723
B ₂ O ₃	Amorphous	2.28	42.10	--	298 - 723
B ₂ O ₃	Liquid	30.45	--	--	900 - 1,800
C	Graphite	4.10	1.02	-2.10	298 - 2,300
N ₂	Gas	6.67	1.0	--	298 - 2,000
Ti	Alpha	5.28	2.4	--	298 - 1,100
Ti	Beta	6.93	--	--	1,100 - 1,350
TiB ₂	--	10.92	7.10	--	298 - 1,200
TiC	--	11.83	0.80	-3.58	298 - 1,800
TiO	Alpha	10.57	3.6	-1.86	298 - 1,264
TiO	Beta	11.85	3.0	--	1,264 - 1,800
Ti ₂ O ₃	Alpha	7.31	53.52	--	298 - 473
Ti ₂ O ₃	Beta	34.68	1.3	-10.2	473 - 1,800
Ti ₃ O ₅	Alpha	35.47	29.50	--	298 - 450
Ti ₃ O ₅	Beta	41.60	8.0	--	450 - 1,400

TABLE C-4
SOME DATA ON THERMAL CONDUCTIVITY AND SPECIFIC HEATS

Substance	Temperature, T (°C)	Specific Heat C_p (j/g°K)	Thermal Conductivity, k (w/m°K)
Al (99% pure)	100	--	209
Al (99.5% pure)	100	--	218
Al	20	900	238
	100	938	238
	200	984	238
	300	1030	238
	400	1076	238
	660	1080	94.03
	700	1080	95.37
	800	1080	98.71
	900	1080	102.05
	1000	--	105.35
B	2077	2910	--
Ti	20	519	16
	100	540	15
	200	569	15
	400	619	4
	600	636	13
	800	682	13

TABLE C-5
SOME DATA ON VAPOR PRESSURE CONSTANTS

$$\log P = -\frac{A}{T} + B + C \log T + 10^{-3} DT$$

Substance	P(mm Hg)				T (°K)
	A	B	C	D	
Al	16,450	12.36	-1.023	--	1,200 -
2,800					
B	29,900	13.88	-1.0	--	100 - T_m
Bi ₂ O ₃	23,200	11.74	-0.66	--	$T_m - T_b$
Ti (α)	24,400	13.18	-0.91	--	1,155 - T_m
Ti (β)	16,960	6.64	--	--	1,300 -
1,650					

TABLE C.6
SOME DATA ON TOTAL NORMAL RADIATIVE EMISSIVITY

Temperature (°C)	Emissivity (fractional)		
	Al	Ti	Al ₂ O ₃
100	0.038	0.11	--
200	--	--	0.11
400	--	--	0.15
500	0.064	--	--
600	--	--	0.19

GLOSSARY OF TERMS

C_p :	Specific Heat
gmol:	Gram mole
ΔG :	Gibbs free energy
H:	Enthalpy
J:	Joule
k:	Thermal conductivity
$^{\circ}\text{C}$:	Degrees centigrade
$^{\circ}\text{K}$:	Degrees Kelvin
L_m :	Latent heat of fusion
L_s :	Latent heat of sublimation
L_t :	Latent heat of transition
L_v :	Latent heat of vaporization
m:	Meters
mmHg:	Millimeters mercury (pressure)
s:	Entropy
T:	Temperature
T_b :	Boiling temperature
T_m :	Melting temperature
T_s :	Sublimation temperature
T_t :	Transition temperature
V:	Volume
ΔV_m :	$\frac{V_{\text{liquid}} - V_{\text{solid}}}{V_{\text{solid}}}$
W:	Watts

Appendix D
BASIC DATA TABULATIONS
FOR REACTANTS AND PRODUCTS

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The units for data reported in Tables D.1 through D.11 follow:

- Temperature, degrees Kelvin
- Enthalpy, calories
- Entropy and Gibbs free energy, calories per °Kelvin

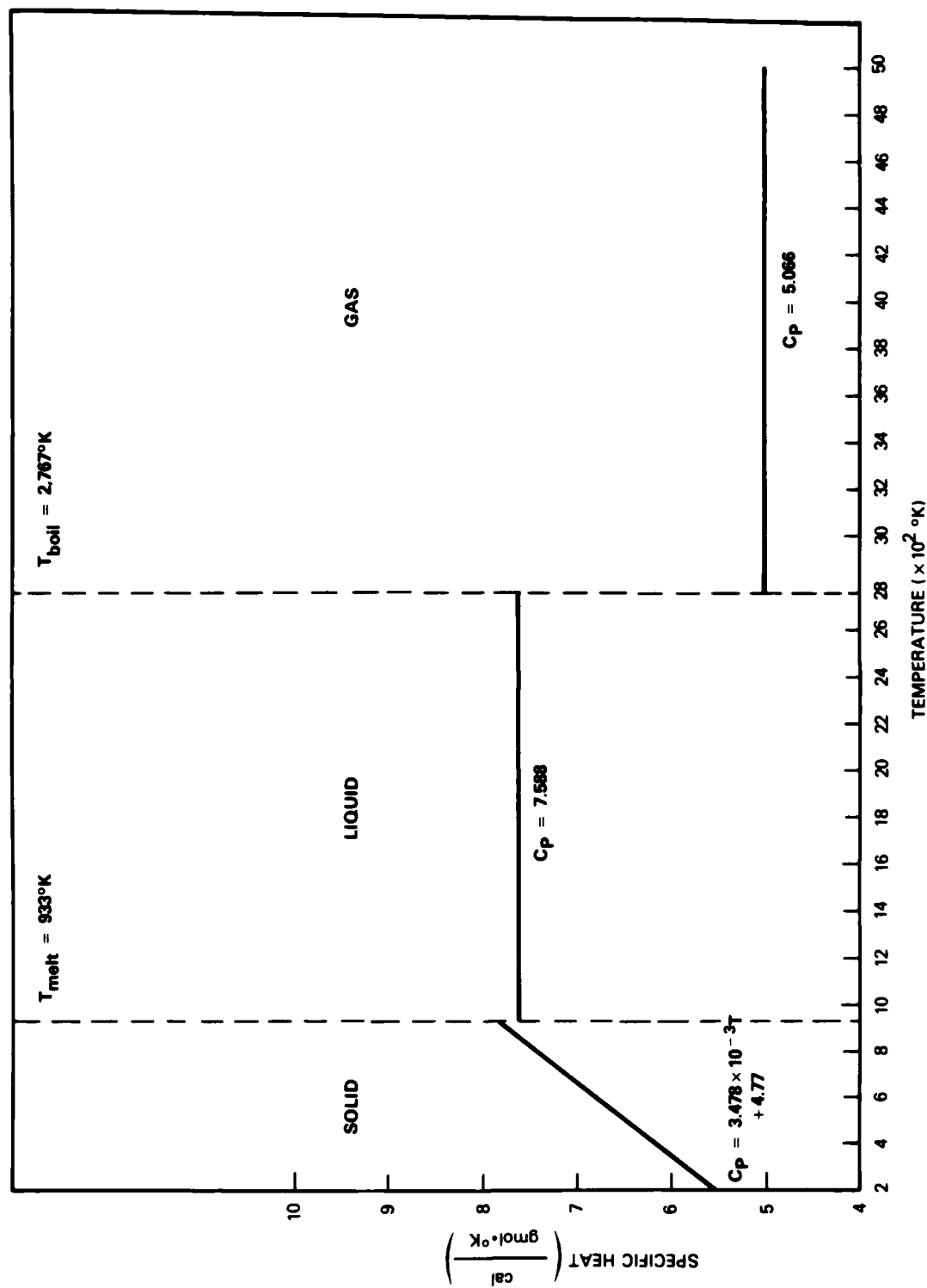


FIGURE D-1.
SPECIFIC HEAT VS TEMPERATURE FOR ALUMINUM

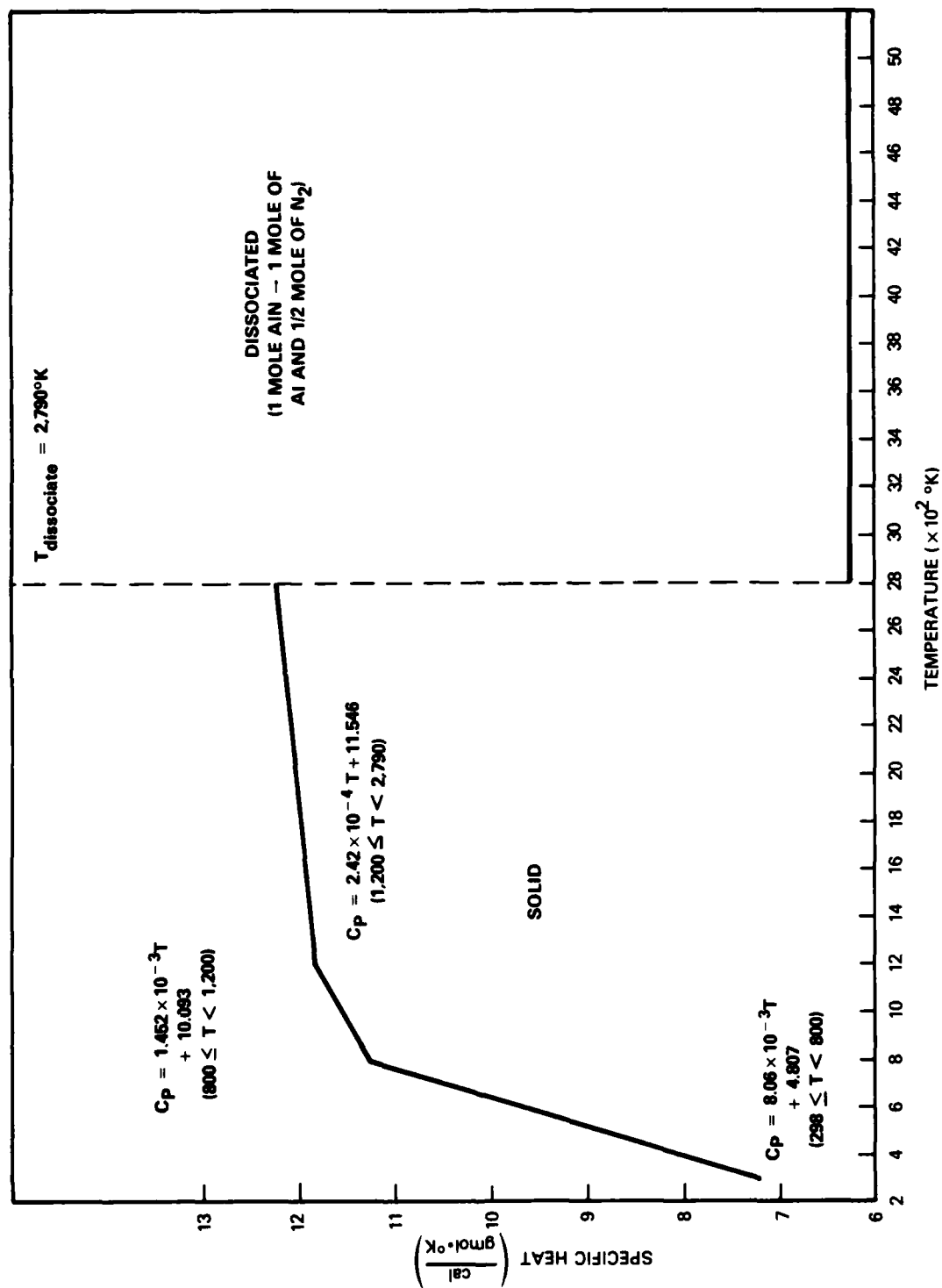


FIGURE D-2.
SPECIFIC HEAT VS TEMPERATURE FOR ALUMINUM NITRIDE (AlN)

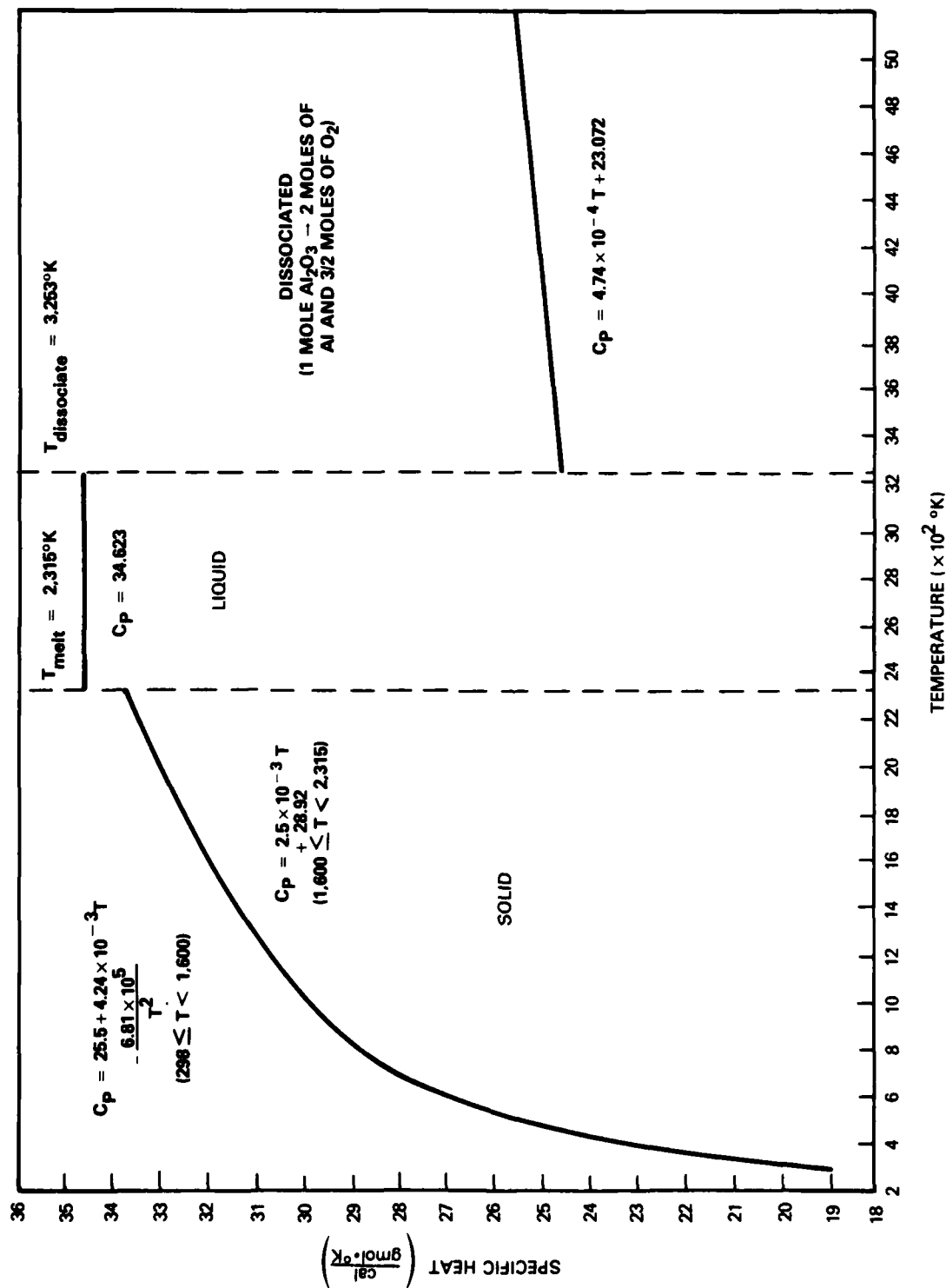


FIGURE D-3.
SPECIFIC HEAT VS TEMPERATURE FOR ALUMINUM OXIDE (Al_2O_3)

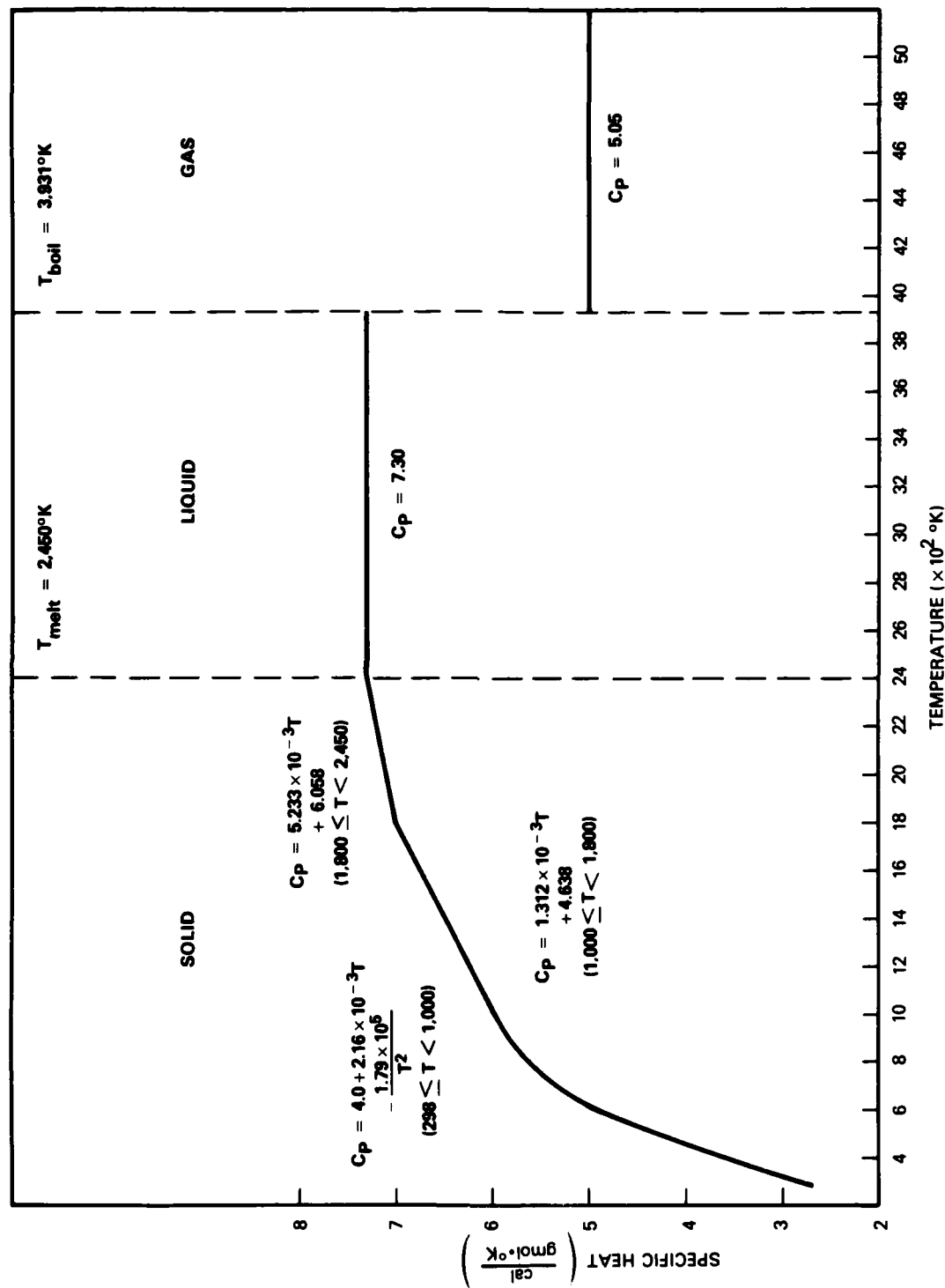


FIGURE D-4.
SPECIFIC HEAT VS TEMPERATURE FOR BORON

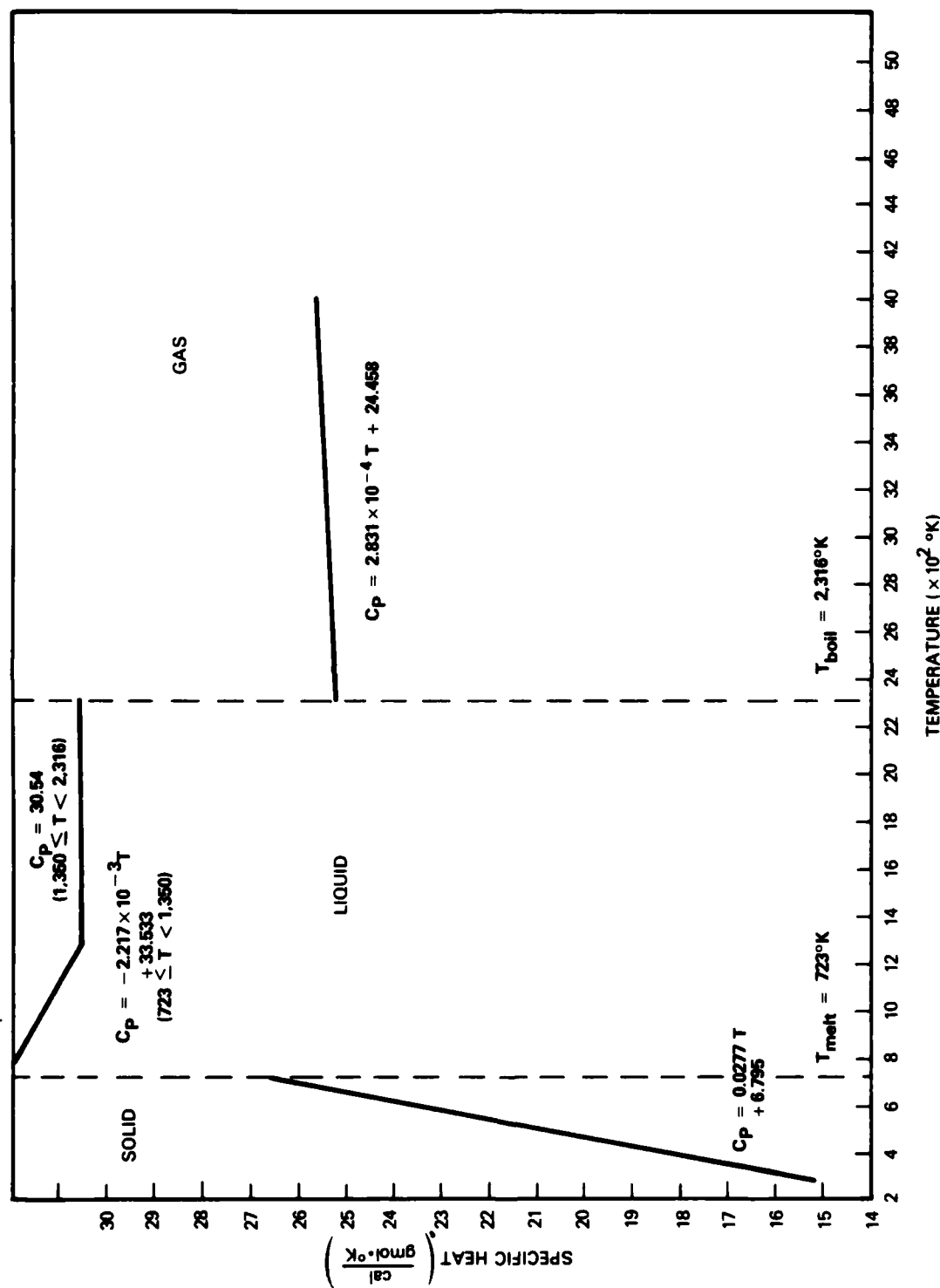


FIGURE D-5.
SPECIFIC HEAT VS TEMPERATURE FOR BORON OXIDE (B_2O_3)

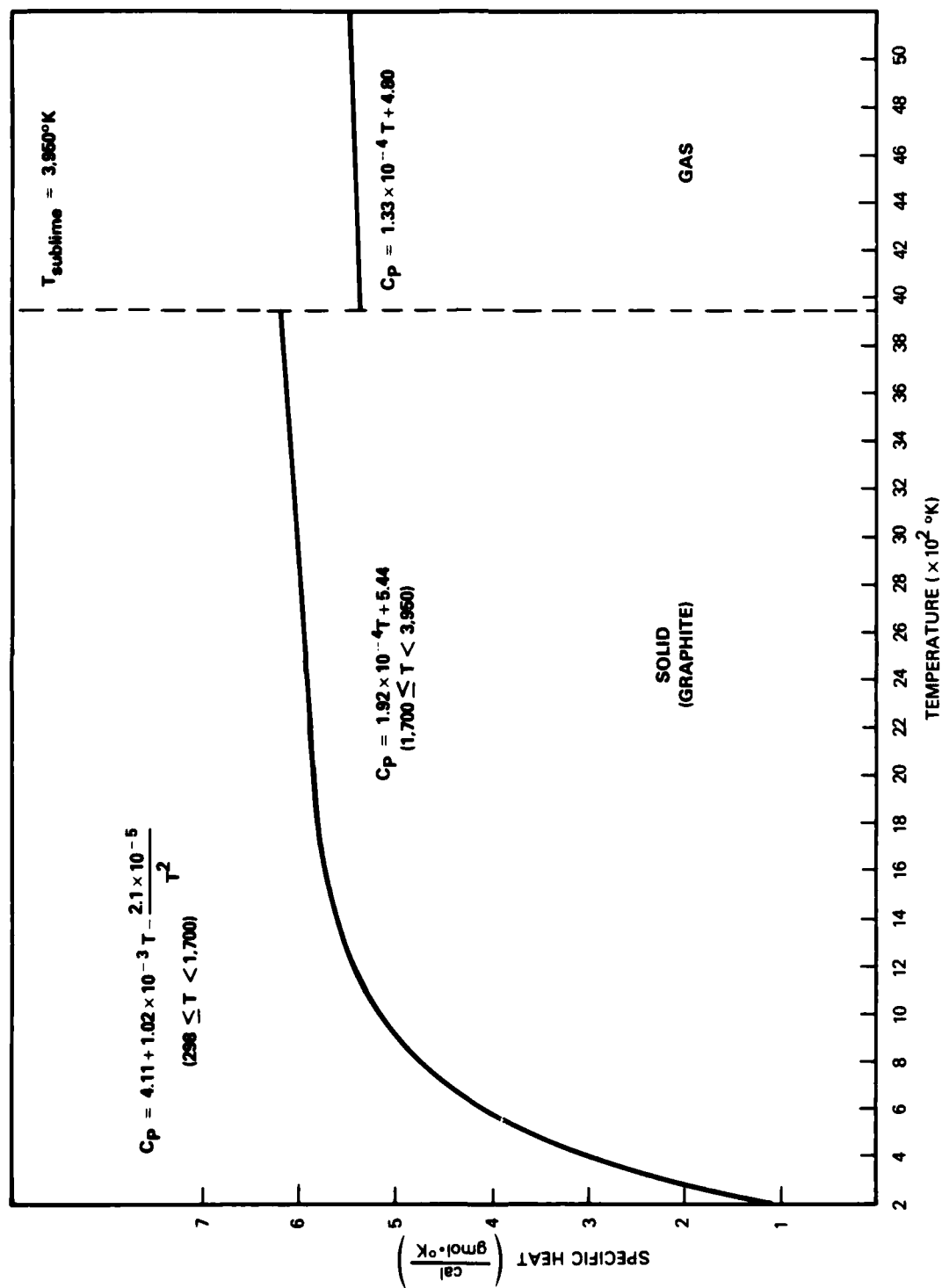


FIGURE D-6.
SPECIFIC HEAT VS TEMPERATURE FOR CARBON

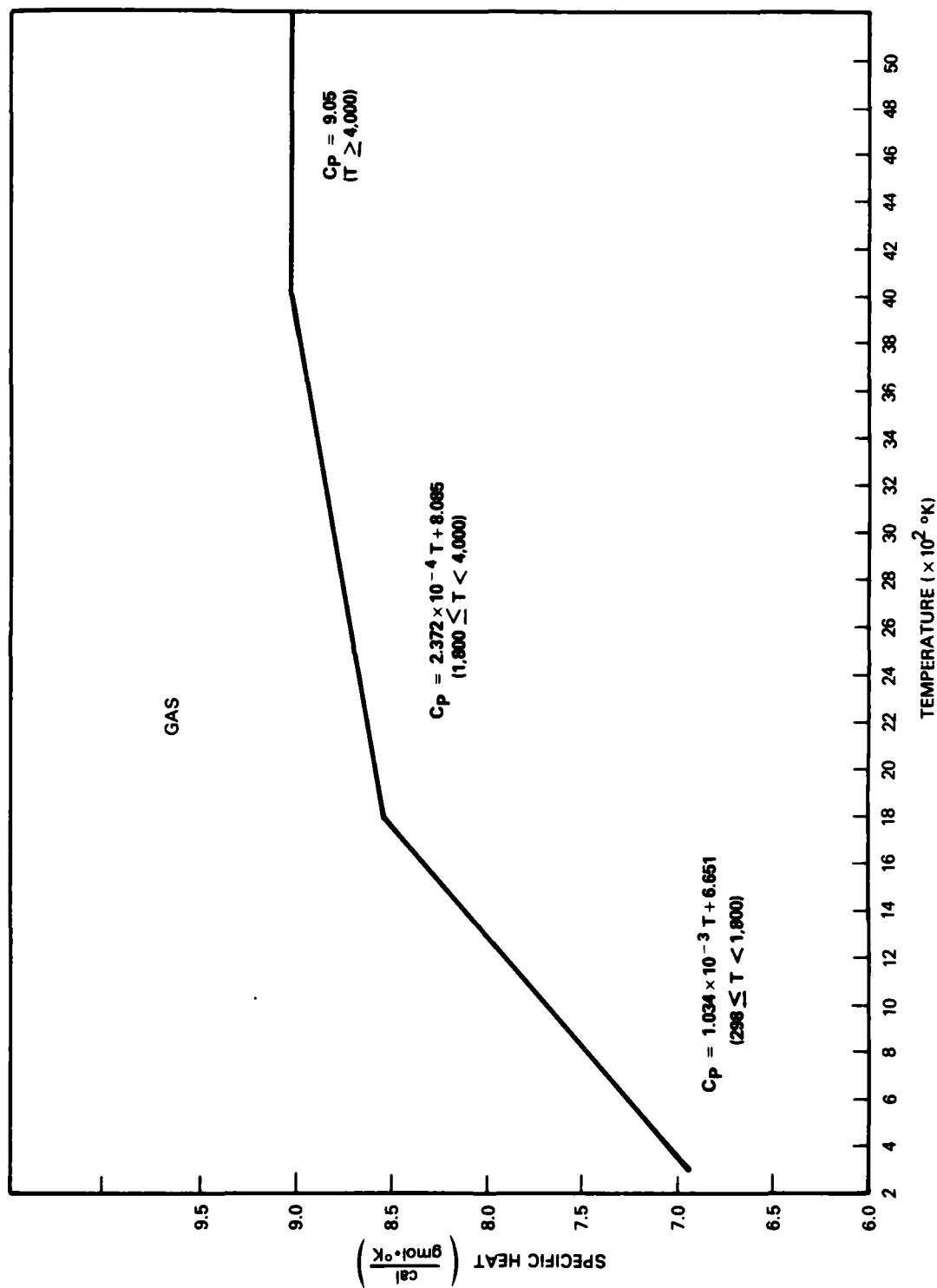


FIGURE D-7.
SPECIFIC HEAT VS TEMPERATURE FOR NITROGEN

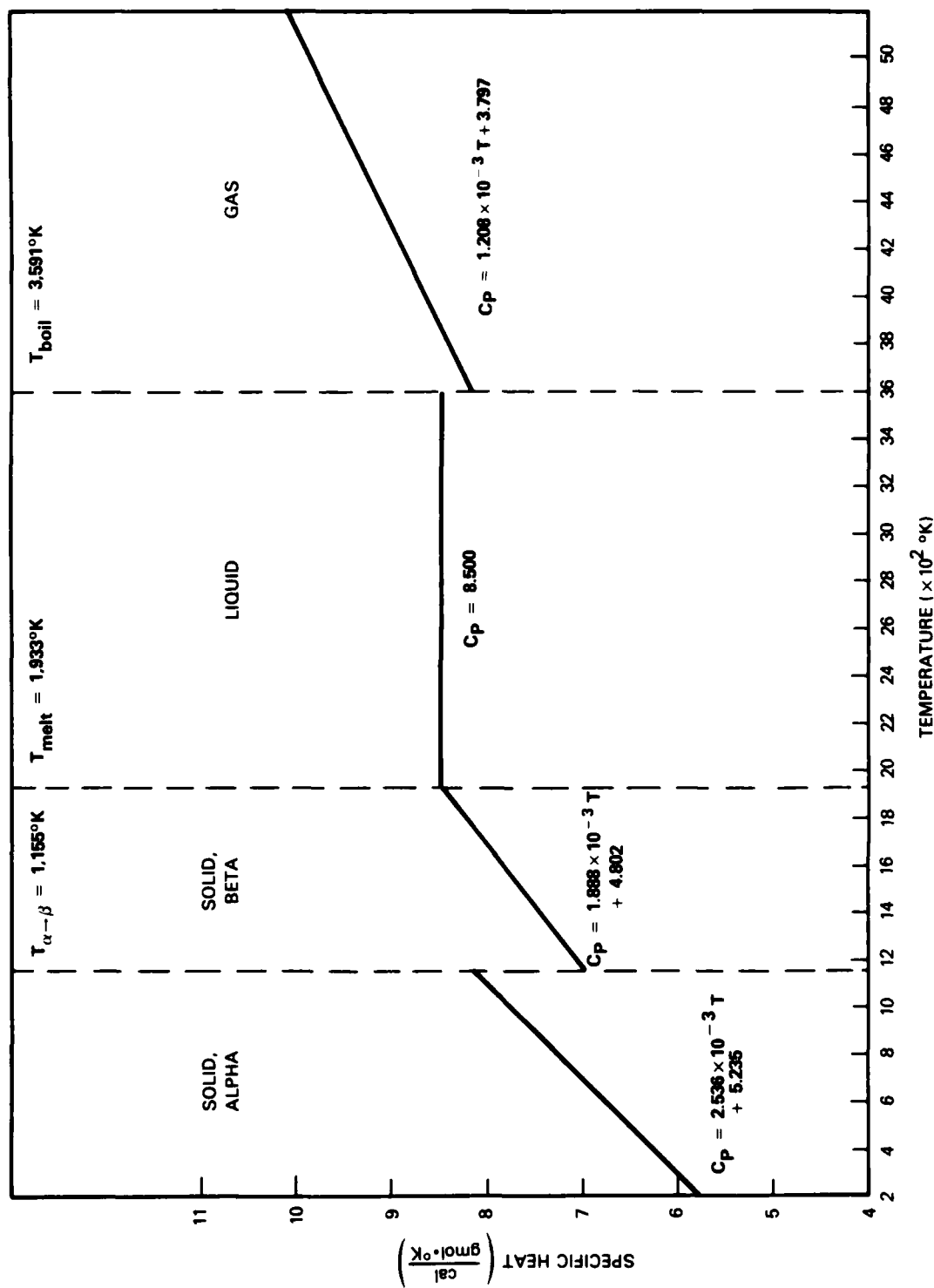


FIGURE D-8.
SPECIFIC HEAT VS TEMPERATURE FOR TITANIUM

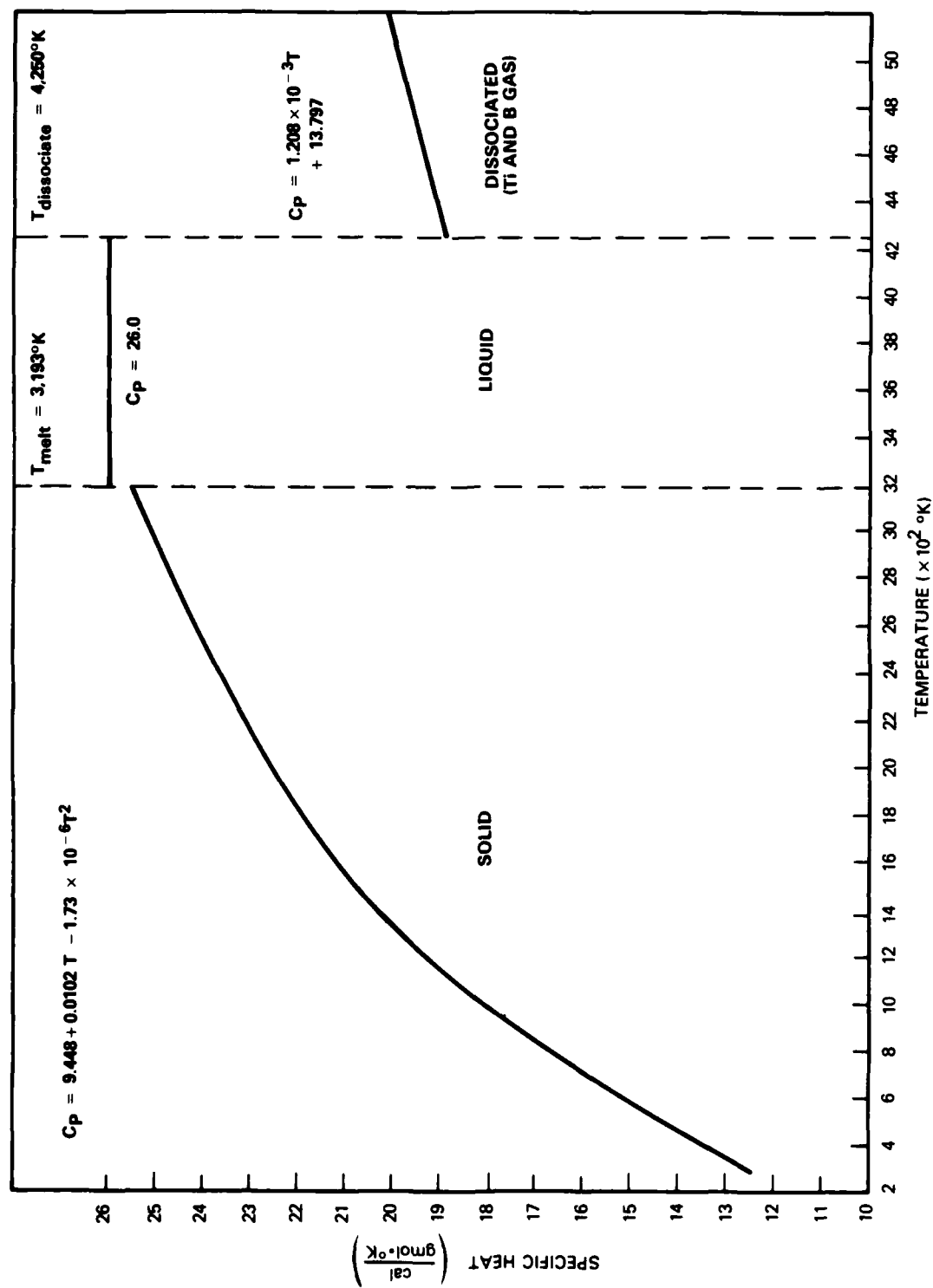


FIGURE D-9.
SPECIFIC HEAT VS TEMPERATURE FOR TITANIUM DIBORIDE (TiB₂)

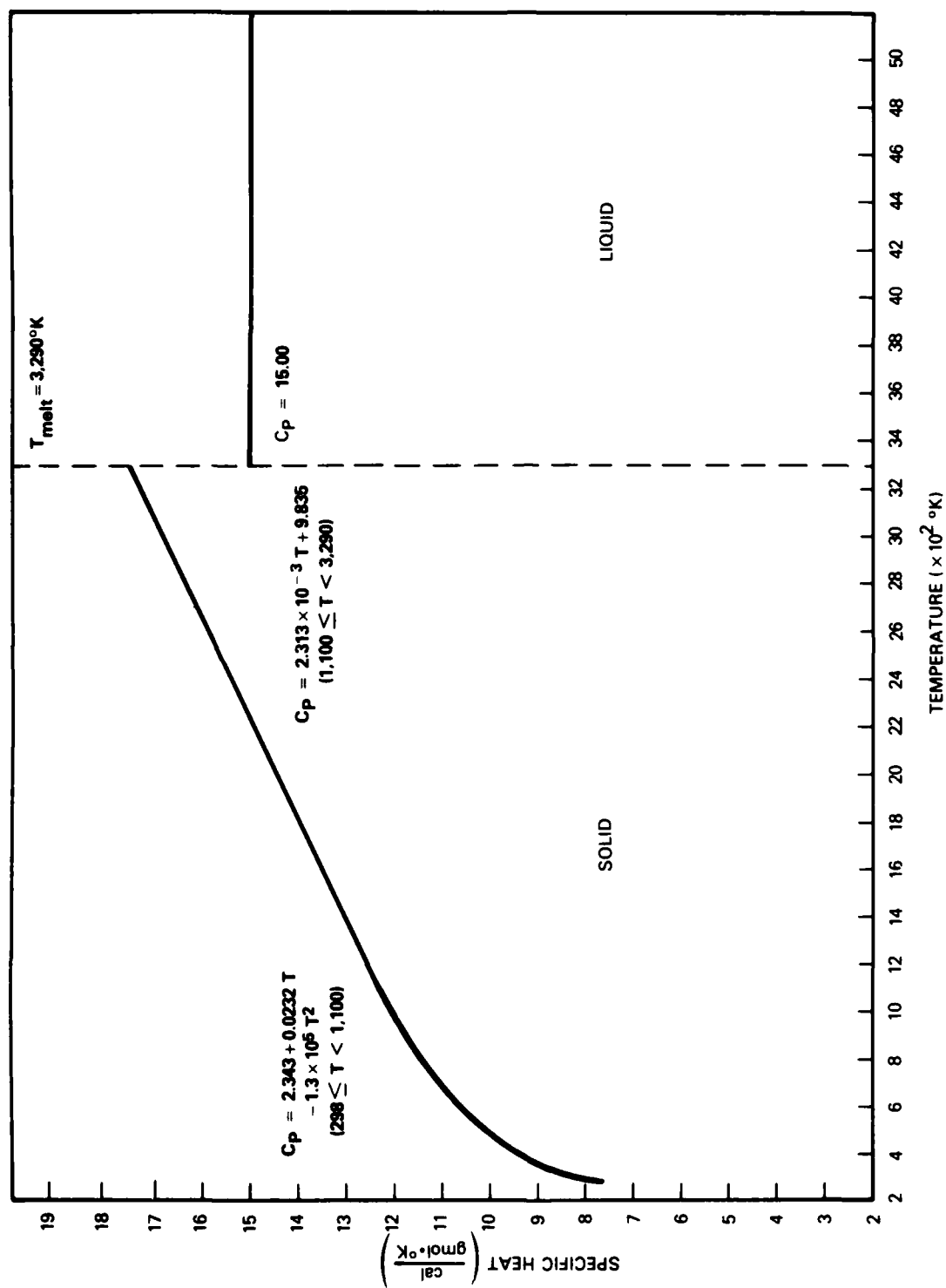


FIGURE D-10.
SPECIFIC HEAT VS TEMPERATURE FOR TITANIUM CARBIDE (TiC)

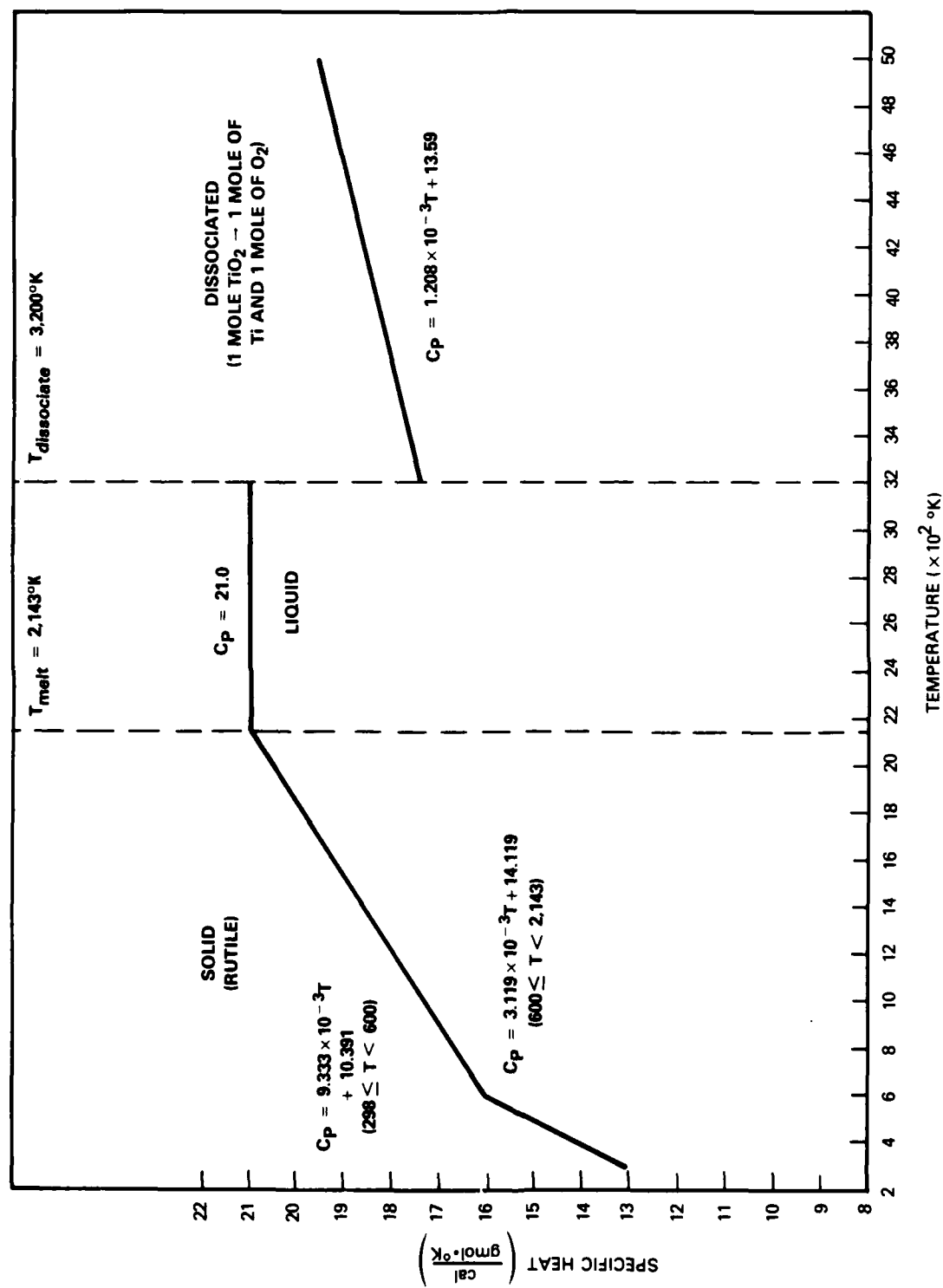


FIGURE D-11.
SPECIFIC HEAT VS TEMPERATURE FOR TITANIUM DIOXIDE (TiO₂)

TABLE D-1
STATE FUNCTIONS DATA FOR ALUMINUM

ALUMINUM

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	10.51	5.91	-2533.00
400.00	609.20	3.53	-2803.00
500.00	1243.00	9.24	-3729.00
600.00	1911.00	11.16	-4785.00
700.00	2614.00	12.24	-5956.00
800.00	3352.00	13.23	-7230.00
900.00	4125.00	14.14	-8599.00
1000.00	4937.00	17.60	-10000.00
1100.00	5756.00	18.32	-11500.00
1200.00	6595.00	18.98	-13060.00
1300.00	7463.00	19.59	-14690.00
1400.00	8340.00	20.15	-16380.00
1500.00	9219.00	20.67	-18120.00
1600.00	10100.00	21.16	-19910.00
1700.00	11000.00	21.62	-21750.00
1800.00	11910.00	22.06	-23640.00
1900.00	12830.00	22.47	-25580.00
2000.00	13760.00	22.86	-27570.00
2100.00	14700.00	23.23	-29610.00
2200.00	15650.00	23.58	-31700.00
2300.00	16610.00	23.92	-33840.00
2400.00	17580.00	24.24	-36030.00
2500.00	18560.00	24.55	-38270.00
2600.00	19540.00	24.85	-40560.00
2700.00	20530.00	25.13	-42900.00
2800.00	21520.00	50.50	-45290.00
2900.00	22510.00	50.68	-47730.00
3000.00	23500.00	50.85	-50220.00
3100.00	24490.00	51.02	-52760.00
3200.00	25480.00	51.13	-55350.00
3300.00	26470.00	51.23	-57990.00
3400.00	27460.00	51.48	-60680.00
3500.00	28450.00	51.63	-63420.00
3600.00	29440.00	51.77	-66210.00
3700.00	30430.00	51.91	-69050.00
3800.00	31420.00	52.06	-71940.00
3900.00	32410.00	52.18	-74880.00

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TABLE D-2
STATE FUNCTIONS DATA FOR ALUMINUM NITRIDE (AlN)

ALUMINUM NITRIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-75990.00	4.36	-77450.00
400.00	-75230.00	7.06	-76050.00
500.00	-74380.00	8.93	-74650.00
600.00	-73450.00	10.61	-73250.00
700.00	-72450.00	12.16	-71850.00
800.00	-71370.00	14.18	-70450.00
900.00	-69940.00	15.51	-69050.00
1000.00	-68790.00	16.72	-67650.00
1100.00	-67630.00	17.83	-66250.00
1200.00	-66420.00	18.88	-64850.00
1300.00	-65240.00	19.83	-63450.00
1400.00	-64050.00	20.71	-62050.00
1500.00	-62860.00	21.53	-60650.00
1600.00	-61670.00	22.30	-59250.00
1700.00	-60480.00	23.02	-57850.00
1800.00	-59290.00	23.71	-56450.00
1900.00	-58080.00	24.36	-55050.00
2000.00	-56880.00	24.97	-53650.00
2100.00	-55670.00	25.56	-52250.00
2200.00	-54470.00	26.12	-50850.00
2300.00	-53260.00	26.66	-49450.00
2400.00	-52050.00	27.18	-48050.00
2500.00	-50830.00	27.67	-46650.00
2600.00	-49620.00	28.15	-45250.00
2700.00	-48400.00	28.51	-43850.00
2800.00	-47180.00	28.84	-42450.00
2900.00	-45950.00	29.26	-41050.00
3000.00	-44720.00	29.47	-39650.00
3100.00	-43480.00	29.58	-38250.00
3200.00	-42240.00	29.68	-36850.00
3300.00	-41000.00	29.77	-35450.00
3400.00	-39750.00	29.86	-34050.00
3500.00	-38500.00	29.94	-32650.00
3600.00	-37250.00	29.91	-31250.00
3700.00	-36000.00	29.79	-29850.00
3800.00	-34750.00	29.65	-28450.00
3900.00	-33500.00	29.12	-27050.00

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TABLE D-3
STATE FUNCTIONS DATA FOR ALUMINUM OXIDE (Al_2O_3)

ALUMINUM OXIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-409400.00	12.28	-4074100.00
400.00	-395300.00	18.40	-4056300.00
500.00	-385900.00	23.74	-4047700.00
600.00	-383300.00	28.40	-4038000.00
700.00	-380600.00	32.51	-4027000.00
800.00	-387900.00	36.17	-4016000.00
900.00	-385100.00	39.49	-4006000.00
1000.00	-382200.00	42.52	-4024700.00
1100.00	-379300.00	45.31	-4029100.00
1200.00	-376300.00	47.91	-4030800.00
1300.00	-373200.00	50.34	-4030700.00
1400.00	-370200.00	52.63	-4030300.00
1500.00	-367300.00	54.79	-4029200.00
1600.00	-3653200.00	57.56	-4028300.00
1700.00	-3639900.00	59.56	-4026700.00
1800.00	-366600.00	61.47	-4027200.00
1900.00	-363200.00	63.28	-4023600.00
2000.00	-349900.00	65.01	-4029900.00
2100.00	-346500.00	66.67	-4036800.00
2200.00	-343000.00	68.27	-4032000.00
2300.00	-339600.00	69.83	-4027100.00
2400.00	-308500.00	83.15	-4026100.00
2500.00	-305000.00	94.56	-4013400.00
2600.00	-301600.00	85.92	-4025000.00
2700.00	-298100.00	87.23	-4033600.00
2800.00	-294700.00	88.49	-4042400.00
2900.00	-291200.00	89.70	-4051300.00
3000.00	-287700.00	90.87	-4060400.00
3100.00	-284300.00	92.01	-4069500.00
3200.00	-280800.00	93.11	-4078600.00
3300.00	225300.00	205.00	-4084400.00
3400.00	227800.00	206.70	-4075000.00
3500.00	230300.00	207.40	-4065700.00
3600.00	232700.00	208.10	-4056000.00
3700.00	235200.00	208.80	-4047400.00
3800.00	237700.00	209.50	-4038300.00
3900.00	240200.00	210.10	-4029300.00

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TABLE D-4
STATE FUNCTIONS DATA FOR BORON

BORON

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	4.37	2.67	-795.40
400.00	331.30	3.60	-1138.00
500.00	739.00	4.51	-1514.00
600.00	1198.00	5.34	-2007.00
700.00	1696.00	6.11	-2560.00
800.00	2226.00	6.82	-3227.00
900.00	2785.00	7.47	-3942.00
1000.00	3427.00	8.03	-4700.00
1100.00	4029.00	8.54	-5522.00
1200.00	4643.00	9.01	-6406.00
1300.00	5271.00	9.46	-7350.00
1400.00	5912.00	9.89	-8359.00
1500.00	6566.00	10.31	-9438.00
1600.00	7233.00	10.73	-10587.00
1700.00	7913.00	11.11	-11760.00
1800.00	8645.00	11.47	-12990.00
1900.00	9348.00	11.82	-14260.00
2000.00	10050.00	12.15	-15580.00
2100.00	10770.00	12.48	-16940.00
2200.00	11490.00	12.79	-18350.00
2300.00	12210.00	13.29	-19810.00
2400.00	12940.00	13.57	-21330.00
2500.00	13670.00	13.85	-22910.00
2600.00	14400.00	14.11	-24550.00
2700.00	15130.00	14.37	-26250.00
2800.00	15860.00	14.62	-28010.00
2900.00	16590.00	14.86	-29830.00
3000.00	17320.00	15.09	-31710.00
3100.00	18050.00	15.31	-33650.00
3200.00	18780.00	15.53	-35650.00
3300.00	19510.00	15.74	-37710.00
3400.00	20240.00	15.95	-39830.00
3500.00	20970.00	16.15	-42010.00
3600.00	21700.00	16.34	-44250.00
3700.00	22430.00	16.53	-46550.00
3800.00	23160.00	16.73	-48910.00
3900.00	23890.00	16.93	-51330.00
4000.00	24620.00	17.13	-53810.00

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TABLE D-5
STATE FUNCTIONS DATA FOR BORON OXIDE (B_2O_3)

BORON OXIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-303600.00	12.96	-307500.00
400.00	-302000.00	17.69	-305000.00
500.00	-300000.00	21.97	-311000.00
600.00	-297800.00	25.98	-313400.00
700.00	-295300.00	29.80	-316200.00
800.00	-287000.00	41.26	-320000.00
900.00	-283800.00	44.99	-324300.00
1000.00	-230700.00	48.30	-329000.00
1100.00	-277600.00	51.28	-334000.00
1200.00	-274500.00	53.97	-339200.00
1300.00	-271400.00	56.43	-344700.00
1400.00	-268300.00	58.70	-350500.00
1500.00	-265300.00	60.81	-356500.00
1600.00	-262200.00	62.78	-362700.00
1700.00	-259200.00	64.63	-369000.00
1800.00	-256100.00	65.37	-375500.00
1900.00	-253100.00	68.02	-382300.00
2000.00	-250000.00	69.59	-389200.00
2100.00	-247000.00	71.08	-396200.00
2200.00	-243900.00	72.50	-403400.00
2300.00	-240900.00	73.86	-410700.00
2400.00	-150700.00	112.80	-421400.00
2500.00	-148200.00	113.80	-432800.00
2600.00	-145700.00	114.80	-444200.00
2700.00	-143100.00	115.30	-455700.00
2800.00	-140600.00	116.70	-467400.00
2900.00	-138100.00	117.60	-479100.00
3000.00	-135600.00	118.40	-490900.00
3100.00	-133000.00	119.30	-502800.00
3200.00	-130500.00	120.10	-514700.00
3300.00	-127900.00	120.90	-526800.00
3400.00	-125400.00	121.60	-538900.00
3500.00	-122900.00	122.40	-551100.00
3600.00	-120300.00	123.10	-563400.00
3700.00	-117800.00	123.90	-575700.00
3800.00	-115200.00	124.40	-588100.00
3900.00	-112700.00	125.10	-600500.00

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TABLE D-6
STATE FUNCTIONS DATA FOR CARBON

CARBON

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	3.90	1.32	-391.60
400.00	275.60	2.09	-561.00
500.00	627.50	2.87	-310.00
600.00	1025.00	3.60	-1134.00
700.00	1452.00	4.26	-1527.00
800.00	1902.00	4.86	-1984.00
900.00	2370.00	5.41	-2497.00
1000.00	2855.00	5.92	-3064.00
1100.00	3354.00	6.39	-3680.00
1200.00	3866.00	6.84	-4342.00
1300.00	4391.00	7.26	-5047.00
1400.00	4929.00	7.66	-5793.00
1500.00	5477.00	8.04	-6578.00
1600.00	6038.00	8.40	-7400.00
1700.00	6696.00	8.76	-8198.00
1800.00	7274.00	9.09	-9090.00
1900.00	7854.00	9.40	-10020.00
2000.00	8435.00	9.70	-10970.00
2100.00	9018.00	9.99	-11950.00
2200.00	9604.00	10.26	-12970.00
2300.00	10190.00	10.52	-14010.00
2400.00	10780.00	10.77	-15070.00
2500.00	11370.00	11.01	-16160.00
2600.00	11960.00	11.25	-17270.00
2700.00	12560.00	11.47	-18410.00
2800.00	13160.00	11.69	-19570.00
2900.00	13750.00	11.90	-20750.00
3000.00	14350.00	12.10	-21950.00
3100.00	14960.00	12.30	-23170.00
3200.00	15560.00	12.49	-24410.00
3300.00	16170.00	12.68	-25660.00
3400.00	16780.00	12.86	-26940.00
3500.00	17390.00	13.04	-28240.00
3600.00	18000.00	13.21	-29550.00
3700.00	18610.00	13.38	-30880.00
3800.00	19230.00	13.54	-32230.00
3900.00	19850.00	13.70	-33590.00

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TABLE D-7
STATE FUNCTIONS DATA FOR NITROGEN

NITROGEN

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	12.83	45.81	-16785.00
400.00	714.10	47.83	-16420.00
500.00	1426.00	49.42	-16020.00
600.00	2148.00	50.73	-15590.00
700.00	2880.00	51.95	-15120.00
800.00	3623.00	52.85	-14620.00
900.00	4376.00	53.74	-14090.00
1000.00	5139.00	54.54	-13530.00
1100.00	5913.00	55.29	-12940.00
1200.00	6697.00	55.95	-12320.00
1300.00	7491.00	56.53	-11670.00
1400.00	8296.00	57.03	-11000.00
1500.00	9111.00	57.45	-10310.00
1600.00	9935.00	57.79	-9600.00
1700.00	10770.00	58.05	-8870.00
1800.00	11710.00	58.22	-8120.00
1900.00	12650.00	58.34	-7360.00
2000.00	13410.00	58.42	-6590.00
2100.00	14270.00	58.46	-5810.00
2200.00	15130.00	58.48	-5020.00
2300.00	15990.00	58.48	-4220.00
2400.00	16860.00	58.46	-3410.00
2500.00	17720.00	58.42	-2590.00
2600.00	18590.00	58.36	-1760.00
2700.00	19460.00	58.28	-920.00
2800.00	20340.00	58.18	900.00
2900.00	21210.00	58.06	1620.00
3000.00	22090.00	57.92	2340.00
3100.00	22970.00	57.76	3060.00
3200.00	23860.00	57.58	3780.00
3300.00	24740.00	57.39	4500.00
3400.00	25630.00	57.18	5220.00
3500.00	26520.00	56.95	5940.00
3600.00	27410.00	56.70	6660.00
3700.00	28310.00	56.43	7380.00
3800.00	29210.00	56.14	8100.00
3900.00	30110.00	55.83	8820.00

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TABLE D-8
STATE FUNCTIONS DATA FOR TITANIUM

TITANIUM

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	10.62	7.36	-2197.00
400.00	622.90	9.12	-2025.00
500.00	1260.00	10.54	-1810.00
600.00	1923.00	11.75	-1512.00
700.00	2612.00	12.81	-1135.00
800.00	3326.00	13.76	-768.00
900.00	4065.00	14.63	-410.00
1000.00	4829.00	15.44	-56.00
1100.00	5619.00	16.19	-121.00
1200.00	6436.00	16.89	-181.00
1300.00	7290.00	17.54	-236.00
1400.00	8181.00	18.15	-286.00
1500.00	9110.00	18.72	-331.00
1600.00	10087.00	19.26	-371.00
1700.00	11113.00	19.77	-406.00
1800.00	12189.00	20.25	-437.00
1900.00	13316.00	20.70	-463.00
2000.00	14495.00	21.13	-485.00
2100.00	15827.00	21.53	-503.00
2200.00	17313.00	21.91	-517.00
2300.00	18964.00	22.27	-527.00
2400.00	20791.00	22.61	-533.00
2500.00	22805.00	22.93	-536.00
2600.00	24917.00	23.24	-536.00
2700.00	27138.00	23.53	-532.00
2800.00	29469.00	23.81	-525.00
2900.00	31921.00	24.07	-515.00
3000.00	34495.00	24.32	-502.00
3100.00	37193.00	24.56	-486.00
3200.00	40017.00	24.79	-467.00
3300.00	42969.00	25.00	-445.00
3400.00	46051.00	25.20	-420.00
3500.00	49265.00	25.39	-392.00
3600.00	52613.00	25.57	-361.00
3700.00	56107.00	25.74	-327.00
3800.00	59749.00	25.90	-290.00
3900.00	63541.00	26.05	-250.00

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TABLE D-9
STATE FUNCTIONS DATA FOR TITANIUM DIBORIDE (TiB₂)

TITANIUM DIBORIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-66360.00	5.63	-66360.00
400.00	-66520.00	13.31	-66520.00
500.00	-64210.00	13.36	-70090.00
600.00	-62760.00	16.91	-72360.00
700.00	-61220.00	18.37	-74060.00
800.00	-59610.00	20.52	-76030.00
900.00	-57920.00	22.51	-78180.00
1000.00	-56170.00	24.36	-80530.00
1100.00	-54340.00	26.10	-82060.00
1200.00	-52450.00	27.74	-83740.00
1300.00	-50500.00	29.30	-85500.00
1400.00	-48500.00	30.79	-87350.00
1500.00	-46440.00	32.21	-89280.00
1600.00	-44330.00	33.57	-91290.00
1700.00	-42170.00	34.88	-93380.00
1800.00	-39970.00	36.14	-95550.00
1900.00	-37730.00	37.35	-97800.00
2000.00	-35460.00	38.51	-100120.00
2100.00	-33150.00	39.64	-102520.00
2200.00	-30810.00	40.73	-104990.00
2300.00	-28450.00	41.78	-107530.00
2400.00	-26060.00	42.79	-110140.00
2500.00	-23650.00	43.78	-112810.00
2600.00	-21230.00	44.73	-115550.00
2700.00	-18800.00	45.64	-118360.00
2800.00	-16360.00	46.53	-121240.00
2900.00	-13910.00	47.39	-124190.00
3000.00	-11460.00	48.22	-127210.00
3100.00	-9010.00	49.02	-130300.00
3200.00	-6560.00	50.79	-133460.00
3300.00	-4110.00	52.52	-136690.00
3400.00	-1660.00	54.21	-139990.00
3500.00	800.00	55.87	-143360.00
3600.00	3210.00	57.50	-146800.00
3700.00	5420.00	59.10	-150310.00
3800.00	7630.00	60.67	-153890.00
3900.00	9840.00	62.21	-157540.00
4000.00	12050.00	63.73	-161260.00

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TABLE D-10
STATE FUNCTIONS DATA FOR TITANIUM CARBIDE (TiC)

TITANIUM CARBIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-44000.00	5.84	-45730.00
400.00	-43110.00	8.38	-45470.00
500.00	-42100.00	10.64	-45220.00
600.00	-40980.00	12.67	-44980.00
700.00	-39790.00	14.50	-44740.00
800.00	-38550.00	16.16	-44500.00
900.00	-37280.00	17.65	-44270.00
1000.00	-36020.00	18.98	-44050.00
1100.00	-34960.00	19.96	-43840.00
1200.00	-33710.00	21.05	-43640.00
1300.00	-32440.00	22.37	-43450.00
1400.00	-31140.00	23.83	-43270.00
1500.00	-29820.00	23.94	-43100.00
1600.00	-28480.00	24.80	-42940.00
1700.00	-27120.00	25.63	-42790.00
1800.00	-25730.00	26.42	-42650.00
1900.00	-24320.00	27.19	-42520.00
2000.00	-22880.00	27.92	-42400.00
2100.00	-21430.00	28.63	-42290.00
2200.00	-19950.00	29.32	-42190.00
2300.00	-18440.00	29.99	-42100.00
2400.00	-16920.00	30.64	-42020.00
2500.00	-15370.00	31.27	-41950.00
2600.00	-13790.00	31.39	-41890.00
2700.00	-12200.00	32.49	-41840.00
2800.00	-10580.00	33.08	-41800.00
2900.00	-8925.00	33.66	-41770.00
3000.00	-7259.00	34.22	-41750.00
3100.00	-5583.00	34.78	-41740.00
3200.00	-3859.00	35.32	-41740.00
3300.00	14410.00	40.79	-41750.00
3400.00	15910.00	41.23	-41760.00
3500.00	17410.00	41.67	-41770.00
3600.00	13910.00	42.09	-41780.00
3700.00	20410.00	42.50	-41790.00
3800.00	21910.00	42.90	-41800.00
3900.00	23410.00	43.29	-41810.00

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TABLE D-11
STATE FUNCTIONS DATA FOR TITANIUM DIOXIDE (TiO₂)

TITANIUM OXIDE

T (K)	ENTHALPY	ENTROPY	GIBBS
300.00	-225600.00	12.11	-225400.00
400.00	-224400.00	13.03	-224200.00
500.00	-222900.00	13.99	-222600.00
600.00	-221300.00	22.35	-221000.00
700.00	-219700.00	24.33	-219400.00
800.00	-218000.00	27.33	-217600.00
900.00	-216300.00	29.31	-215800.00
1000.00	-214600.00	30.31	-214000.00
1100.00	-212900.00	32.46	-212200.00
1200.00	-211100.00	34.33	-210400.00
1300.00	-209300.00	35.46	-208600.00
1400.00	-207500.00	36.33	-206800.00
1500.00	-205600.00	38.09	-204900.00
1600.00	-203700.00	39.31	-203000.00
1700.00	-201800.00	40.48	-201100.00
1800.00	-199800.00	41.60	-199200.00
1900.00	-197800.00	42.68	-197300.00
2000.00	-195800.00	43.71	-195300.00
2100.00	-193800.00	44.71	-193300.00
2200.00	-191800.00	53.36	-191300.00
2300.00	-189800.00	54.29	-189300.00
2400.00	-187800.00	55.19	-187300.00
2500.00	-185800.00	56.04	-185300.00
2600.00	-183800.00	56.87	-183300.00
2700.00	-181800.00	57.66	-181300.00
2800.00	-179800.00	58.42	-179300.00
2900.00	-177800.00	59.16	-177300.00
3000.00	-175800.00	59.87	-175300.00
3100.00	-173800.00	60.56	-173300.00
3200.00	-171800.00	61.24	-171300.00
3300.00	-169800.00	126.63	-169300.00
3400.00	-167800.00	126.73	-167300.00
3500.00	-165800.00	126.83	-165300.00
3600.00	-163800.00	127.00	-163300.00
3700.00	-161800.00	127.13	-161300.00
3800.00	-159800.00	127.23	-159300.00
3900.00	-157800.00	127.33	-157300.00
4000.00	-155800.00	127.43	-155300.00

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