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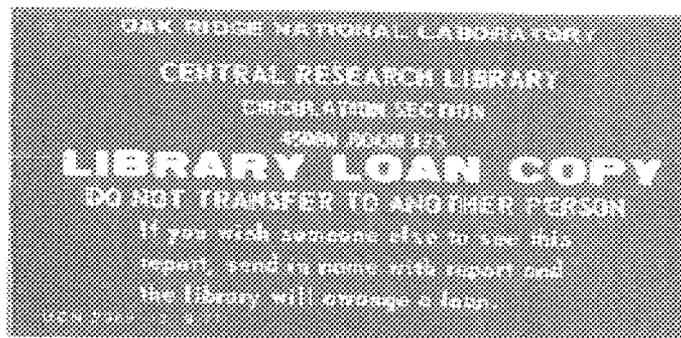
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Chemical Vapor Deposition in the Silicon-Carbon and Boron-Carbon-Nitrogen Systems

T. M. Besmann



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BORON-CARBON-NITROGEN SYSTEMS

T. M. Besmann

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CHEMICAL VAPOR DEPOSITION IN THE SILICON-CARBON AND
BORON-CARBON-NITROGEN SYSTEMS*

T. M. Besmann

ABSTRACT

The chemical vapor deposition of SiC from methyl-trichlorosilane was studied using a combination of measurement and analytical techniques. Equilibrium analysis and mass spectrometric measurements were used to identify gas-phase species and determine their concentrations. Analysis of kinetic data coupled with a thermokinetic assessment allowed determination of rate-limiting mechanisms.

The preparation of a two-phase coating of B₄C-BN was addressed as a potential wear coating, because of its likelihood of having a high fracture toughness resulting from its composite nature and inherent lubrication resulting from the presence of BN. Equilibrium analysis identified appropriate deposition conditions; however, deposited coatings were found to be single-phase BN with a high degree of substitution of carbon for nitrogen.

INTRODUCTION

This report is an account of work performed on the Energy Conversion and Utilization Technologies Program from October 1, 1985, to September 30, 1987. The efforts are divided into two related areas. The first area was a study of the fundamental, rate-limiting processes in the deposition of SiC coatings. This included thermochemical analysis and experimental determination of gas phase compositions. The second area was an investigation of the preparation of two-phase B₄C-BN as a potential wear coating. Equilibrium analysis was performed to determine likely deposition conditions, and coatings were prepared and analyzed.

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SiC DEPOSITION PROCESSES

The understanding of rate-limiting processes in the chemical vapor deposition (CVD) of SiC from methyltrichlorosilane (MTS) has been developed using a combination of measurement and analytical techniques. These involve equilibrium analysis, mass spectrometric measurements of gas-phase species in the CVD reactor, analysis of kinetic data, and thermokinetic assessment.

EQUILIBRIUM ANALYSIS

An equilibrium analysis was performed for the system of MTS diluted with either hydrogen or an inert gas. Individual calculations were performed utilizing the SOLGASMIX-PV computer code (Besmann, 1977), considering 81 gaseous species and 6 condensed phases. Thermodynamic data were obtained for all species from the JANAF Thermochemical Tables, with the exception that those for MTS were derived from Aleman et al. (1985). The calculations indicated equilibrium partial pressures and stable condensed phases. An example of these results is shown in Fig. 1, which is a plot of reactant and equilibrium partial pressures as a function of temperature. It is apparent from the calculations that MTS is a relatively unstable species and that it readily decomposes to SiCl_4 and CH_4 . In addition, single-phase SiC forms under all the conditions explored, with HCl the expected product gas.

MASS SPECTROMETRIC MEASUREMENTS

The deviation from equilibrium in the SiC CVD system must be determined experimentally. This was accomplished by measurement of species partial pressures in the CVD reactor, using mass spectrometry. A simple, but versatile, CVD system was constructed for the deposition of SiC from MTS and is shown schematically in Fig. 2. A probe for a quadrupole mass spectrometer was inserted into the reactor on the exhaust side of the system. Measurements made continuously during SiC CVD runs gave generally consistent concentration values throughout their durations.

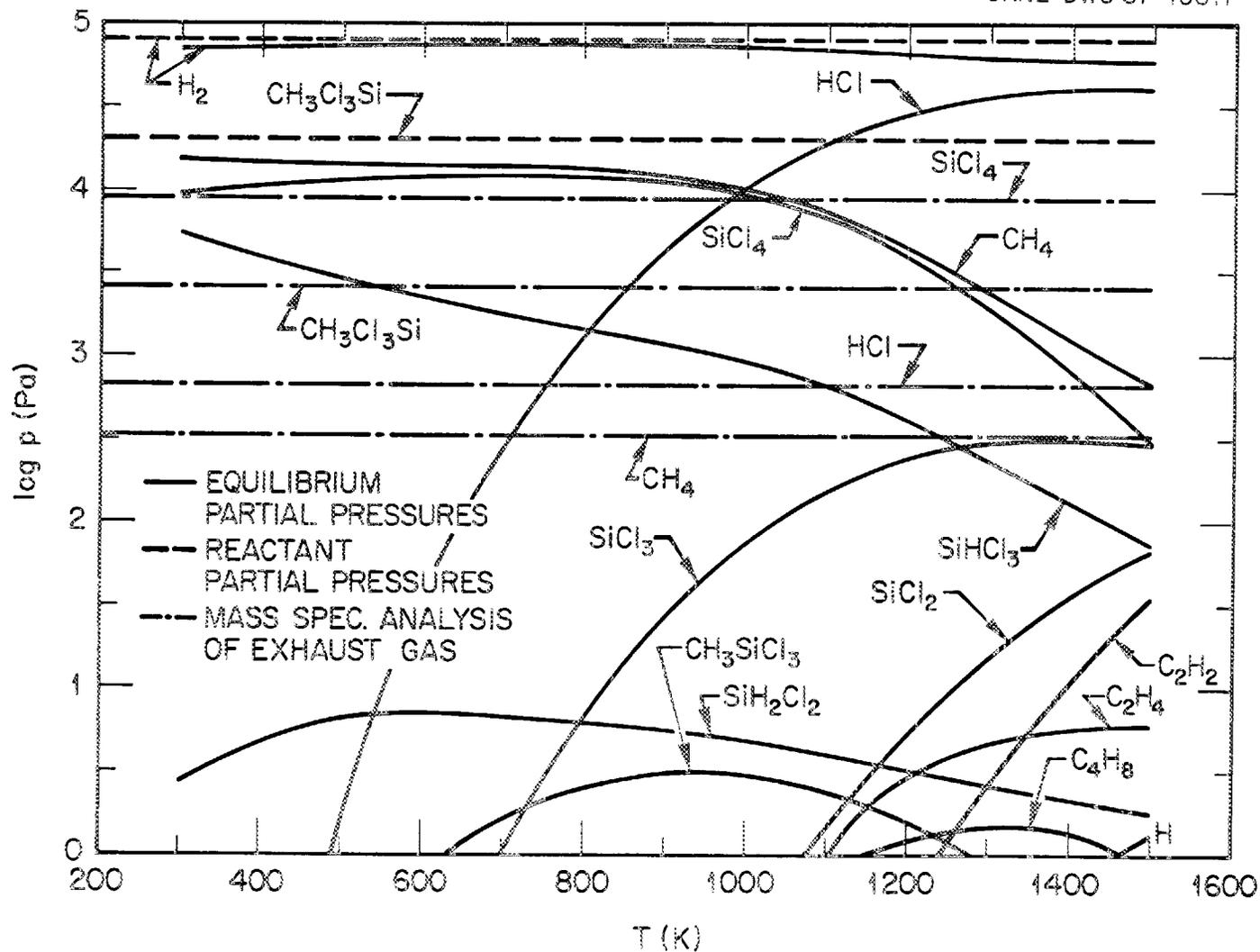
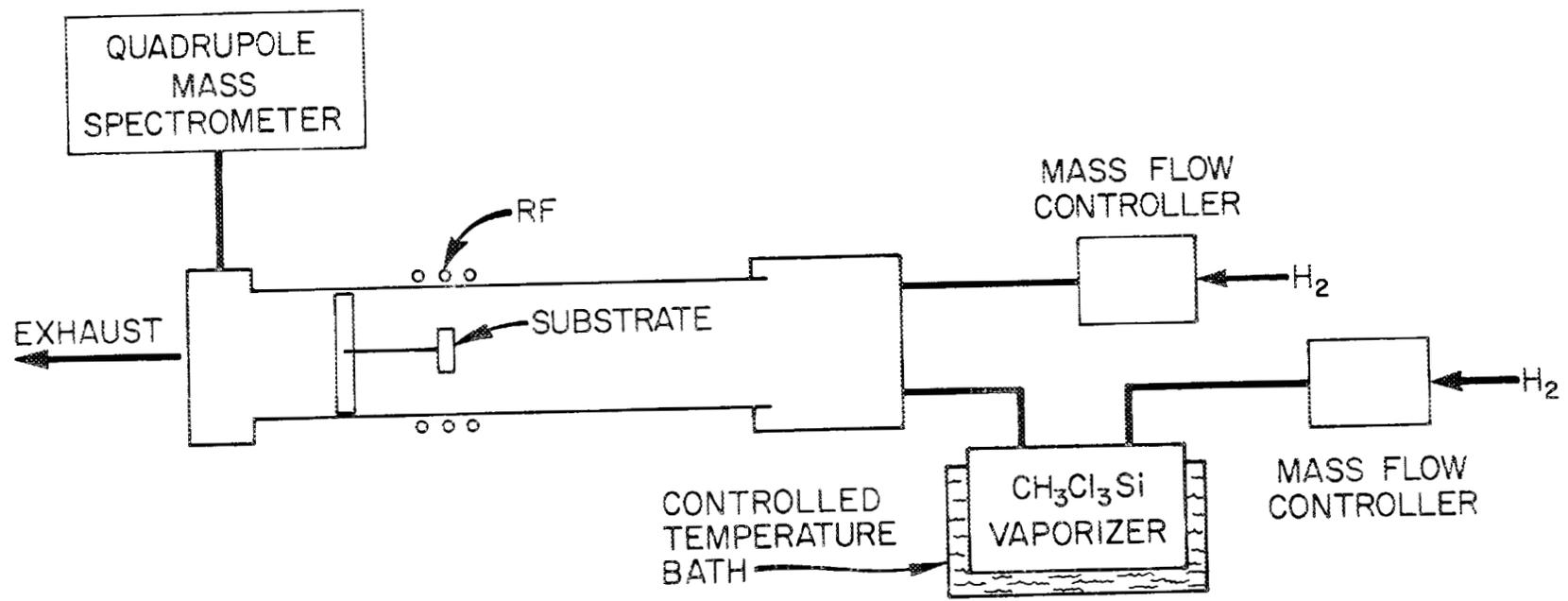


Fig. 1. Species vapor pressures for the reactant system of MTS in hydrogen, showing the reactant, calculated equilibrium, and mass spectrometrically measured (1300 K substrate temperature) partial pressures.



4

Fig. 2. Cold-wall reactor for the CVD of SiC from MTS and hydrogen. A quadrupole mass spectrometer is installed to sample the exhaust gas.

The major species identified were MTS, SiCl_4 , CH_4 , and HCL; their measured pressures at 1300 K are shown in Fig. 1. The most significant difference between the calculated and measured values was in the pressure of MTS. Although thermodynamically the species should decompose to an extremely low partial pressure, it remained present at significant concentrations. It is likely that much of the gas stream did not heat sufficiently to overcome the kinetic barrier to MTS decomposition, since only the 2.5-cm-diam graphite substrate was at an elevated temperature in the cold-wall CVD reactor used (Fig. 2).

In an attempt to obtain partial pressures more indicative of the CVD reaction mechanism, the mass spectrometer probe was inserted into a hole that extended through the graphite substrate so that the probe entrance was flush with the front surface of the substrate. Vapor species were thus sampled directly from the CVD growth surface. The results, however, closely matched those obtained from sampling the exhaust gases, indicating that either the compositions were similar or that any high-temperature species did not remain stable during transport through the capillary probe to the mass spectrometer vacuum chamber.

The results shown in Fig. 1 confirm, as noted above, that MTS is an unstable reactant that quickly decomposes to SiCl_4 and CH_4 at elevated temperatures. In essence, these latter species are thus the CVD reactants which reach the substrate surface and thus are likely to be important in discerning the rate-limiting mechanisms.

ANALYSIS OF KINETIC DATA

Another basis for this mechanistic study is the development of kinetic parameters from deposition rate data. For CVD systems this is inherently difficult, since gas-phase diffusion of reactants through a boundary layer above the substrate is typically rate controlling. Limiting surface or gas-phase reactions, which are potentially more important than gas-phase diffusion with regard to growth habit and composition mechanisms, are rapid compared with the gas-phase diffusion, and thus they are masked.

Brennfleck et al. (1984) have determined rate data in the absence of gas-phase diffusion effects, by depositing SiC on a graphite wire that was

vibrating. The relatively high velocity of the vibrating wire results in an exceptionally small boundary layer between the bulk gas and the substrate, allowing gas-phase diffusion to be rapid and deposition rates to be limited by other CVD mechanisms. Brennfleck et al. determined data for the CVD of SiC from MTS diluted with either hydrogen or argon, and the results are shown in Figs. 3 and 4.

In one set of measurements, deposition rates were determined as a function of MTS concentration. The linear behavior with respect to MTS partial pressure in the systems diluted with hydrogen or argon indicates that deposition is first order with respect to MTS concentration for both. Brennfleck et al. (1984) also determined that the logarithms of the deposition rates were linear with respect to reciprocal absolute temperature (Figs. 3 and 4), and thus the Arrhenius relationship was usable (Benson, 1976). The slope of the plots yielded activation energies, which they reported as 120 and 400 kJ/mol for MTS plus hydrogen and for MTS plus argon, respectively. The difference in the activation energies is, naturally, a reflection of the difference in the deposition rates, and it is thus apparent that hydrogen catalyzes the CVD of SiC from MTS.

The data determined by Brennfleck et al. (1984) were refit to an Arrhenius relationship that included both the first-order dependence on MTS concentration and a frequency factor:

$$r = C_{\text{MTS}} A \exp(-E/RT) , \quad (1)$$

where r is the deposition rate, C_{MTS} is the MTS concentration, A is the frequency factor, E is the activation energy, R is the ideal gas law constant, and T is the absolute temperature. It is apparent from the comparative results shown in Table 1 that the frequency factors for the two systems are, like the activation energies, significantly different. As expected, the activation energies computed by Brennfleck et al. are equivalent to those recalculated here.

The magnitude of the frequency factor has been observed to be descriptive of the nature of the rate-limiting process. Baetzold and Somorjai (1976) have correlated experimentally determined frequency factors with various processes. When compared with the correlation, the values in Table 1 indicate that the deposition of SiC from MTS in the presence of

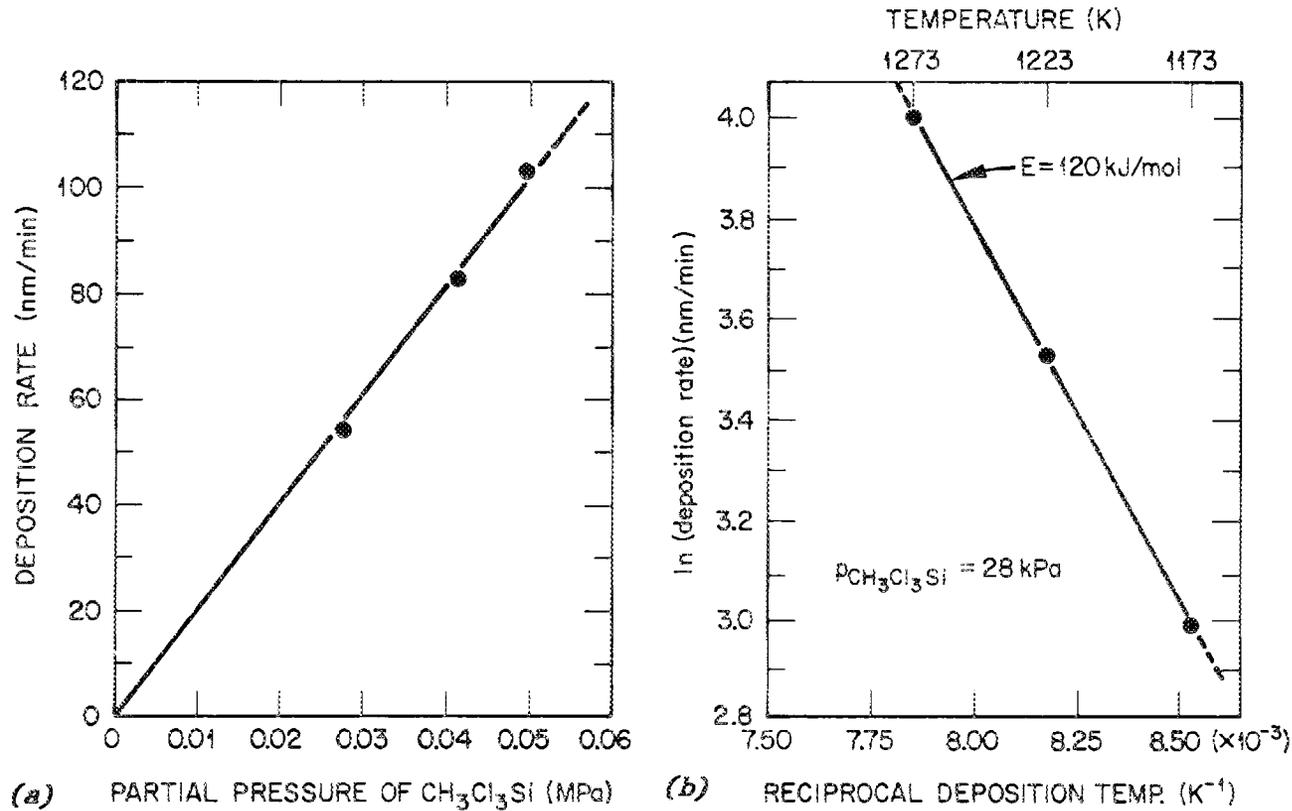


Fig. 3. Deposition rate data of Brennfleck et al. (1984) for the CVD of SiC from MTS in the presence of hydrogen, showing (a) the linear dependence of deposition rate on MTS concentration and (b) the linear behavior of the logarithm of the deposition rate vs reciprocal absolute temperature, with the activation energy derived from the slope.

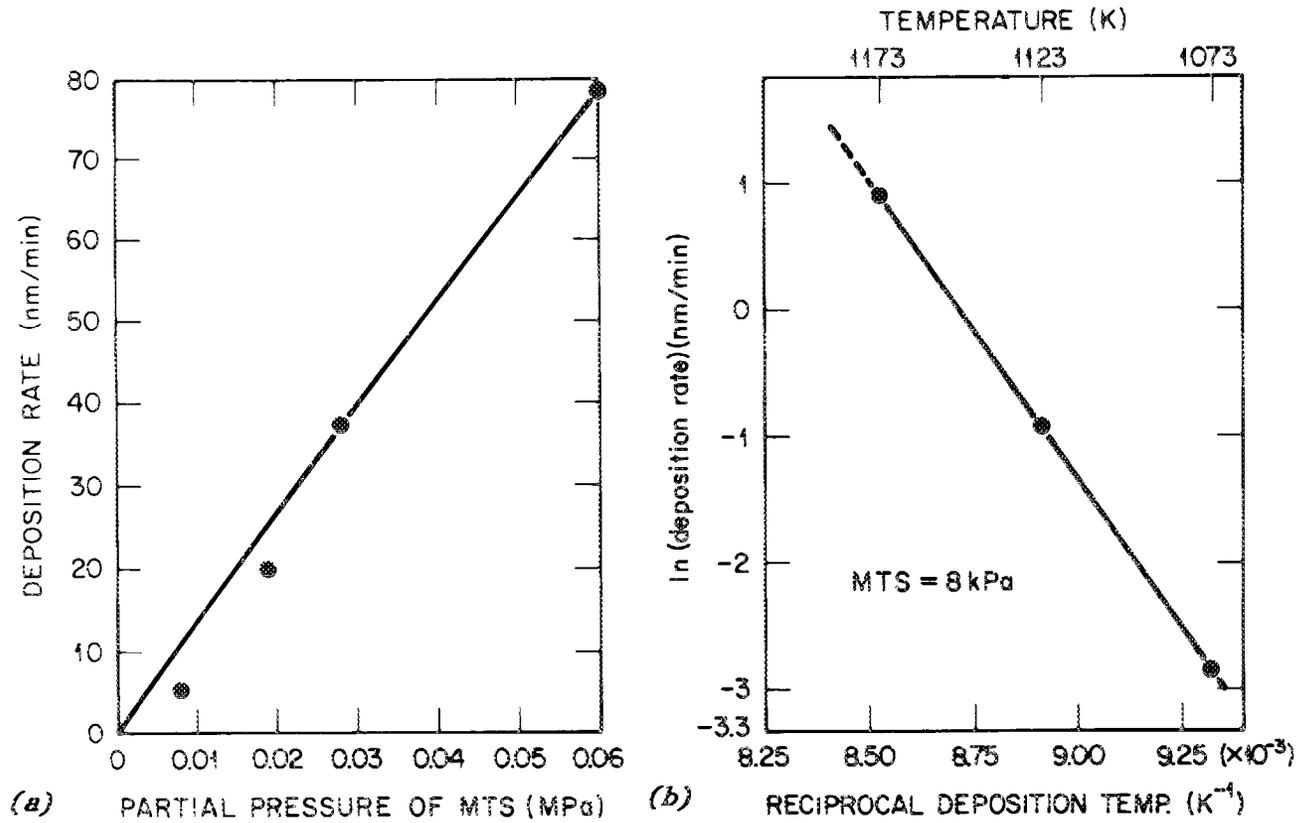


Fig. 4. Deposition rate data of Brennfleck et al. (1984) for the CVD of SiC from MTS diluted with argon, showing (a) the linear dependence of deposition rate on MTS concentration and (b) the linear behavior of the logarithm of the deposition rate vs reciprocal absolute temperature, with the activation energy derived from the slope.

Table 1. Derived activation energies of Brennfleck et al. (1984) and the activation energies and frequency factors rederived from their data

Diluent	Brennfleck et al.	Recalculated	
	E (kJ/mol)	E (kJ/mol)	Ln A
H ₂	120	134 ± 7	10.9 ± 0.7
Ar	400	405 ± 23	37.7 ± 2.5

hydrogen is limited by adsorption or surface diffusion, whereas the deposition of SiC from MTS diluted with an inert gas is limited by a unimolecular surface or gas-phase reaction.

THERMOKINETIC ANALYSIS

Thermokinetic analysis can be used to identify rate-limiting reactions from derived Arrhenius parameters. Activation energies and frequency factors are equated to the thermodynamic values for specific rate-limiting reactions:

$$\ln K_{\text{rate}} = \ln A - E/RT, \quad (2)$$

$$\ln K_{\text{equil}} = \Delta S^\circ/R - \Delta H^\circ/RT, \quad (3)$$

and

$$\ln K_{\text{rate}} = \ln K_{\text{equil}}, \quad (4)$$

where K_{rate} is the rate constant, K_{equil} is the equilibrium constant, and ΔS° and ΔH° are the entropy change and the enthalpy change, respectively, for the rate-limiting reaction. Values of entropy and enthalpy for specific reactions can thus be compared with the determined frequency

factor and activation energy, using the appropriate class of processes chosen via the frequency factor correlations, to then identify likely rate-limiting reactions.

Since the rate-limiting process for the deposition of SiC from MTS in hydrogen is adsorption or surface diffusion, no rate-limiting reaction can be written for which tabulated thermodynamic data can be used to derive entropy and enthalpy changes. Any further elucidation of this process will thus depend on further in situ analysis of the deposition process.

The rate-limiting process for the CVD of SiC from MTS diluted in argon is a unimolecular gas-phase or surface reaction, and thus candidate reactions can be examined for applicability utilizing tabulated thermodynamic data. Thermodynamic calculations were performed assuming that there is equilibrium in the gas phase, but that no SiC forms, in order to obtain partial pressures in the system in which SiC formation is constrained by intermediate reactions. The major and minor species listed in Table 2 were derived from the equilibrium calculations and were taken to be candidates for rate-limiting process reactants.

All conceivable reactions in the system were then written, using the species listed in Table 2 as unimolecular reactants. The thermodynamic calculations for each were performed, using the reactant partial pressures of Table 2 and the equilibrium thermodynamic codes in the FACT interactive system, to derive entropy and enthalpy changes at 1300 K. Four reactions were found to best match the frequency factor and the activation energy with the entropy change and the enthalpy change, respectively. These reactions are listed in Table 3. These, therefore, are primary candidates for the mechanism controlling the deposition of SiC from MTS diluted with an inert gas.

TWO-PHASE COATINGS

The well-known increase in fracture toughness in ceramic bodies due to the presence of a second phase is thought to extend to ceramic coatings as well. Coatings with improved fracture toughness could solve one of the most difficult problems in the use of ceramic protective coatings, the cracking and spalling that result from the difference in thermal expansion

Table 2. Major species equilibrium partial pressures calculated at 1300 K and 0.101 MPa for the MTS system diluted with inert gas. It is assumed that no condensed phases are present

Species	Partial pressure (kPa)
H ₂	5.3
SiCl ₃	3.1
SiCl ₂	2.1
SiCl ₄	1.4
C ₆ H ₆	0.92
HCl	0.75
SiHCl ₃	0.74
CH ₄	0.63
C ₂ H ₂	0.28
C ₄ H ₈	0.13

Table 3. Possible rate-limiting reactions for SiC CVD from MTS plus argon

Reaction	$\Delta H^\circ{}^a$	$\Delta S^\circ{}^b$
(SiCl ₂) → <Si> + 2(Cl)	420	342
1/2(C ₂ H ₄) → <C> + 2(H)	430	377
(H ₂) → 2(H)	448	344
(SiCl ₄) → (SiCl ₃) + (Cl)	374	288

$${}^aE = (405 \pm 23) \text{ kJ/mol.}$$

$${}^bR \ln A = (313 \pm 21) \text{ J mol}^{-1} \text{ K}^{-1}.$$

coefficient between coating and substrate. In particular, it was postulated that coatings of B_4C -BN would be attractive as protection against oxidation, corrosion, wear, and erosion. The major phase, B_4C , is exceptionally hard and would provide wear and erosion protective qualities, whereas the presence of the substantially softer minor phase, hexagonal BN, would improve the fracture toughness.

PREVIOUS WORK

Earlier work on the CVD of SiC - $TiSi_2$ was very encouraging (Stinton et al. 1984). Coatings produced on graphite exhibited fracture toughnesses approximately double those of the major phase, SiC (Fig. 5). In addition, it was demonstrated that the morphology of the coatings could be controlled to some extent by controlling the reactant concentrations and deposition temperature. Deposits were also produced using fluidized bed deposition; these were more fine-grained and equiaxed, although the fracture toughness remained equivalent to that of the columnar coatings shown in Fig. 5.

EQUILIBRIUM ANALYSIS OF THE B-C-N CVD SYSTEM

An extensive equilibrium analysis was performed using the SOLGASMIX-PV code (Besmann, 1977) and varying reactant concentrations, total pressure, and temperature. It was assumed that deposition would take place from the reactants BCl_3 , CH_4 , NH_3 , and hydrogen. Figure 6 illustrates some of the results of those calculations, in this case showing the effect of a low hydrogen concentration. Low nitrogen content is seen to result in three deposited phases, with higher values causing the disappearance of B_4C . Significantly increasing the hydrogen content, however, allows the free carbon to form hydrocarbons, and a large compositional area of the desired phases B_4C -BN emerges (Fig. 7). Both deposition temperature and pressure appear to have minor effects on the deposition system equilibria.

DEPOSITION EXPERIENCE

A CVD system for the deposition of B_4C -BN was constructed and is depicted schematically in Fig. 8. Deposition runs were performed to

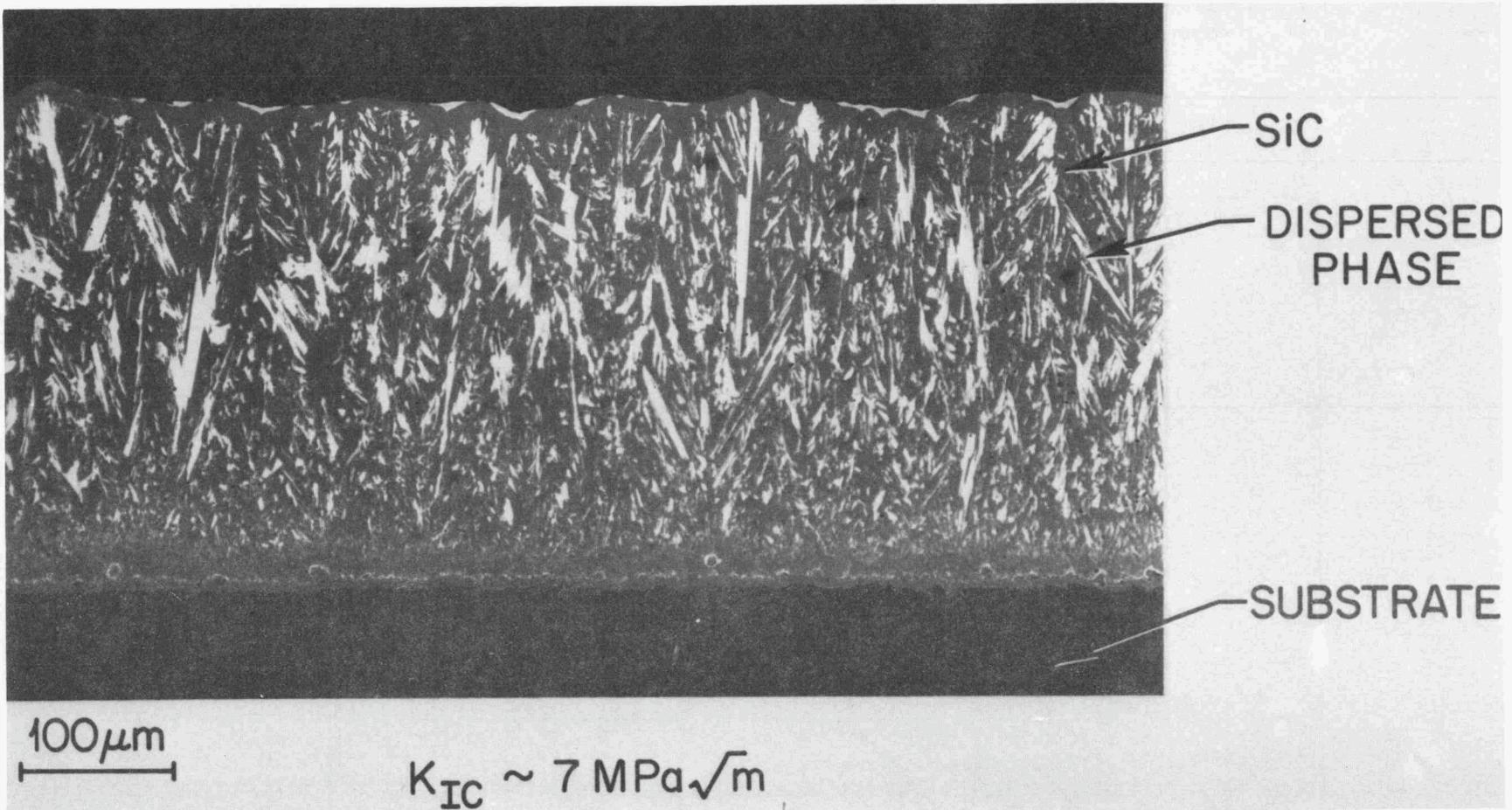


Fig. 5. Two-phase coating of SiC-TiSi₂ on graphite.

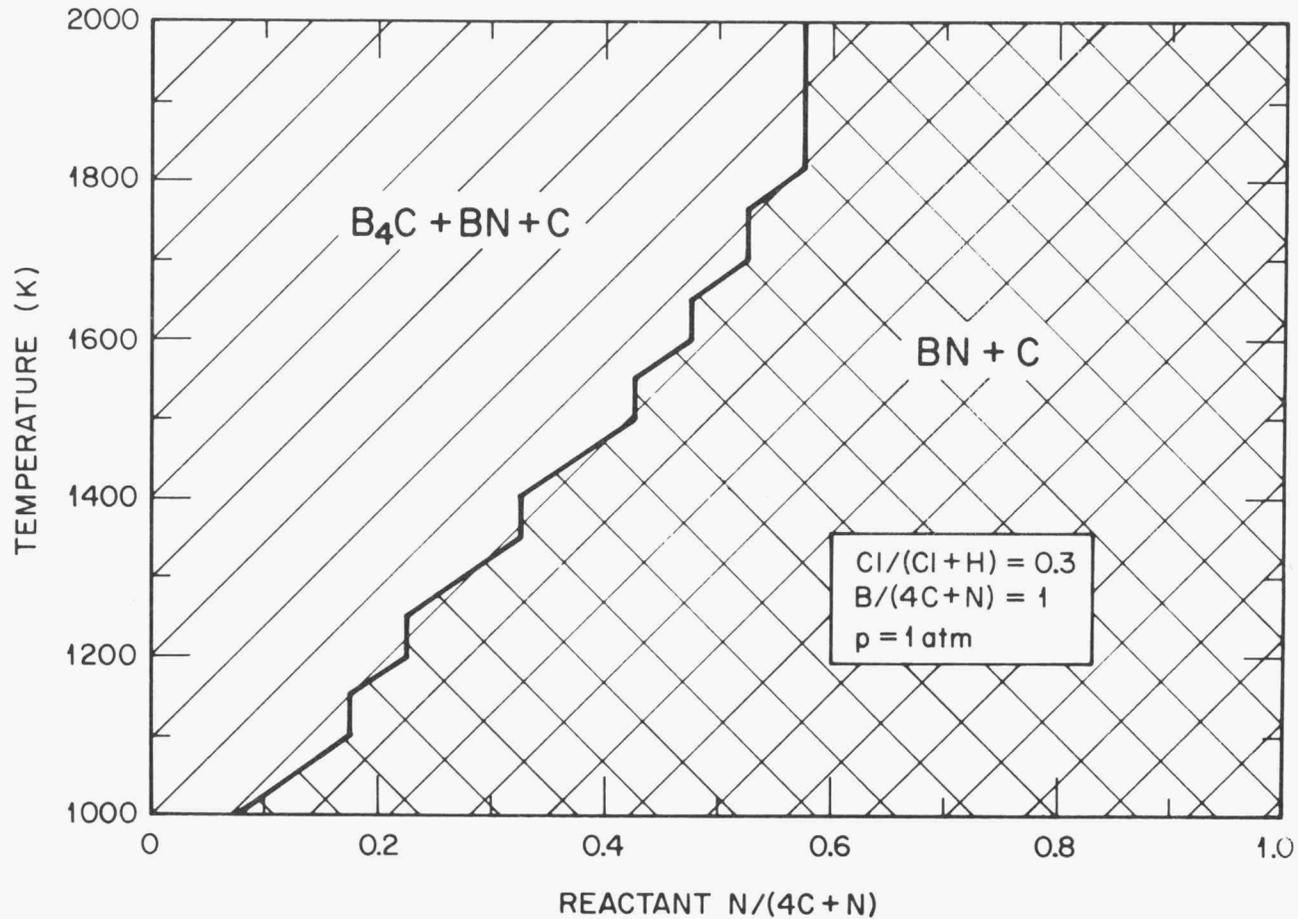


Fig. 6. Equilibrium CVD phase diagram for deposition of B-C-N phases plotted with gram-atomic concentration of reactant $N/(4C + N)$ vs temperature for specific gram-atomic concentrations of reactants $Cl/(Cl + H)$ and $B/(4C + N)$. Note the relatively low reactant hydrogen concentration [$Cl/(Cl + H) = 0.3$].

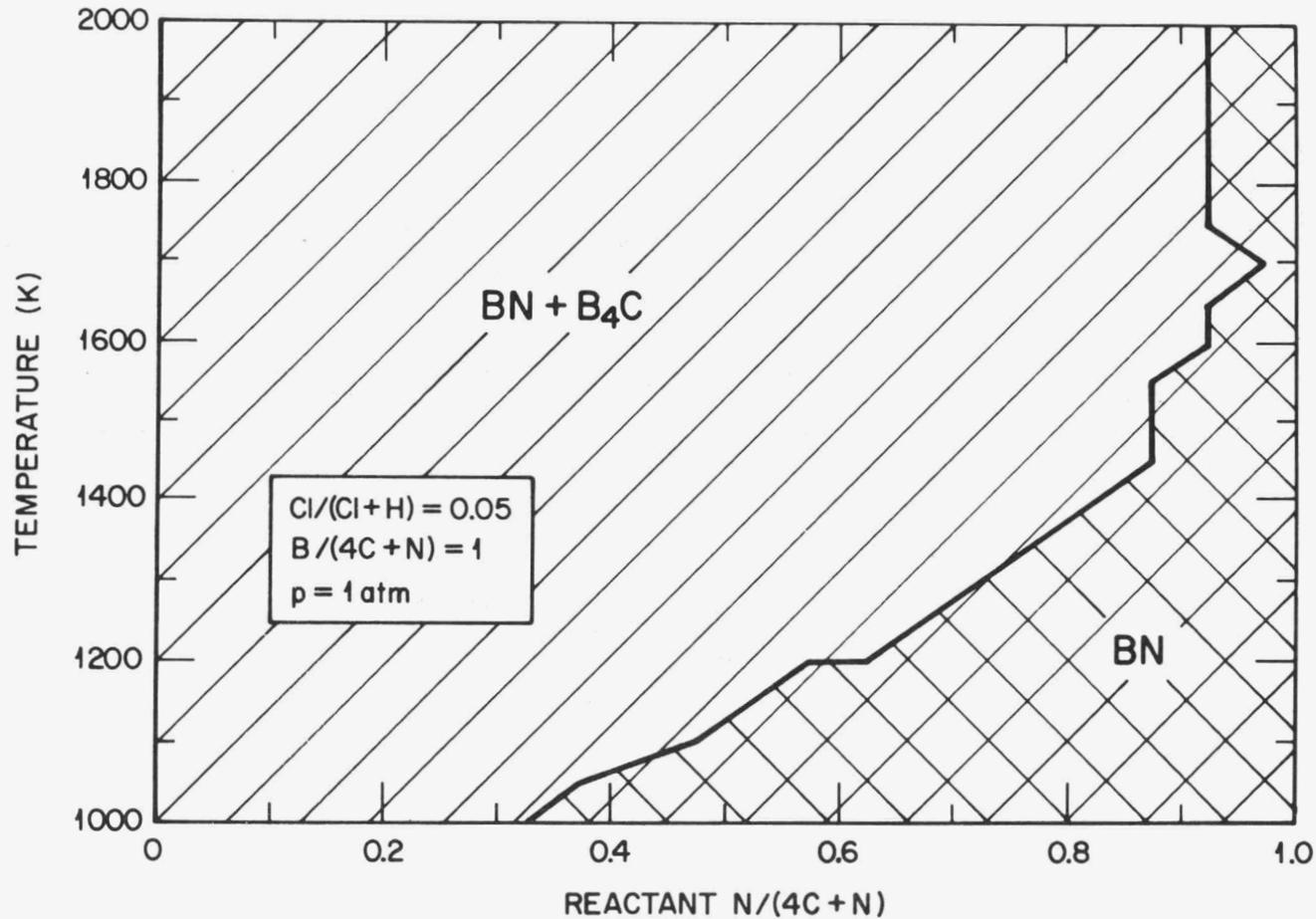


Fig. 7. Equilibrium CVD phase diagram for deposition of B-C-N phases plotted with gram-atomic concentration of reactant $N/(4C + N)$ vs temperature for specific gram-atomic concentrations of reactants $Cl/(Cl + H) = 0.05$ and $B/(4C + N) = 1$. The substantially larger hydrogen concentration [$Cl/(Cl + H) = 0.05$] allows the formation of the desired two-phase system, B₄C-BN.

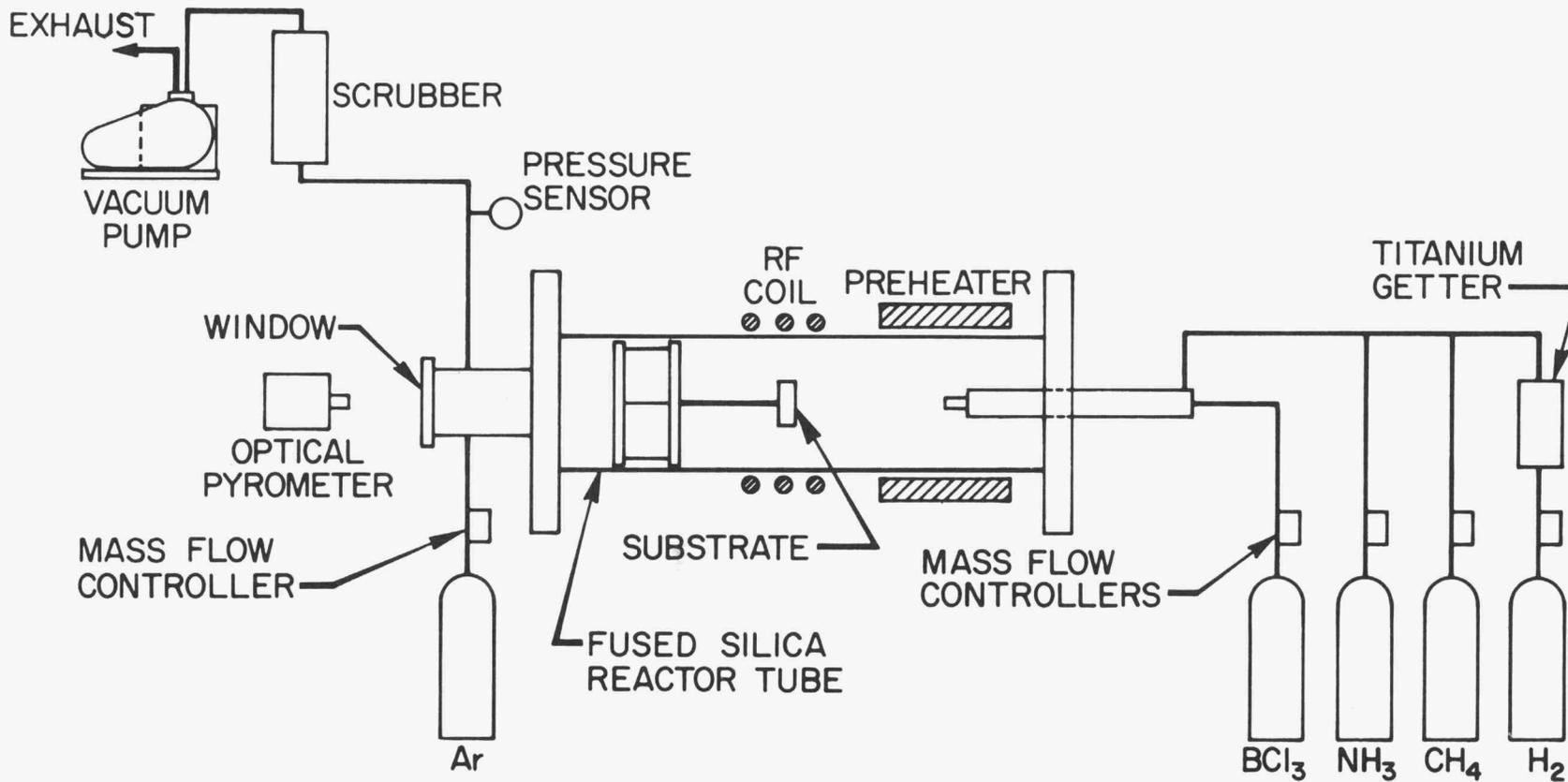


Fig. 8. The cold-wall CVD reactor used to deposit B-C-N phases. The preheater prevents ammonium chlorides from precipitating, and the vacuum system allows deposition under controlled, reduced pressures.

separately produce B_4C and BN on graphite substrates to prove the system and demonstrate that each phase could be prepared. These runs were successful, although it was determined that the high hydrogen concentrations predicted to be necessary from the equilibrium calculations to deposit B_4C resulted in a porous, friable coating (Fig. 9). Substantially reducing the hydrogen flow produced dense, single-phase B_4C , and it is postulated that free carbon must be kinetically hindered in its formation from methane, as has been observed by others (Cartwright and Popper, 1970). All runs were made at reduced pressure, 3.3 kPa (25 torr), to improve coating uniformity.

Experimental runs were next performed to deposit two-phase coatings with a variety of compositions. Predicted phase contents ranged from 50 to 10 mol % BN. The results, however, were unexpected. All deposits were single-phase when subjected to examination by metallography (Fig. 10) and X-ray diffractometry. The X-ray diffraction patterns were also found to be equivalent to that determined by Badzian et al. (1972), who interpreted it to indicate a graphitic structure which was turbostratic. A turbostratic structure is one in which the graphite-like planes are highly ordered; however, there is little order between planes. Thus the hexagonal BN apparently formed its typical graphite-like structure in the *a* and *b* directions, with little orientation in the *c* direction.

Scanning Auger electron spectroscopy was performed on fracture surfaces of the coatings. The results confirmed the uniformity of the coating, with the average composition determined from a spot size over $100 \mu m^2$ equivalent to that from a spot size of square-nanometer scale. A typical sample composition was $BC_{0.43}N_{0.29}$, indicating a likely substitution of carbon for nitrogen in the hexagonal BN structure.

Microindentation of the cross section of the coatings indicated a relatively soft material (Vickers hardness of ~430). In addition, relaxation of the indentation after removal of the load was observed, which indicates that the material is substantially more elastic than B_4C would be expected to be.

Reciprocal sliding tests were performed on the surface of a typical coating to determine its coefficient of friction. The counterface material

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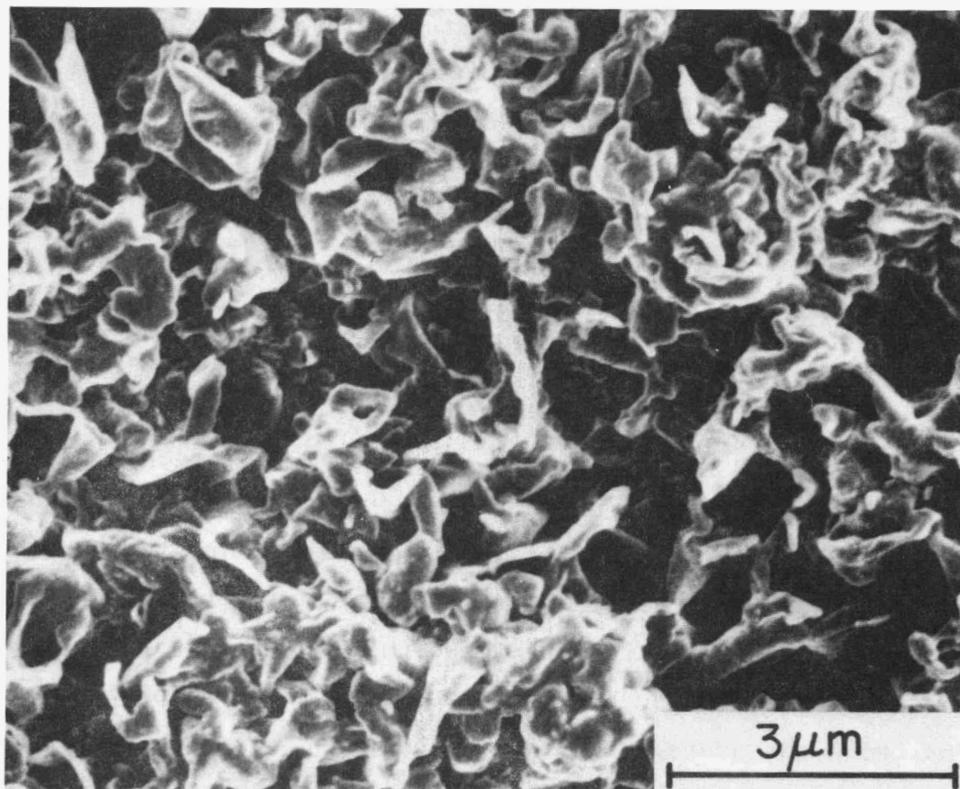


Fig. 9. Scanning electron micrograph of the porous, friable coating of B₄C deposited using a high concentration of hydrogen.

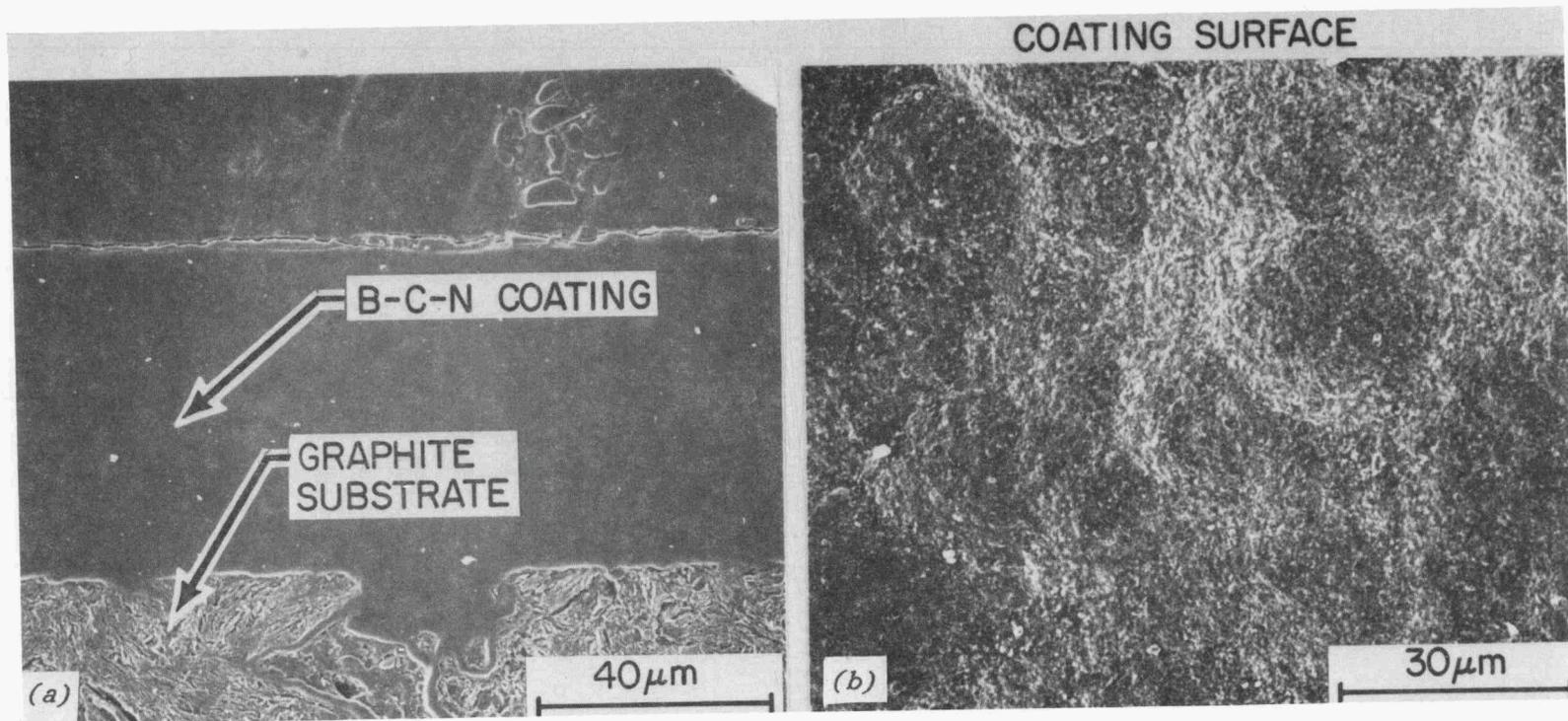


Fig. 10. Scanning electron micrographs of (a) polished cross section and (b) top surface of a B-C-N coating.

was alumina. Coefficient of friction values of ~ 0.39 were measured, which agree well with the room-temperature value reported for BN of 0.4 (Rabinowicz, 1965).

SUMMARY

Equilibrium analysis calculations, experimentally determined gas-phase composition, and analysis of kinetic data coupled with thermokinetic analysis were used to develop an understanding of the CVD of SiC from MTS. The rate-limiting process for SiC deposited from MTS diluted with hydrogen (which acts as a catalyst) appears to be adsorption or surface diffusion. The rate-limiting process for the CVD of MTS diluted with argon is a unimolecular gas-phase or surface reaction, and the four most probable reactions have been identified.

The CVD of B-C-N yields a single-phase, turbostratic coating. Scanning Auger analysis has revealed a substoichiometric (in the nonmetals) B(C,N) phase. Microindentation indicates the coating to be somewhat elastic, and reciprocal sliding measurements against an alumina counterface give a coefficient of friction of ~ 0.39 .

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REFERENCES

- Aleman, H., S. C. L. Lau, and J. Lielmezs, *Thermochim. Acta* **84**, 57 (1985).
- Badzian, A. R., S. Appenheimer, T. Niemyski, and E. Olkusnik, "Graphite-Boron Nitride Solid Solutions by Chemical Vapor Deposition," pp. 747-53 in *Proc. Third Intl. Conf. Chemical Vapor Deposition*, ed. F. A. Glaski, American Nuclear Society, Hinsdale, Ill., 1972.

Baetzold, R. C., and G. A. Somorjai, *J. Catal.* 45, 94 (1976).

Benson, S. W., *Thermochemical Kinetics*, John Wiley and Sons, New York, 1976.

Besmann, T. M., *SOLGASMIX-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL/TM-5775, April 1977.

Brennfleck, K., E. Fitzer, G. Schoch, and M. Dietrich, "CVD of SiC-Interlayers and Their Interaction with Carbon Fibers and with Multilayered NbN-Coatings," pp. 649-62 in *Proc. Ninth Intl. Conf. Chemical Vapor Deposition, 1984*, eds. McD. Robinson, C. H. J. van den Brekel, G. W. Cullen, J. M. Blocher, Jr., and P. Rai-Choudhury, The Electrochemical Society, Pennington, N.J., 1984.

Cartwright, B. S., and P. Popper, "The Deposition of Pyrolytic Silicon Carbide From Methyltrichlorosilane," pp. 473-99 in *Proc. Fifth Intl. Conf. Science of Ceramics*, eds. C. Brosset and E. Knopp, Swedish Institute for Silicate Research, Gothenburg, Sweden, 1970.

Rabinowicz, E., *Friction and Wear of Materials*, John Wiley and Sons, New York, 1965, p. 310.

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