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DISCONTINUOUS PHASE FORMATION AND SELECTIVE ATTACK OF SiC MATERIALS EXPOSED TO LOW OXYGEN PARTIAL PRESSURE ENVIRONMENTS

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ABSTRACT. Three SiC materials were exposed to gas mixtures containing N₂, H₂, and CO at 1000-1300°C, 1-740 torr for a few to 1000 h. Kinetic and thermodynamic studies indicate that CO is the predominant oxidizing species. A variety of corrosion processes were observed, including surface and internal pit formation, needle growth, grain boundary attack, and attack of impurities and surrounding material. In the case of a siliconized SiC, impurities such as Ca, Al, and Fe diffused rapidly through the Si matrix forming complex calcium aluminosilicates on the surface, leaving behind internal voids. Evaluation of the mechanical properties, including fractography, revealed a variety of degradative phenomena. Efforts to identify causes of pit formation suggested that the overall process was complex. Pits formed during attack of grain boundaries and regions containing transition metal impurities. Studies of single crystals showed preferential attack near impurities and crystalline defects, indicating that damaged crystals or certain crystal orientations in the polycrystalline materials are susceptible to attack. In addition, under some conditions where pit formation was observed, the strength of certain materials increased apparently due to flaw healing. It is suggested that flaws can heal in the absence of mechanical stress due to their high surface energy. However, second phases observed within partially healed surface cracks suggest impurities also contribute to the flaw healing processes.

1. Introduction

Silicon Carbide materials are candidates for a variety of high-temperature combustion applications. This study was initiated out of concern for the durability of SiC materials in low pO₂ metallurgical heat treatment environments. Typically, Si-based ceramics are not considered for use in low pO₂ atmospheres where active oxidation may occur. However, recently the heat treatment industry has begun using SiC radiant tubes in indirect gas-fired heat treating operations. In such systems, the tubes are internally heated by combustion burners and radiate heat to some external work load, such as an ingot of alloy, which is isolated from the combustion atmosphere. The heat treatment atmospheres, which surround the outer surface of the radiant tube, are frequently comprised of N₂, H₂, and CO often with significant percentages of CH₄, CO₂, and H₂O. For a review of heat treatment environments the reader is referred to a review by the ASM Committee on Furnace Atmospheres.¹

Jacobson² has suggested that in combustion environments there are five main mechanisms of corrosive degradation any of which may operate simultaneously: passive oxidation, deposit-induced corrosion, active oxidation, scale/substrate interactions, and scale volatility. Of course, the engineer or furnace operator of a combustion system is primarily concerned with the effects that these phenomena have on the useful life of his materials. Uniform corrosion is not particularly deleterious in that the primary degradation mechanism is the

gradual loss of component dimensions or cross-section and, therefore, loss of load-bearing capacity. Selective attack, such as pitting, is of great concern since it can result in a significant reduction in component strength with only a small amount of material loss.

In previous publications³⁻⁶ we described the thermodynamics and kinetics of reactions, and the effects on mechanical properties, of SiC materials exposed to N₂-H₂-CO heat treatment environments. In this paper we discuss certain interesting aspects of the observed heterogeneous reactions that were not previously covered in detail in an effort to foster discussion in this relatively unexplored area of ceramics corrosion research. The emphasis of the discussion is on those processes, and their kinetics, which lead to a loss of strength.

2. Experimental Procedures

Two heat treatment gases were used in these studies, an endothermic gas and a nitrogen-based gas. The calculated equilibrium compositions of both gases at 1300°C are summarized in table 1. These atmospheres were selected because they represent opposite ends of the compositional spectrum of industrial heat treatment gases. Studies were done at 1000 to 1350°C at 1-740 torr for up to 1000 h. As described in table 1, three SiC materials were used in these studies, a B-doped sintered SiC (Hexoloy SA, Carborundum Co., Niagara Falls, NY), an Al-doped sintered SiC (Elektroschmelzwerk Kempton GmbH, FRG), and a siliconized SiC (SCRB210, Coors Ceramics Co., Golden, CO).

Table 1. Physical properties data for the experimental SiC materials.

<u>Property/Analysis</u>	<u>Siliconized SiC*</u>	<u>B-Doped SiC</u>	<u>Al-Doped SiC</u>
Density, g/cc	3.05	3.16	3.14
% Porosity	0	<2	<3
SiC Grain Size, μm	2-5 and 25-75	2-8	2-5 and 80-200**
Major Impurities (0.5-2%)	Al, Fe, Ca	B	Al
Minor Impurities (0.01-0.49%)	Mg, Ti, V, Cr, Ni, Zr	Fe, Mg, Al, Ca, Cr	Ti, Ni, Fe, V Ca, Mg, Zr

* The siliconized SiC contained 19% free silicon by volume.

**The large grains were platelets of SiC and comprised <10% of the composition by volume.

Table 2. Calculated 1300°C thermodynamic equilibrium of gaseous species in the experimental heat treatment atmospheres.

<u>Component</u>	<u>Volume Fraction in Gas</u>	
	<u>Nitrogen-Based</u>	<u>Endothermic*</u>
N ₂	0.982	0.378
H ₂	1.2x10 ⁻²	0.411
CO	6.0x10 ⁻³	0.211
CO ₂	6.0x10 ⁻⁷	1.6x10 ⁻⁵
CH ₄	5.5x10 ⁻⁹	2.9x10 ⁻⁴
H ₂ O	9.0x10 ⁻⁵	3.5x10 ⁻⁶
O ₂	1.9x10 ⁻¹⁸	1.1x10 ⁻¹⁸

*Solid carbon is predicted to deposit out of the endothermic atmosphere.

The broad experimental approach to this corrosion problem involved correlating the thermodynamics and kinetics of reactions with changes in mechanical properties. The thermodynamics of reactions were modeled using the program SOLGASMIX⁶ and thermodynamic data from the JANAF tables^{7,8} and other sources.⁹⁻¹¹ The kinetics of

reactions were studied using thermogravimetric techniques (TGA) and by exposing specimens to the heat treatment atmospheres for long durations in a large vacuum furnace and measuring the resulting weight changes. Corroded specimens were then fractured at room temperature or 1300°C in argon. Fractography and microstructural characterization techniques were used to correlate changes in strength with changes in flaw populations. The strength studies described in this paper were done by fracturing 25.4x3.6x3.2 mm bars at room temperature using a 4-point bend configuration.

3. Thermodynamics of Reactions Between SiC Materials and N₂-H₂-CO Gases

Thermodynamic calculations are presented as plots of concentration of product species versus total system pressure at 1300°C. Figures 1 and 2 show plots of the calculated compositions when excess SiC is reacted with the nitrogen-based and endothermic gases, respectively. By having a large solid/gas ratio the calculated partial pressures represent the equilibrium partial pressures above the solid. These figures represent the static equilibrium between the respective solid phase and the input gases and are not meant to depict boundary layer effects that can occur in a flowing gas environment. Calculations which do simulate a flowing gas environment have been reported elsewhere.^{3,6}

In the case of the nitrogen-based gas (figure 1), the following net etching reaction between the gas and SiC is predicted to be important at the experimentally used pressures, based on the magnitudes of the calculated partial pressures:

Figure 1. Calculated composition when excess SiC is reacted with the nitrogen-based gas at 1300°C, shown as a function of total system pressure.

Figure 2. Calculated composition when excess SiC is reacted with the endothermic gas at 1300°C, shown as a function of total system pressure.

In the case of the endothermic gas, at 133 Pa total pressure (figure 2), SiO is predicted to form along with solid carbon according to the reaction:

In addition to reaction 2, at the higher pressure of 98.7 kPa, silica is predicted to form when the endothermic gas is in thermodynamic equilibrium with SiC according to the reaction:

The actual transition pressure above which silica was predicted to become thermodynamically stable is ≈ 40 kPa. Note that HCN is not predicted to be a product of reactions between SiC and the endothermic gas as was the case for the nitrogen-based gas. Rather, the levels of HCN shown in figure 2 correspond to the equilibrium partial pressures in the endothermic gas itself.

As discussed elsewhere,^{3,6} similar thermodynamic calculations were done for reactions between silicon and the heat treatment gases. It was found that the partial pressures of the product gases SiO and Si are orders of magnitude higher above Si than above SiC in both heat treatment gases, indicating that volatilization of species from solid Si should be more rapid than from SiC. At 133 Pa the following net reaction was predicted to be important in both gases, based on the calculated magnitudes of the product partial pressures:

Reaction 4 is an etching reaction in that there is a loss of solid phase of 16.07 amu per reaction. At the higher total pressure of 98.7 kPa, the following reaction was also predicted to be important:

The transition pressures above which silica was predicted to become thermodynamically stable in the nitrogen-based and endothermic gases were ≈ 40 and 1 kPa, respectively.

4. Kinetics of Corrosion of SiC Materials in N₂-H₂-CO Gases

4.1 CORROSION OF THE SILICONIZED SiC MATERIAL

The kinetics of corrosion of the siliconized SiC were generally complex owing to its two phase microstructure and relatively high impurity content (table 1). Figures 5 and 6 show TGA weight change measurements made during exposures to the nitrogen-based and endothermic gases at 1 torr total pressure. Note, as discussed in detail elsewhere,^{3,6} in the endothermic gas (figure 6) there was significant deposition of carbon and silica on the upper portions of the hangdown assembly which was subtracted from the observed TGA profiles. The siliconized SiC experienced etching in both atmospheres, apparently by reaction (4). The rapid initial weight loss was due to the rapid removal of Si phase as shown in figures 7 and 8.

Figure 5. TGA profiles of weight loss kinetics of the siliconized SiC exposed to the nitrogen-based gas at 1 torr total pressure.

Figure 6. TGA profiles of weight loss kinetics of the siliconized SiC exposed to the endothermic gas at 1 torr total pressure.

The complex, non-linear weight loss behavior of the siliconized SiC (figures 5 and 6) was associated with a number of factors: •As the silicon phase is removed the area fraction of Si directly exposed to the atmosphere decreases. •Once most of the Si has been removed from the surface (to $\approx 100\text{ }\mu\text{m}$), further removal requires gaseous diffusion through surface porosity. •At long times, when the activity of Si at the surface is sufficiently low, the corrosion rate is determined by the rate of removal of SiC phase. •And, despite the rapid etching, a significant population of discontinuous phases formed on the surface and in porosity near the surface (see brief periods of weight gain in figures 5 and 6).

Figure 7. Optical micrograph of a polished cross-section of the siliconized SiC following exposure to the nitrogen-based gas at 1300°C , 1 torr for 8 h. (Dark regions=SiC, light regions=Si.)

Figure 8. SEM micrograph of the surface morphology of the siliconized SiC following exposure to the nitrogen-based gas at 1300°C , 1 torr for 150 h. (Note the etching of individual SiC grains.)

Figure 9. Back scattered (left) and secondary (right) electron micrographs of a large aluminosilicate nodule and silicate whiskers that formed on the surface of the siliconized SiC during exposure to the nitrogen-based gas at 1300°C , 740 torr for 100 h.

Impurity sinks contained throughout the Si matrix were the sources of most of the discontinuous phases that formed during corrosion. TEM and SEM/EDX studies⁶ demonstrated that the silicon phase contained significant percentages of locally concentrated Ca, Al, and Fe. Iron and Si form a eutectic at 1207°C .¹³ It was observed that at temperatures above $\approx 1200^{\circ}\text{C}$, Fe, Ca, and Al easily diffused to the surface via channels of

liquid phase. Once at the surface, complex calcium aluminosilicates, such as anorthite and gehlenite, formed due to their high negative free energy of formation (see figure 9). To further illustrate the mechanism of nodule formation, figure 10 shows a specimen that failed at a large Si inclusion (see arrows) above which a calcium aluminosilicate nodule has formed. Figure 11 shows a cross-section through a specimen on which a large nodule had grown. The light colored, mushroom-shaped region in the middle of the specimen is a silicon inclusion. The void near the bottom of the inclusion was an impurity sink from which the impurities migrated to the surface through a channel of liquid.

Thus, the complex reaction kinetics of the siliconized SiC (figures 5 and 6) were primarily associated with the simultaneous etching of the Si matrix and formation of discontinuous phases on the surface. Etching of Si occurred nonlinearly as the Si/gas interface moves away from the specimen surface. The formation of discontinuous phases occurs in small bursts (as suggested by the short periods of weight gain) as pockets of liquid impurities periodically escape to the surface.

Figure 10. Failure origin (98 MPa) in the siliconized SiC originating from a large Si inclusion above which a calcium aluminosilicate nodule has formed (1200°C, 1 torr, 100 h, nitrogen-based gas).

Figure 11. Optical micrograph of a Silicon inclusion from which impurities have migrated through a channel of liquid. The arrow shows the location of a nodule lost during post-mortem sample preparation.

4.2 CORROSION OF THE SINTERED SiC MATERIALS

The corrosion of the sintered SiC materials was not as complex as that of the siliconized material due to their more homogenous makeup. For example, in the nitrogen-based gas at 1 torr, the sintered materials experienced relatively linear etching (figure 12), apparently due to reaction (1), at times less than ≈ 100 h.^{3,6} However, longer term exposures revealed that all three materials actually exhibit non-linear behavior. Figure 13 compares the corrosion rates of all three materials exposed to the nitrogen-based gas for times up to 1000 h. Between 0 and ≈ 300 h the Al-doped and B-doped SiC materials exhibited nearly identical rates of weight change (as was observed in all the environments studied). However, between 300 and 1000 h of exposure the Al-doped material was etched at a significantly slower rate than the B-doped SiC. X-ray photoelectron spectroscopy and secondary ion mass spectroscopy⁶ indicated that the surface of the Al-doped SiC was comprised of a thin (on the order of $10\text{\AA}$) layer of discontinuous AlN_x and/or AlO_xN_y phase, which apparently provided some protection. In the case of the B-doped SiC, no such phases were identified. It is interesting to note that, although the siliconized SiC experienced significantly more etching than the sintered materials, the B-doped SiC and siliconized SiC were etched at nearly identical rates between 300 and 1000 h, suggesting that at long exposure times the rate of corrosion of the siliconized SiC is controlled by the rate of removal of SiC phase.

Exposures of the sintered SiC materials to the endothermic gas resulted in generally more complex reaction kinetics (figures 14 and 15) compared to that observed in the nitrogen-based gas. At 1 torr in the endothermic gas (figure 14) both sintered materials experienced non-linear weight loss due to simultaneous etching and carbon formation, apparently by reaction (2). SEM inspection (figure 16) and Raman spectroscopy indicated that the surfaces were covered with layers of amorphous carbon soot. Removal of the soot using a wire brush and/or by vibrating ultrasonically in water, revealed the presence of discontinuous graphitic carbon strongly bonded to the SiC. As suggested by reaction (2), the source of the carbon was believed to be both from the SiC and the endothermic gas. Removal of Si from the SiC surface was apparently rate limited or partially rate limited by gaseous diffusion through the relatively porous surface carbon. At very long exposure times in a tube furnace^{3,6} the sintered SiC materials actually gained weight as the rate of deposition was significantly more rapid than the rate of etching.

Figure 12. SEM micrograph of the etched surface of the B-doped SiC exposed to the nitrogen based gas at 1300°C, 1 torr for 150 h.

Figure 13. Weight change kinetics of the three SiC materials exposed to the nitrogen-based gas at 1300°C, 1 torr for up to 1000 h.

Figure 14. TGA data for the B-doped SiC exposed to the endothermic gas at 1 torr.

Figure 15. TGA data for the three SiC materials exposed to the endothermic gas at 1300°C, 1 torr.

At 740 torr in the endothermic gas all three SiC materials gained weight relatively rapidly (figure 15) due to the simultaneous formation of silica needles and deposition of carbon (figure 17), and, in the case of the siliconized SiC, the formation of discontinuous calcium

aluminosilicates. In the case of the sintered materials, the carbon and silica apparently formed by reaction (3). Despite the formation of SiO_2 , the weight gain profiles of the sintered materials appear similar to that observed during carbon deposition on catalytic surfaces.¹⁴ The deposition of carbon on a surface is strongly affected by the presence of, for example, catalysts, hydrogen, and cyanogens.¹⁴ Often the deposition process is characterized by a so-called initial induction period, followed by a period of linear weight gain. The cause of the initial induction period is not clear, but it has been argued that it is caused by either the slow desorption of unreactive adsorbed species from active sites, or may be inherent in the nucleation process itself.¹⁴

Figure 16. SEM micrograph of the B-doped SiC surface covered with amorphous carbon after exposure to the endothermic gas at 1300°C, 1 torr for 100 h.

Figure 17. SEM micrograph of the B-doped SiC surface covered with amorphous carbon and silica needles after exposure to the endothermic gas at 1300°C, 740 torr, for 90 h.

4.3 CORROSION OF SINGLE CRYSTAL SiC

Despite their apparent uniformity (i.e., their lack of grain boundaries and additive phases) both black and light green single crystals of SiC also experienced selective attack in the N_2 - H_2 -CO atmospheres.⁶ Pitting occurred on the surface of the single crystal materials by localized attack near impurities (vanadium in particular) and apparently by attack of crystal defects such as stacking faults and screw dislocations intersecting the {0001}. Figure 18 shows a V impurity in the as received black SiC after exposure to the nitrogen-based gas. As shown in the figure, there was localized attack at the inclusion/SiC interface. If this specimen were exposed for a longer duration, the inclusion would eventually become dislodged from the sample leaving behind a surface pit. Figure 19 shows a relatively large hexagonal etch pit on the surface of the black SiC that apparently formed due to preferential attack of a screw dislocation. Etch pits were typically hexagonal or distorted hexagonal in shape, owing to the 3m and 6m symmetry of the hexagonal and rhombohedral polytypes of the SiC. It is interesting to note that the hexagonal etch pits tended to grow laterally with exposure time, but tended not to become significantly deeper after ≈ 100 h of exposure, indicating that the crystal etched more rapidly in the $\langle 0001 \rangle$ directions.

5. Effects of Corrosion on Mechanical Properties and Dominant Flaw Populations

In the discussion above a number of mechanisms of corrosion and selective attack were identified. Of course, we are concerned with how these processes affect mechanical properties and long term durability. Figures 20 and 21 show the time dependence of strength of all three SiC materials exposed to the endothermic gas at 1300°C, 1 and 740

torr, respectively. (Compare these figures to figures 6, 14-17.) Note that the numbers next to the data points represent the number of failures from surface pits per total number of specimens tested. At 1 torr (figure 20), all three materials lost a significant amount of strength during the first 100 h of corrosion, but between 100 and 300 h there was no statistically significant decrease in strength. This non-linear behavior has significant engineering implications: if it is known that the strength of a material asymptotically approaches a constant value then a system can be designed to operate below that stress state.

Figure 18. A vanadium-rich inclusion on the surface of black single crystal SiC showing localized attack at the inclusion/SiC interface. (nitrogen-based gas, 1300°C, 1 torr, 150 h.)

Figure 19. A large hexagonal etch pit on the surface of black single crystal SiC apparently caused by preferential attack of a screw dislocation. (nitrogen-based gas, at 1300°C, 1 torr, 1000 h.)

Figure 20. Room temperature strength versus time for the SiC materials exposed to the endothermic gas at 1300°C, 1 torr.

Figure 21. Room temperature strength versus time for the SiC materials exposed to the endothermic gas at 1300°C, 740 torr.

The primary cause of failure in corroded specimens was surface, and in the case of the siliconized SiC, internal pits.^{4,6} Numerous efforts were made to identify the specific mechanisms of pit initiation and growth. In the case of the siliconized SiC, the primary cause of pitting was the removal of Si matrix phase, as shown in figure 22, or impurity sinks as discussed above. In the case of the sintered materials, we were able to directly determine that pitting was at least associated attack of grain boundaries and localized attack near regions containing transition metal impurities. Figure 23 shows a pit on the surface of the Al-doped material where one can see localized attack of grain boundaries and individual

grains. At the upper region of the pit there was a nickel-rich impurity (shown by arrow). Although we were never able to directly observe the effects of nickel on pitting, numerous pits were found to have similar regions. As discussed elsewhere,^{4,6} we also directly observed pit formation at Ti-rich inclusions on the surface of the Al-doped SiC, and on one occasion we observed failure in the B-doped material at a region rich in Fe.

Figure 22. Corrosion pit from which failure occurred in the siliconized SiC at 223.5 MPa (300 h, 1 torr, 1300°C, endothermic gas).

Figure 23. Pit on the surface of the Al-doped SiC showing attack of grains and grain boundaries near a nickel-rich particle (50 h, 1 torr, 1300°C, endothermic gas).

Figure 24. Percentage of failures from (a) surface pits and (b) surface cracks in the Al-doped SiC. Each data point represents a particular long term heat treatment as tabulated elsewhere.^{4,6}

Although significant pitting occurred in the SiC materials in almost all the test environments, in some cases an increase in strength was observed. As illustrated in figure 24, in the case of the Al-doped SiC, regardless of whether the average strength increased or decreased during corrosion, there was an increase in the percentage of failures from surface pits and a corresponding decrease in the number of failures from surface cracks. Microstructural studies indicated that crack healing was occurring under some conditions. This was particularly evident in the case of the Al-doped SiC. Studies of indentation cracks before and after corrosion (figure 25) showed the cracks healed under certain conditions.^{4,6} Fractography of the Al-doped SiC showed that some specimens failed from what appeared to be surface cracks partially healed by titanium aluminosilicate phases such as that shown in

figure 26. Although impurities appeared to play a role in the crack healing process, we proposed^{4,6} that cracks may also heal in low oxygen partial pressure environments due purely to their surface energy as described by the well known Kelvin equation:

$$\ln\left(\frac{p}{p_0}\right) \approx \left(\frac{2\gamma\Omega}{rRT}\right) \quad (6)$$

where γ is the surface energy of the material, Ω is the molar volume, r is the radius of curvature (a negative number for a crack tip), and RT has its usual meaning. The term p_0 represents the equilibrium vapor pressure of gaseous species above a plane surface and p represents the equilibrium pressure above a curved surface. Since the molar volume of SiC equals 18.39 cc/mol and assuming an average surface energy for polycrystalline SiC of ≈ 2000 mJ/m², the ratio p/p_0 may be calculated for any crack tip radii using equation 6. For example, for an atomically sharp crack ($r \approx 5\text{\AA}$) the drop in the equilibrium vapor pressure from a flat surface to a crack tip would be approximately five orders of magnitude implying a large driving force for vaporization-condensation (or surface diffusion) from the surface of the SiC materials to sharp crack tips during gas phase etching. Please see other references for a more detailed discussion of crack healing.^{4,6}

Figure 25. Healed indentation crack on a polished surface of the Al-doped SiC (24 h, 1 torr, 1350°C, nitrogen-based gas).

Figure 25. Failure origin in the Al-doped SiC showing surface crack partially healed by a titanium aluminosilicate phase (205.9 MPa, 100 h, 740 torr, 1200°C, nitrogen-based gas).

6. Concluding Remarks

In N₂-H₂-CO heat treatment gases, etching, pitting, and the simultaneous formation of non-protective or semi-protective condensed phases was experimentally observed. However, in the particular atmospheres studied, the rates of attack were relatively slow and the severity of pits tends not to increase significantly beyond a certain period of heat treatment time (<100 hours) as evidenced by time-dependent strength studies. The results of kinetic studies and mechanical properties testing indicate that the long term durability of SiC materials should be relatively good in N₂-H₂-CO heat treatment gases at temperatures up to approximately 1300°C providing the retained strength after short term exposure is adequate for the particular stress state.

A full understanding of the kinetics of material degradation in low pC₂ environments requires an understanding of the mechanisms of selective attack, in particular, processes that lead to pitting. In this study we identified several sites or mechanisms for pit formation including rapid attack of a second phase (Si), grain boundaries, transition metal impurities,

and crystalline defects. However, it is unlikely that these are the only preferred sites for pit formation, and it could not be concluded from these studies that all of these sites actually lead to flaws more severe than those already present in the material, although certainly some of these mechanisms did lead to strength limiting flaws. Thus, further research is still needed in this area.

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References

1. ASM Committee on Furnace Atmospheres, "Furnace Atmospheres," pp. 389-416 in *Metals Handbook*, 9th ed., Vol. 4. American Society of Metals, Metals Park, OH, 1981.
2. N. S. Jacobson, "Corrosion of Silicon-Based Ceramics in Combustion Environments," *J. Am. Ceram. Soc.*, **76** [1] 3-28 (1993).
3. D. P. Butt, R. E. Tressler, and K. E. Spear, "Corrosion of SiC Materials in N₂-H₂-CO Gaseous Environments: I, Thermodynamics and Kinetics of Reactions," *J. Am. Ceram. Soc.*, **75** [12] 3257-3267 (1992).
4. D. P. Butt, R. E. Tressler, and K. E. Spear, "Corrosion of SiC Materials in N₂-H₂-CO Gaseous Environments: II, Durability and Mechanical Properties," *J. Am. Ceram. Soc.*, **75** [12] 3268-3277 (1992).
5. D. P. Butt, R. E. Tressler, and K. E. Spear, "Corrosion of Silicon Carbide Materials in Metallurgical Heat-Treatment Environments," *Am. Ceram. Soc. Bull.*, **71** [11] 1683-1690 (1992).
6. D. P. Butt, "Thermodynamics, Kinetics, and Durability of Silicon Carbide Materials in Nitrogen-Hydrogen-Carbon Monoxide Gaseous Environments at Elevated Temperatures"; Ph.D. Thesis. The Pennsylvania State University, University Park, PA, 1991.
7. G. Eriksson, "Thermodynamic Studies of High Temperature Equilibria," *Chemica Scripta*, **8**, 100-103 (1975).
8. *JANAF Thermochemical Tables*, 3rd Ed., M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, Editors, Am. Chem. Soc. and the Am. Institute of Phys. for the NBS, Volume 14, 1985.
9. Personal correspondence with M.W. Chase, NIST, Gaithersburg, MD: corrections to erroneous data for CN and C₂H₂ in reference 8.
10. I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Germany 1973.
11. M. B. Fegley, Jr., "The Thermodynamic Properties of Silicon Oxynitride," *J. Am. Ceram. Soc.*, **64** [9] C124-126 (1981).
12. D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, 1969.
13. R. Schmid, "Thermodynamic Analysis of the Melting Equilibria in the Iron-Silicon System," *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, **4** [2] 101-108 (1980).
14. P.L. Walker, Jr. and J. M. Thomas, "The Catalyzed Disproportionation of Carbon Monoxide," *Carbon*, **8** [1] 103-104 (1969).

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