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Thermochemical analysis of chemical processes relevant to the stability and processing of SiC-reinforced Si_3N_4 composites

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Chemical processes relevant to the stability and processing of SiC-reinforced Si_3N_4 composites are examined from a thermochemical point of view. The thermodynamic stability of various interfaces, such as SiC–Si_3N_4, SiC–Si_3N_4–Si_2ON_2, and SiC–Si_3N_4–SiO_2, is examined as a function of temperature. The temperatures above which these interfaces become unstable are calculated, and the degradation of SiC during the processing of the composite is examined. The processing routes considered in this study include the reaction-bonded silicon nitride process, as well as pressure-assisted sintering processes in the presence of suitable sintering additives.

1. Introduction

Ceramic matrix composites are becoming increasingly important as high-temperature structural materials, due to their enhanced mechanical properties in terms of strength and fracture toughness. One system that has received considerable attention in recent years [1–4] is the SiC-reinforced Si_3N_4 composite.

The addition of SiC whiskers [1, 2] and monofilament SiC fibres [3, 4] to Si_3N_4 results in increased fracture toughness, as compared to that for monolithic silicon nitride. Although the potential of the SiC-reinforced Si_3N_4 composite system as a high-temperature structural material has been demonstrated, the long-term stability of this material has yet to be determined.

The long-term stability of a composite material is determined by three factors [5]: firstly, internal stability, which is the stability of the internal constituents of the composite; secondly, the stability of the reinforcement material–matrix interface; and thirdly, environmental stability, such as stability in oxidizing environments for high-temperature engine applications.

The internal stability of Si_3N_4 is the same as that of the monolithic Si_3N_4 ceramic and need not be discussed here. The internal stability of SiC fibres or whiskers is a function of the impurities introduced during the processing of the reinforcement material. For example, the SiC fibres produced from polymeric precursors contain SiO_2 and excess carbon, and are inherently unstable above about 1773 K [6]. Because the internal stabilities of different commercially available SiC fibres and whiskers are expected to be different, no attempt will be made to discuss them here.

Thus the long-term stability issues for the SiC/Si_3N_4 composite system examined in this paper are the stability of the SiC/Si_3N_4 interface; and stability in oxidizing atmospheres, such as the atmosphere in commercial jet engines.

As well as the stability of the composite under conditions of use, the chemical stability of a fibre during the processing of the composite is also important. Chemical degradation of a fibre during processing can decrease its strength and is clearly undesirable. The other objective of this work is to examine the chemical stability of SiC fibres during the processing of SiC–Si_3N_4 composites.

Several processing techniques can be employed for the manufacture of Si_3N_4–SiC composites. These include nitriding a Si–SiC compact at high temperatures, as in the reaction-bonded silicon nitride (RBSN) process [3], or sintering Si_3N_4–SiC compacts at high temperatures under pressure, such as hot pressing and hot isostatic pressing (HIP), with the aid of suitable sintering additives [1, 2]. The degradation of SiC fibres for both these processing routes will be examined in this paper.

2. Stability of the Si_3N_4–SiC interface

There are no known compounds between SiC and Si_3N_4. The solubility of SiC in Si_3N_4 and *vice versa* is not known, and is probably negligible. In the absence of any compound formation and interdiffusion between SiC and Si_3N_4, the stability of the SiC/Si_3N_4 interface would be governed by the pressure of N_2 at this interface,

$$3SiC + 2N_2 = Si_3N_4 + 3\underline{C} \quad (1)$$

where the underline denotes that the element can be present at a reduced activity, i.e. at an activity less than unity. The equilibrium constant (K_1) for Reaction 1 is

$$K_1 = (a_C)^3/(p_{N_2})^2 \quad (2)$$

where a_C and p_{N_2} represent the activity of carbon in

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SiC and the partial pressure of N_2, respectively. Thus, the partial pressure of N_2 at the SiC/Si_3N_4 interface is governed by the activity of carbon in SiC.

The carbon activity in SiC is governed by the equilibria for the reaction

$$\underline{Si} + \underline{C} = SiC \quad (3)$$

The minimum possible value of carbon activity in SiC corresponds to a situation where the activity of Si is unity, i.e., SiC is in equilibrium with free Si, or in other words, SiC is saturated with Si. The maximum possible value for C activity in SiC is, obviously, unity, corresponding to a situation where SiC is in equilibrium with free C (SiC saturated with carbon). The C activity in SiC that is not saturated with either Si or C would lie somewhere in between these two limits, and would be a function of the processing conditions.

The upper and lower carbon activity limits in SiC are shown in Fig. 1 as a function of temperature. Fig. 2 shows the equilibrium N_2 partial pressures at the SiC/Si_3N_4 interface as a function of temperature for these two carbon activity limits.

The equilibrium N_2 pressure at the SiC/Si_3N_4 interface increases with carbon activity in SiC, and reaches 0.1 MPa (1 atm) at about 1713 K for carbon-saturated

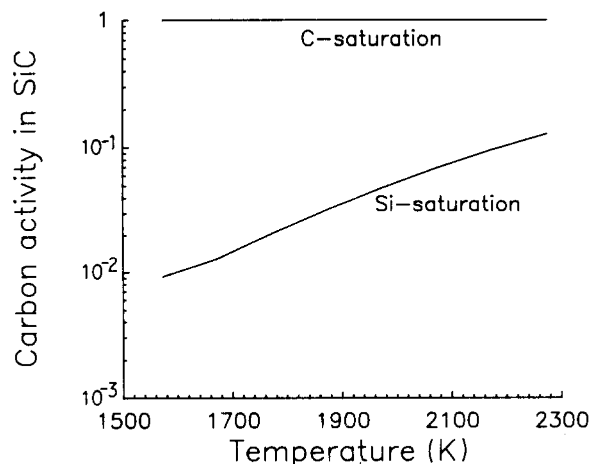


Figure 1 Carbon activities as a function of temperature for Si-saturated and C-saturated SiC.

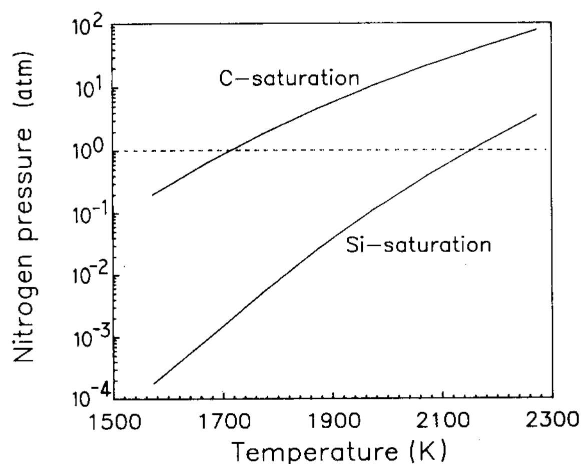


Figure 2 Partial pressure of N_2 at the Si_3N_4–SiC interface as a function of temperature for C-saturated and Si-saturated SiC fibres.

SiC. The removal of gases from the SiC/Si_3N_4 interface depends on the availability of open paths to the outside environment, such as continuous pores in the matrix and cracks at the reinforcement–matrix interface. For the situations where the equilibrium N_2 pressure at the SiC/Si_3N_4 interface is less than 0.1 MPa, the interface would become saturated with N_2 if there are no open paths to the outside for the gas to diffuse out, and the interface can then be considered to be stable. However, this may not be the case if the equilibrium pressure of N_2 at the interface is greater than 0.1 MPa. Even if there are no open paths for gas diffusion to the outside, a gas pressure > 0.1 MPa at the SiC/Si_3N_4 interface can create cracks at the interface. In such situations, the interface can be considered to be unstable.

Based on the criteria that the partial pressure of N_2 at the SiC/Si_3N_4 interface must be less than 0.1 MPa for the interface to the stable, the upper temperature limit in terms of interfacial stability can be obtained from Fig. 2. For SiC saturated with carbon, the upper temperature limit is of the order of 1713 K, as compared to 2153 K for SiC saturated with Si. Note that these temperatures correspond to the intrinsic thermodynamic stability limits for the SiC/Si_3N_4 interface. A temperature such as 2153 K is clearly not possible for two reasons: firstly, Si-saturated SiC means that SiC reinforcement material contains free Si, and Si melts at 1685 K; and secondly, both Si_3N_4 and SiC depend upon a SiO_2 layer for oxidation protection, and SiO_2 melts at 1996 K.

The practical implications of the upper temperature limits described above are that, for SiC reinforcements with carbon activities closer to (but greater than) that corresponding to Si-saturation, the upper use temperature limits would be dictated by factors other than the interfacial stability, such as oxidation resistance. On the other hand, for SiC/Si_3N_4 composites with carbon activities in SiC closer to that corresponding to C-saturation, the upper temperature limit might, at least partially, be dictated by the stability of the SiC/Si_3N_4 interface.

3. Stability in oxidizing environments

Both Si_3N_4 and SiC depend on a SiO_2 layer for oxidation protection. The intrinsic thermodynamic stability limits for the SiC–SiO_2 and Si_3N_4–SiO_2 interfaces [7] are 2073 K for the Si_3N_4–SiO_2 interface; 2083 K for the SiC–SiO_2 interface with excess Si; and 1790 K for the SiC–SiO_2 interface with excess C. These temperatures correspond to those at which the total pressure of gases at the Si_3N_4– or SiC–SiO_2 interface exceeds 0.1 MPa. It would be of interest to determine how these intrinsic stability limits are affected by the presence of both SiC and Si_3N_4 at the composite–oxide interface.

The oxidation products for the Si_3N_4/SiC composite would depend on the phase stabilities in the Si–C–N–O system. Such stabilities have recently been analysed by Wada *et al.* [8] as a function of oxygen and nitrogen partial pressures. Based on thermodynamic stability considerations, the Si_3N_4/SiC interface

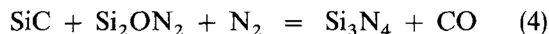
cannot be in direct contact with SiO_2 for temperatures greater than ~ 1473 K. An intermediate layer of Si_2ON_2 would always be present between the composite and the outer SiO_2 layer. Thus the pressure of gases at the Si_3N_4–SiC–Si_2ON_2 interface would probably determine the intrinsic thermodynamic stability limits in oxidizing atmospheres.

Although from purely thermodynamic arguements a layer of Si_2ON_2 is to be expected at the Si_3N_4–SiO_2 interface, this layer has rarely been observed during the oxidation of Si_3N_4. Only recently, Du *et al.* [9] have observed a very thin layer of Si_2ON_2 at the Si_3N_4–SiO_2 interface. In the absence of a layer of Si_2ON_2, the Si_3N_4/SiC/SiO_2 equilibrium becomes important for the thermodynamic stability of the composite–SiO_2 interface. Probably the Si_3N_4/SiC/SiO_2 equilibrium can be called a metastable one. In this study, the equilibrium partial pressure of gases at both the interfaces, i.e., at the Si_3N_4/SiC/Si_2ON_2 and at the Si_3N_4/SiC/Si_2ON_2 interfaces, will be examined.

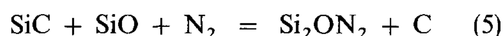
The major gaseous species at both Si_3N_4–SiC–Si_2ON_2 and Si_3N_4–SiC–SiO_2 interfaces would be N_2, SiO and CO. The equilibrium composition of the gases corresponding to the four-phase (three solids and one gas) equilibria in the Si–C–N–O system can be calculated at a given temperature for fixed carbon activities, as by Wada *et al.* [8] in their analysis of the Si_3N_4–SiC–Si_2ON_2 equilibrium.

3.1. Stability of the Si_3N_4–SiC–Si_2ON_2 interface

The partial pressure of N_2 at the Si_3N_4–SiC–Si_2ON_2 interface is the same as that for the SiC–Si_3N_4 equilibrium. The partial pressures of CO and SiO can then be calculated from the equilibria for the reactions



$$SiC + Si_2ON_2 + N_2 = Si_3N_4 + CO \quad (4)$$



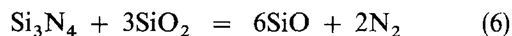
$$SiC + SiO + N_2 = Si_2ON_2 + \underline{C} \quad (5)$$

The total pressure at the Si_3N_4/SiC/Si_2ON_2 interface would be the sum of the partial pressures of N_2, SiO, and CO.

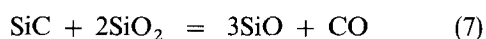
The total pressure of gases at the SiC/Si_3N_4/Si_2ON_2 interface for both Si-saturated and C-saturated SiC, shown in Figs 3 and 4, respectively, is nearly the same as the partial pressure of N_2 at this interface. Thus the intrinsic thermodynamic stability for the SiC/Si_3N_4/Si_2ON_2 interface is the same as that of the SiC/Si_3N_4 interface.

3.2. Stability of the Si_3N_4–SiC–SiO_2 metastable interface

The partial pressure of N_2 at the Si_3N_4–SiC–SiO_2 interface is the same as that corresponding to the Si_3N_4–SiC equilibria. The partial pressures of SiO and CO at the SiC–Si_3N_4–SiO_2 interface are determined from the equilibria for the reactions



$$Si_3N_4 + 3SiO_2 = 6SiO + 2N_2 \quad (6)$$



$$SiC + 2SiO_2 = 3SiO + CO \quad (7)$$

The partial pressures of N_2, CO, and SiO, as well as

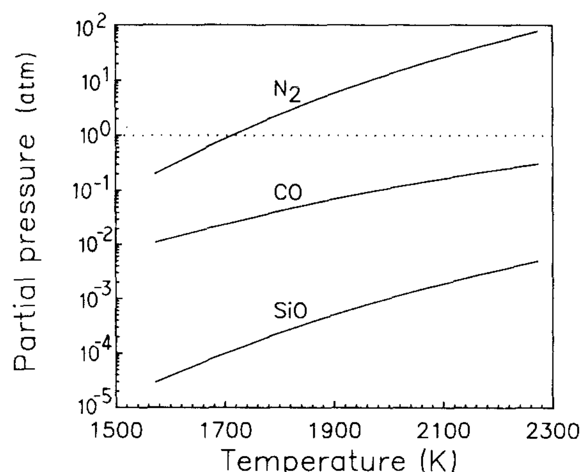


Figure 3 Partial pressures of N_2, CO and SiO for the SiC–Si_3N_4–Si_2ON_2 equilibria as a function of temperature for SiC saturated with carbon.

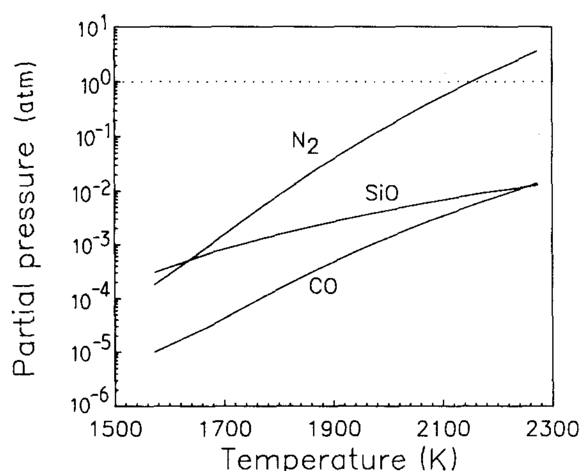


Figure 4 Partial pressures of N_2, SiO and CO for the SiC–Si_3N_4–Si_2ON_2 equilibria as a function of temperature for SiC saturated with Si.

the total pressure at the Si_3N_4/SiC/SiO_2 interface, are shown in Figs 5 and 6 for situations corresponding to C-saturation and Si-saturation, respectively.

For the Si_3N_4/C-saturated SiC/SiO_2 interface, the equilibrium partial pressure of CO is comparable to that of N_2, and the total pressure at this interface reaches 0.1 MPa at 1683 K. Thus the Si_3N_4/SiC/SiO_2 interface for carbon-saturated SiC would become thermodynamically unstable above this temperature. Note that this temperature is 30 K lower than the corresponding temperature for the SiC/Si_3N_4 interface. Also, this temperature is substantially lower (by about 100 K) than that corresponding to the instability of the C-saturated SiC/SiO_2 interface. Thus, the presence of Si_3N_4 at the SiC–SiO_2 interface decreases the stability of this interface.

The total pressure at the Si_3N_4/SiC/SiO_2 interface for Si-saturated SiC reaches 0.1 MPa at 2053 K, which is about 100 K lower than the corresponding temperature for the Si_3N_4/SiC (Si-saturated) equilibrium. Because the temperature of 2053 K is higher than the melting point of SiO_2 (1996 K), the thermodynamic stability limit for the Si_3N_4/SiC/SiO_2 interface for Si-saturated SiC has no practical implications.

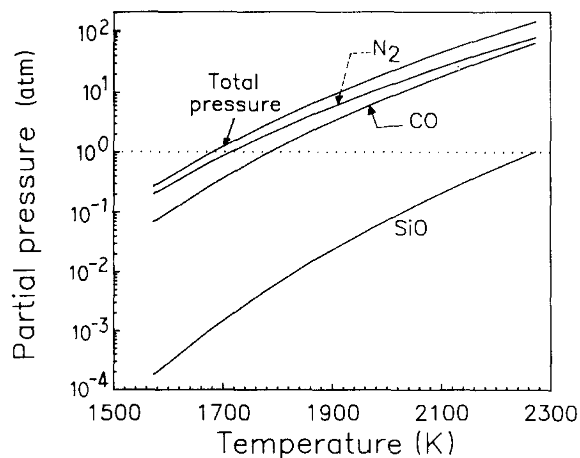


Figure 5 Partial pressures of N_2, CO, SiO, and total gas pressure at the $SiC–Si_3N_4–SiO_2$ interface as a function of temperature for SiC saturated with carbon.

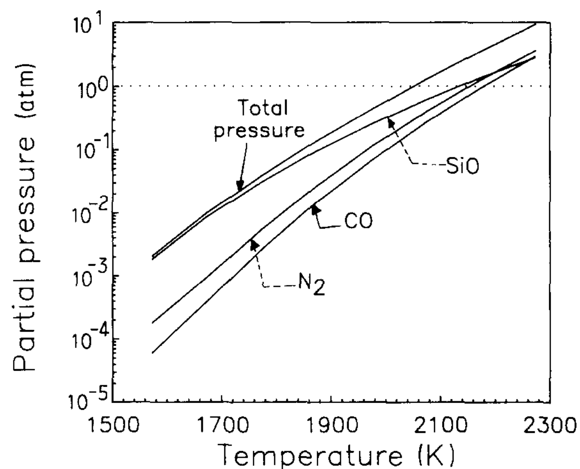


Figure 6 Partial pressures of N_2, CO, SiO, and total gas pressure at the $SiC–Si_3N_4–SiO_2$ interface as a function of temperature for SiC saturated with Si.

In summary, for carbon activities in SiC closer to that corresponding to Si-saturation, both $SiC/Si_3N_4/Si_2ON_2$ and $SiC/Si_3N_4/SiO_2$ interfaces are thermodynamically stable up to temperatures greater than the melting point of SiO_2. Thus the intrinsic thermodynamic stability limits for C activities closer to Si-saturation have no practical implications. However, for C activities in SiC closer to unity, the intrinsic thermodynamic stability limits for the $Si_3N_4/SiC/Si_2ON_2$ and $Si_3N_4/SiC/SiO_2$ interfaces would probably dictate the upper-use temperature limits for the SiC/Si_3N_4 composite in oxidizing atmospheres.

4. Stability of SiC fibres during processing

Two processing routes will be considered in this paper. One is the process for making SiC–RBSN composites in which a Si–SiC compact is nitrided in a N_2 atmosphere at high temperatures. Normally, the nitriding is carried out in 0.1 MPa N_2 and at temperatures ranging from 1473 to 1673 K. These conditions will be referred to as normal RBSN processing conditions.

The other processing route is pressure-assisted sintering, such as hot pressing or/and HIP, of $SiC–Si_3N_4$ composites in the presence of suitable sintering additives. The sintering aids normally used are [10–13] MgO, Al_2O_3, Y_2O_3, ZrO_2, CeO_2, and BeO. To prevent decomposition of Si_3N_4, a N_2 atmosphere is maintained during sintering. The maximum sintering temperature for 0.1 MPa N_2 is of the order of ~ 2153 K, which is the decomposition temperature for Si_3N_4. Sintering at higher temperatures requires N_2 pressures greater than 0.1 MPa. Two sintering situations will be considered in this study. One is sintering under 0.1 MPa in the temperature range 1973 to 2153 K; the other is sintering at 2273 K under high N_2 pressures. Note that the N_2 pressure must be greater than 0.364 MPa at 2273 K to prevent the decomposition of Si_3N_4.

There are two primary modes of chemical degradation for the SiC reinforcement materials during processing. These are firstly, reaction with the N_2, which is the atmosphere during nitriding as well as during sintering, and secondly, reaction with the sintering additives.

4.1. Reaction of SiC with N_2

The reaction of SiC with N_2 is governed by the equilibria for Reaction 1 and is a function of both N_2 pressure and the carbon activity of the SiC fibres. The equilibrium C activity at the Si_3N_4–SiC interface for a given N_2 pressure can be calculated from Equation 2. The extent of the reaction between the SiC fibre and the N_2 atmosphere is a function of the difference between the equilibrium C activity at the interface and the C activity in the SiC fibre.

Firstly, consider the reaction of SiC during the RBSN process. The equilibrium partial pressure of N_2 for the Si_3N_4–SiC–C equilibrium (the upper curve in Fig. 1) is less than 0.1 MPa for temperatures lower than 1713 K. Thus under normal RBSN processing conditions, i.e., 0.1 MPa N_2 and temperatures in the range of 1473 to 1673 K, SiC would react with N_2 to form Si_3N_4 and free carbon. This is irrespective of the starting carbon activity in the fibre.

The reaction of SiC during nitriding can be prevented by controlling the N_2 pressure during nitriding. As an example, consider a carbon-saturated SiC reinforcement material. To avoid the reaction of this fibre during nitriding, the N_2 pressure should be maintained at a level equal to that corresponding to the Si_3N_4–SiC–C equilibrium. The equilibrium partial pressures of N_2 for this equilibrium are 0.005, 0.02, and 0.065 MPa for temperatures 1473, 1573, and 1673 K, respectively. Lowering the N_2 partial pressures to very low levels is likely to have an adverse effect on the rate of nitridation of Si powders. Thus at lower temperatures such as 1473 K, lowering the N_2 partial pressure to 0.005 MPa may not be a practical solution. On the other hand, at higher temperatures such as 1673 K, lowering the N_2 partial pressure to levels on the order of 0.065 MPa may not have an adverse effect on the silicon nitridation kinetics.

Next, consider the reaction of SiC with N_2 during sintering. Table I shows the C activities at the Si_3N_4–SiC interface as a function of temperature for sintering under 0.1 MPa N_2. The equilibrium C activities are of the order of 0.1 to 0.2 for sintering under 0.1 MPa N_2. Thus if the C activity in the SiC fibre is different from this value, some chemical degradation of the fibre can be expected. However, because the deviations from stoichiometry for the compound SiC are negligible, the fibre degradation due to the change in C activity, say from 0.7 to 0.2, is probably negligible. In the event there is free C on the surface, i.e., if the SiC is saturated with C, Si_3N_4 would react with free carbon to form SiC until the C activity becomes equal to the equilibrium value.

Table II shows the equilibrium C activity at the Si_3N_4–SiC interface as a function of N_2 pressure for sintering at 2273 K under high N_2 pressures, in the range of 0.5 to 8.0 MPa. The activity of C at the interface is again less than unity, unless a very high N_2 pressure, of the order of 8.0 MPa, is maintained during sintering. Thus for N_2 pressures less than 8.0 MPa, the degradation of the SiC reinforcement would probably be negligible provided there is no free C at the fibre surface. At N_2 pressures greater than 8.0 MPa, SiC is likely to react with N_2 to form Si_3N_4 and free C and significant degradation of SiC fibre/whisker can occur.

The N_2 pressure during the nitriding and sintering processes has another important effect on composite properties. That is, the N_2 pressure during processing controls the carbon activity at the Si_3N_4–SiC interface which, as discussed earlier, affects the stability of the composite. The C activity at the interface for composites processed under normal RBSN processing conditions is unity. Thus, a carbon-rich layer would always be present at the fibre–matrix interface, irrespective of the starting carbon activity in the fibre, for composites processed under normal RBSN conditions. On the other hand, for composites processed by sintering in 0.1 MPa N_2, the C activity at the interface would be of the order of 0.1 to 0.2. Thus, the stability would be different for composites processed under different conditions.

TABLE I Equilibrium carbon activities at the Si_3N_4/SiC interface as a function of temperature for sintering under 0.1 MPa N_2

Temperature (K)	Activity of carbon
1973	0.21
2023	0.16
2073	0.13
2123	0.10

TABLE II Equilibrium carbon activities at the Si_3N_4/SiC interface as a function of N_2 pressure for sintering at 2273 K

Pressure of N_2 (MPa)	Activity of carbon
0.5	0.16
1.0	0.25
2.0	0.40
3.0	0.53
4.0	0.64
5.0	0.74
6.0	0.83
7.0	0.92
7.9	1.00

4.2. Reaction of SiC with the sintering additives

Consolidation of Si_3N_4 requires the addition of suitable sintering aids such as MgO, Al_2O_3, BeO, CeO_2, ZrO_2, and Y_2O_3. It is believed [14] that these sintering aids combine with SiO_2, which is always present on the Si_3N_4 powders, to form a glassy phase which helps in the densification process. Interaction of Si_3N_4 with the sintering additives has been studied by several investigators [15–17] and therefore will not be discussed in this paper. The prime concern of this study is to examine the interaction of SiC reinforcement materials with the sintering additives.

Because a multi-component glass phase is formed during the sintering process, the degradation of SiC fibres by this glass phase needs to be examined. However the chemical and thermodynamic properties of the glassy phase are not known, and therefore the interaction of SiC with the individual components of the glassy phase will be examined, assuming unit activity for these components. Firstly, the interaction of SiC with SiO_2 will be described; subsequently the interaction of SiC with the additives such as MgO, Al_2O_3, Y_2O_3, CeO_2, ZrO_2 and BeO will be detailed.

4.2.1. Interaction of SiC with SiO_2

Gaseous products such as SiO and CO are formed by the reaction of SiC with SiO_2. The equilibrium partial pressure of SiO at the SiC–SiO_2 interface is dictated by the C activity in SiC via the equilibria for the reaction

$$SiC + SiO_2 = 2SiO + \underline{C} \quad (8)$$

The carbon activity, in turn, is governed by the N_2 pressure and can be calculated from the equilibrium for Reaction 1. Once the partial pressure of SiO is known, the equilibrium partial pressure of CO can be calculated from the equilibrium for the reaction

$$SiC + 2SiO_2 = 3SiO + CO \quad (9)$$

Firstly, consider the sintering of the composite under 0.1 MPa N_2. Fig. 7 shows the equilibrium partial pressures of CO and SiO, and the total pressure of SiO plus CO at the SiC–SiO_2 interface, for carbon activities corresponding to 0.1 MPa N_2. The partial pressures of CO and SiO are appreciable at these sintering temperatures. During the initial stages of sintering, the pores in the matrix would be interconnected, and thus the gaseous species can diffuse to the outside via the interconnected pores and some chemical degradation of the fibre is expected. On the other hand, during the final stages of sintering, when only closed pores are present, the gaseous products cannot escape to the outside. However if the pressure of the gases inside the pores is greater than that of the

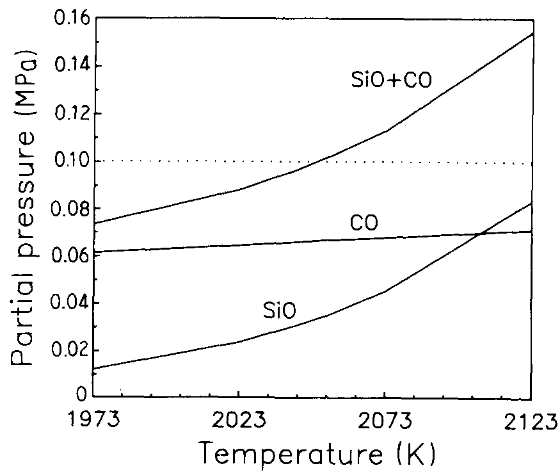


Figure 7 Partial pressures of SiO, CO, and total SiO + CO pressure at the SiC–SiO_2 interface as a function of temperature for sintering under 0.1 MPa of N_2.

TABLE III Equilibrium partial pressures of SiO, CO, and total pressure (SiO + CO) at the SiC–SiO_2 interface as a function of N_2 pressure for sintering at 2273 K

Nitrogen pressure (MPa)	p_{SiO} (MPa)	p_{CO} (MPa)	$p_{SiO} + p_{CO}$ (MPa)
0.5	0.256	0.404	0.660
1.0	0.204	0.807	1.011
2.0	0.161	1.620	1.781
3.0	0.141	2.437	2.578
4.0	0.128	3.243	3.371
5.0	0.119	4.054	4.173
6.0	0.112	4.863	4.975
7.0	0.106	5.675	5.781
7.9[a]	0.102	6.379	6.481

[a] Carbon saturation

outside atmosphere, the pores remain stable and complete pore closure becomes difficult.

As seen from Fig. 7, the total pressure of gases at the SiC–SiO_2 interface is more than 0.1 MPa for temperatures greater than 2053 K. Thus if the Si_3N_4–SiC composite is sintered under 0.1 MPa N_2 at temperatures greater than 2053 K, there are likely to be pores near the SiC–Si_3N_4 interface, particularly near the region where the glassy phase comes in contact with the reinforcement material.

Next, consider sintering under high N_2 pressures at 2273 K. Table III shows the equilibrium partial pressures of SiO and CO, and the total CO + SiO pressure at the SiC–SiO_2 interface, for carbon activities corresponding to different N_2 pressures in the range of 0.5 to 8.0 MPa. The equilibrium partial pressure of CO is appreciable for all N_2 pressures, and therefore some degradation of the SiC fibres can be expected during the initial stages of sintering. The total pressure of gases (CO + SiO) is higher than the ambient for N_2 pressures up to about 1.0 MPa. Thus if sintering at 2273 K is done under N_2 pressures less than ~ 1.0 MPa, pores are likely to be present at the SiC–Si_3N_4 interface. Maintaining N_2 pressures significantly higher than 1.0 MPa would eliminate the pores at the SiC–Si_3N_4 interface.

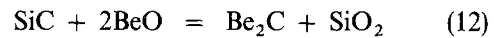
4.2.2. *Interaction of SiC with the sintering additives*

The reaction of SiC with the oxide additives can occur via two different modes: one involving the formation of new condensed phases, and the other involving the formation of gaseous products.

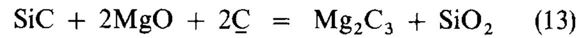
Several possible reactions in which new condensed phases would form are shown below:

$$3SiC + 2Al_2O_3 = Al_4C_3 + 3SiO_2 \quad (10)$$

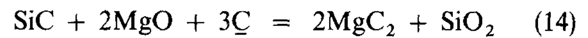
$$SiC + ZrO_2 = ZrC + SiO_2 \quad (11)$$



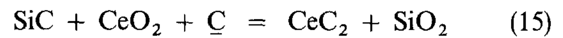
$$SiC + 2BeO = Be_2C + SiO_2 \quad (12)$$



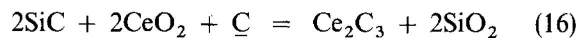
$$SiC + 2MgO + 2\underline{C} = Mg_2C_3 + SiO_2 \quad (13)$$



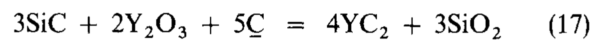
$$SiC + 2MgO + 3\underline{C} = 2MgC_2 + SiO_2 \quad (14)$$



$$SiC + CeO_2 + \underline{C} = CeC_2 + SiO_2 \quad (15)$$



$$2SiC + 2CeO_2 + \underline{C} = Ce_2C_3 + 2SiO_2 \quad (16)$$

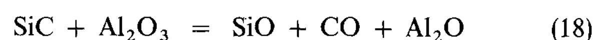


$$3SiC + 2Y_2O_3 + 5\underline{C} = 4YC_2 + 3SiO_2 \quad (17)$$

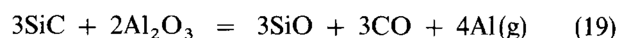
Reactions 10 to 12 are independent of the C activity in SiC, whereas reactions 13 to 17 are dependent on such activity. Table IV gives the equilibrium activity of the metal carbide M_xC_y (M = Al, Zr, Be, Mg, Ce or Y) for reactions 10 to 17 at 2073 and 2273 K, assuming unit activity for SiO_2 and the oxide additive. For the reactions which are dependent on carbon activity in SiC, the equilibrium metal-carbide activity values are given for C-saturated as well as for Si-saturated SiC.

The equilibrium metal-carbide activities shown in Table IV are less than unity for all the reactions. This means that the metal carbides would either be dissolved in SiC or form a binary carbide compound with SiC. The extent of reaction of an oxide with SiC would be governed by the equilibrium activity of the metal carbide. The lower the equilibrium values for the metal-carbide activities, the lesser the extent of the reaction. The equilibrium metal-carbide activities for the reactions of CeO_2, ZrO_2, and Y_2O_3 with SiC are of the order of 0.1 to 0.2, suggesting that the extent of the reaction for these oxides would be significant. On the other hand, the equilibrium metal-carbide activities for reactions of oxides such as Al_2O_3, BeO, and MgO are quite low. As a result, the extent of the reaction between SiC and these oxides is expected to be insignificant. Although the present calculations are done with the assumption of unit activity for SiO_2 and the oxide additive, the general trend concerning the reactivity of a particular oxide towards SiC would still remain the same.

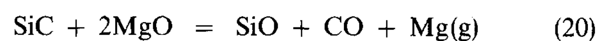
Gaseous reaction products can also be formed by the reaction of SiC with the oxides. The possible reactions are:



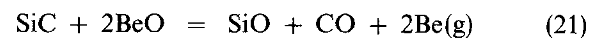
$$SiC + Al_2O_3 = SiO + CO + Al_2O \quad (18)$$



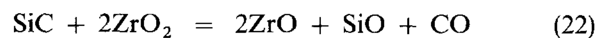
$$3SiC + 2Al_2O_3 = 3SiO + 3CO + 4Al(g) \quad (19)$$



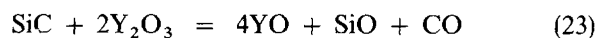
$$SiC + 2MgO = SiO + CO + Mg(g) \quad (20)$$



$$SiC + 2BeO = SiO + CO + 2Be(g) \quad (21)$$



$$SiC + 2ZrO_2 = 2ZrO + SiO + CO \quad (22)$$



$$SiC + 2Y_2O_3 = 4YO + SiO + CO \quad (23)$$

TABLE IV Equilibrium activities for metal carbides M_xC_y (M = Mg, Al, Ce, Zr, Y or Be) for reaction of oxides with SiC

Reaction	Activity of M_xC_y			
	C-saturation		Si-saturation	
	2073 K	2273 K	2073 K	2273 K
$SiC + 2MgO + 2\underline{C} = Mg_2C_3 + SiO_2$	5.48×10^{-8}	5.84×10^{-7}	2.61×10^{-10}	9.57×10^{-9}
$SiC + 2MgO + 3\underline{C} = 2MgC_2 + SiO_2$	2.31×10^{-5}	9.96×10^{-5}	4.19×10^{-7}	4.56×10^{-6}
$SiC + CeO_2 + \underline{C} = CeC_2 + SiO_2$	0.104	0.254	7.23×10^{-3}	0.032
$SiC + 2CeO_2 + \underline{C} = Ce_2C_3 + 2SiO_2$	2.36×10^{-3}	0.015	1.63×10^{-4}	1.91×10^{-3}
$3SiC + 2Y_2O_3 + 5\underline{C} = 4YC_2 + 3SiO_2$	0.121	0.397	4.29×10^{-3}	0.03
$3SiC + 2Al_2O_3 = Al_4C_3 + 3SiO_2$	8.47×10^{-13}	2.47×10^{-11}	Same as C-sat[a]	Same as C-sat[a]
$SiC + ZrO_2 = ZrC + SiO_2$	0.072	0.104	Same as C-sat[a]	Same as C-sat[a]
$SiC + 2BeO = Be_2C + SiO_2$	3.75×10^{-7}	1.28×10^{-6}	Same as C-sat[a]	Same as C-sat[a]

[a] Independent of carbon activity

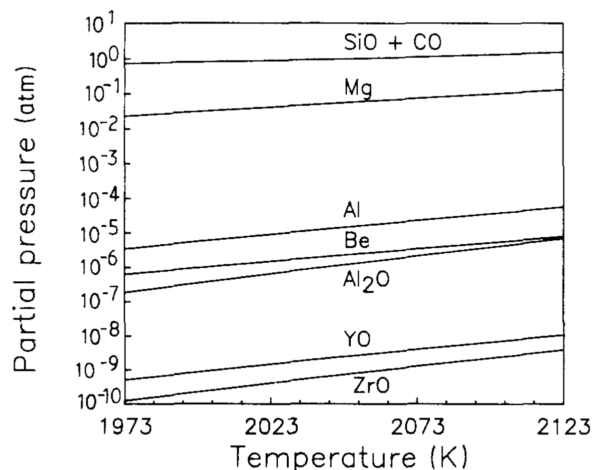


Figure 8 Partial pressures of gaseous reaction products for the reaction of SiC with oxide sintering additives as a function of temperature for sintering under 0.1 MPa N_2.

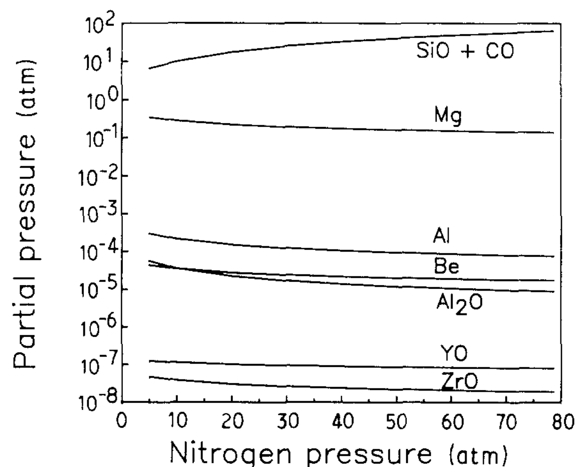


Figure 9 Partial pressures of gaseous reaction products for the reaction SiC with oxide sintering additives as a function of N_2 pressure for sintering at 2273 K.

The equilibrium partial pressures of Al_2O, Al(g), Mg(g), Be(g), ZrO, and YO are functions of the SiO and CO partial pressures. For the equilibrium between SiC and a glass phase consisting of a mixture of SiO_2 and the oxide additive, the partial pressures of SiO and CO are governed by the $SiC–SiO_2$ equilibrium. Thus the partial pressures of SiO and CO, as calculated earlier for the $SiC–SiO_2$ equilibrium, can be used to calculate the equilibrium partial pressures for Al_2O, Al(g), Mg(g), Be(g), ZrO, and YO. Fig. 8 shows the calculated equilibrium partial pressures for these gases as a function of temperature for sintering under 0.1 MPa N_2. The corresponding partial pressures are shown in Fig. 9 as a function of N_2 pressure in the range of 0.5 to 8.0 MPa, for a sintering temperature of 2273 K. The total pressure of SiO plus CO for the $SiC–SiO_2$ equilibrium are also shown in Figs 8 and 9 for comparison.

As seen from Figs 8 and 9, the total pressure of SiO and CO is considerably higher than the other gaseous species. Thus as far as the gaseous reaction products are concerned, the reaction of SiC with SiO_2 is the predominant one. However, some reaction of SiC with the oxide additives can be expected during the initial stage of sintering when the pores are interconnected, the extent of the reaction being greater for MgO than for other additives.

5. Conclusions

The upper-use temperature limit for the $SiC–Si_3N_4$ composite would be a function of the C activity of SiC. For SiC-reinforcement materials with C activities closer to that corresponding to Si-saturation, the upper-use temperature limit will be dictated by factors other than the intrinsic thermodynamic stabilities of different interfaces, such as the protectiveness of the SiO_2 scale. On the other hand, for carbon-saturated SiC-reinforcement materials, the upper-use temperature limit will, at least partially, be dictated by the intrinsic thermodynamic stabilities of the $SiC–Si_3N_4$ and $SiC–Si_3N_4–SiO_2$ interfaces. The upper temperature limit for a C-saturated $SiC–Si_3N_4$ composite, in terms of the stability of the $SiC–Si_3N_4$ interface, is of the order of 1713 K. The corresponding limit for the stability of the $SiC–Si_3N_4–SiO_2$ interface is of the order of 1683 K.

The degradation of SiC-reinforcement materials due to reaction with N_2 during the RBSN, as well as during the pressure-assisted sintering processes, can be prevented by properly controlling the N_2 pressure during processing. For SiC-reinforcement materials with C activities less than unity, i.e., not carbon-saturated, the N_2 pressure during processing should

be maintained at a level below that corresponding to the SiC–Si_3N_4–C equilibrium. On the other hand, for C-saturated SiC reinforcement materials, the N_2 pressure during processing should be maintained at the level same as that corresponding to the SiC–Si_3N_4–C equilibrium.

The reaction of SiC with several oxide sintering aids, such as Al_2O_3, MgO, Y_2O_3, CeO_2, BeO, and ZrO_2, were examined. Among these oxides, Al_2O_3 and BeO would be better choices as sintering aids in terms of reactivity towards SiC. Degradation of the SiC reinforcement material during sintering can also occur by reaction with SiO_2, which is inherently present in the starting Si_3N_4 powders. However, since the reaction products in this case are SiO and CO gases, the reaction can be prevented by maintaining the ambient pressure during sintering significantly above the equilibrium pressure of gases at the SiC–SiO_2 interface.

In summary, three parameters need to be controlled during the processing of the SiC–Si_3N_4 composite. These are firstly, N_2 pressure during processing; secondly, the ambient total pressure during pressure-assisted sintering; and thirdly the C activity in the SiC reinforcement material.

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