

Fabrication of Silicon Carbide-Mullite Composite by Melt Infiltration

Jintao Tian and Kazuhisa Shobu

National Institute of Advanced Industrial Science and Technology (AIST), Kyushu Center, Tosu, Saga 841-0052, Japan

The melt infiltration method was used to fabricate a SiCmullite composite at high temperature. Mullite was successfully obtained from a SiO₂ and Al₂O₃ powder mixture by melting above 1830°C in a BN crucible with a lid. When infiltrated into a porous SiC preform, the mullite significantly reacted with SiC to form gaseous SiO and CO, even at the lowest investigated temperature of 1830°C, consuming SiO₂ and leaving Al₂O₃ and silicon phases in the sample. The relevant reactions were studied in detail. A closed system was adopted to suppress the reaction, and a dense composite was successfully obtained.

I. Introduction

 $S^{\rm ILICON\ CARBIDE\ (SiC)}$ has been recognized as a high-performance material for structural applications because of its unique combination of properties, such as good mechanical properties maintained to high temperature, high wear and oxidation resistance, and high thermal conductivity.^{1,2} Mullite (3Al₂O₃·2SiO₂) is an important ceramic material and is used for a wide range of purposes, including structural, optical, and electrical applications.³ Mullite has a close thermal expansion match and good chemical compatibility with SiC. Thus, the combination of SiC and mullite to form SiC-mullite composites is very attractive. There have been several studies on the subject reported in the literature.⁴⁻⁶ Pressureless sintering or hot pressing commonly has been adopted as the fabrication method. Melt infiltration is an alternative to these conventional methods, with the notable advantage of fabrication of essentially fully dense composites of complex shapes with good geometric and dimensional fidelity.7 Another advantage of melt infiltration is that there is little grainboundary phase in the composite. Furthermore, the method is cost effective; therefore, the fabrication of SiC-mullite composite using the melt infiltration process is attractive. Until now, investigations related to the subject have not been reported in the literature.

In the present study, the fabrication of SiC–mullite composite using melt infiltration was explored. The processing conditions for the fabrication were studied in detail, including the formation of mullite and the reactions with SiC during infiltration.

II. Experimental Procedure

High-purity commercial SiC powder (99% pure, average particle size of ~5 μ m, Showa-Denko, Tokyo, Japan) was molded in a die and kept at 700°C for 1 h in air to remove residual carbon impurities. The relative density of the obtained SiC preform was ~50%. High-purity commercial Al₂O₃ powder (99.5% pure, average particle size of ~0.6 μ m, Sumitomo Chemicals, Tokyo, Japan) and SiO₂ powder (99.5% pure, average particle size of ~5 μ m, Mitsuwa–Kagaku, Tokyo, Japan) were mixed in a weight

ratio of 69:31 in ethyl alcohol using a ball mill for 1 h and then dried at 75°C in an oven (hereafter referred to as $Al_2O_3 + SiO_2$) powder). Formation of mullite and infiltration into the porous SiC preform were conducted in an induction furnace above the mullite melting point of 1830°C under argon at atmospheric pressure. A typical sample with dimensions of 13 mm \times 10 mm \times 6 mm was placed in a boron nitride (BN) crucible with a loose-fitting BN lid and manually heated to 1000°C, then automatically to a temperature >1830°C in 5 min to form molten mullite. The formed molten mullite, as expected, infiltrated into the porous SiC preform via capillary force. After the SiC was infiltrated by mullite, the furnace was cooled to 1000°C in 5 min, followed by natural cooling to room temperature, which led to crystallization of mullite and fabrication of a dense SiC-mullite composite. Crystalline phases of the obtained composite were identified using X-ray diffractometry (XRD). The microstructure of the composite was observed using optical microscopy.

III. Results and Discussion

(1) Formation of Mullite from $Al_2O_3 + SiO_2$ Powder

The formation of mullite from $Al_2O_3 + SiO_2$ powder was studied at temperatures above the melting point of mullite (~1830°C). The experimental details and the results are listed in Table I. Mullite could be synthesized by melting $Al_2O_3 + SiO_2$ powder in a BN crucible with a lid in a temperature range from 1830° to 1900°C. At 1950°C, however, a hold >5 min led to a definite decrease in the SiO₂ content, leaving Al₂O₃ phase in the sample. The lid was found open after the experiment at 1950°C, which indicated extensive gas evolution inside the crucible, whereas the lid stayed closed at lower temperatures. This was explained by the decomposition and evaporation of mullite at high temperature. By assuming molten mullite as an ideal solution of the constituents, where the activities for SiO₂ and Al₂O₃ were simply assumed to be concentrations, and using the thermodynamic data taken from the JANAF Thermochemical Table,⁸ we calculated the equilibrium partial pressures of the gaseous species over molten mullite at high temperature, as shown in Fig. 1. Molten mullite has the main gaseous species SiO, O2, and O, and the total vapor pressures at 1900° and 1950°C are ~ 11 and ~ 21 Pa, respectively. The loose-fitting lid had a weight of 1.84 g and could be open when the gas pressure inside the crucible was higher than that outside the crucible by ~ 10 Pa. The calculated vapor pressure of ~ 21 Pa reasonably explained the opening of the lid at

Table I.Mullite Formation Using $Al_2O_3 + SiO_2$ Powder as the Raw Material

Temperature (°C)	Time (min)	XRD results
1830	10	Mullite
1850	10	Mullite
1875	10	Mullite
1900	10	Mullite
1925	10	Mullite
1950	5	Mullite
1950	10	Al_2O_2 , mullite
1950	20	$Al_2O_3^{3'}$

J. Smialek-contributing editor

Manuscript No. 187365. Received October 29, 2001; approved October 10, 2002. Supported by the Japan Society for the Promotion of Science (JSPS).





Fig. 1. Equilibrium vapor pressures of gas species on molten mullite.



Fig. 2. Equilibrium vapor pressures of gas species on molten mullite with carbon presence.

1950°C. After the lid was open, continuous SiO_2 consumption was attributed to the reaction with carbon from the heating element, which left the Al_2O_3 phase in the sample. This result could be explained by gaseous CO with much higher equilibrium partial pressure over molten mullite in a carbonaceous environment, as shown in Fig. 2.

(2) Reaction between SiC and Mullite

Although it has been well documented that SiO_2 reacts with SiC at high temperatures, we have attempted infiltration of mullite into the SiC preform, hoping that the lower activity of SiO_2 in mullite might result in a successful infiltration, at least just above the melting point of mullite. The infiltration was conducted at temperatures from 1830° to 1950° C in a BN crucible with a lid. Unfortunately, extensive reactions were observed in all the experiments between SiC and mullite, as shown in Table II, and the phases SiC, Al_2O_3 , mullite, and silicon were identified using XRD analysis of the obtained sample. The mullite phase was detected only as a minor phase at the lowest temperatures of 1830° and 1850° C. Many bubbles were observed in the molten infiltrant, and the lid was found open after the experiment, which indicated extensive gas evolution. An additional infiltration experiment was also conducted using mullite powder, which was formerly prepared in the experiment described in Section III(1). The results were almost identical.

Many studies have been conducted theoretically and experimentally on the possible reactions between SiO_2 and $SiC.^{9-11}$ These studies identified some typical reactions, as follows:

$$\operatorname{SiC}(s) + 2\operatorname{SiO}_2(l) \to 3\operatorname{SiO}(g) + \operatorname{CO}(g) \tag{1}$$

$$2\operatorname{SiC}(s) + \operatorname{SiO}_2(l) \to 3\operatorname{Si}(l) + 2\operatorname{CO}(g) \tag{2}$$

$$\operatorname{Si}(l) + \operatorname{SiO}_2(l) \to 2\operatorname{SiO}(g)$$
 (3)

Figure 3 shows the equilibrium total vapor pressures for these reactions as a function of temperature. SiC reacts with SiO₂ via reaction (1) or (2) to form various products: SiO(*g*) and CO(*g*), or Si(*l*) and CO(*g*). Reaction (3) also leads to the consumption of SiO₂. To determine the reaction by which SiC and SiO₂ actually reacted in the present case, experiments were designed and performed as shown in Table III. In experiment A, the powder mixture of SiC and SiO₂ with a mole ratio of 1:2 almost completely disappeared (~99 wt% of the powder), whereas, in experiments B and C, the mixtures with mole ratios of 2:1 and 2:3 lost weights by only ~55 and ~91 wt%, respectively. Thus, reaction (1) appears to have occurred in experiment A, with almost full loss of the sample. However, no single reaction above is responsible for the results of experiments B and C.

An almost complete thermodynamic description of the Si-O-C system is available in the literature,¹² but it is complicated and not easy to understand. We present here a slightly simpler description.

All the possible reactions must actually occur, so that reactions (1)-(3) must be at equilibrium. As shown in Fig. 3, where the equilibrium of each single reaction is assumed, the vapor pressure of reaction (1) is higher than that of reaction (3). This implies that the reverse reaction of reaction (3) is possible, so that the activity of Si(*l*) becomes 1. Three phases—SiC(*s*), SiO₂(*l*), and Si(*l*)—can coexist with the gas phase, but the gas-phase composition and pressure are fixed by the temperature (the phase rule). In the present case, we have only two species, SiC and SiO₂, initially under external atmospheric pressure (101 kPa). With this observation and by equilibrating reactions (1) to (3), we obtain the equilibrium vapor pressure of the system, as shown in Fig. 4, which is a function of SiC and SiO₂: one is a carbon-saturated extreme, where the carbon activity is 1; and the other is a

Table II. SiC Preform Infiltrated with $Al_2O_3 + SiO_2$ and Mullite Powders

Raw material	Preform	Temperature (°C)	Time (min)	XRD results
$Al_2O_3 + SiO_2$ powder	SiC	1830	10	SiC, Al ₂ O ₃ , mullite, silicon
2 5 21	SiC	1850	10	SiC, Al_2O_3 , silicon, mullite
	SiC	1875	10	SiC, Al_2O_3 , silicon
	SiC	1900	10	SiC, Al_2O_3 , silicon
	SiC	1900	15	SiC, silicon, Al ₂ O ₃
	SiC	1950	10	SiC, silicon, Al_2O_3
Mullite powder	SiC	1830	10	SiC, Al ₂ O ₃ , mullite, silicon
	SiC	1850	10	SiC, Al_2O_3 , silicon, mullite
	SiC	1875	10	SiC, silicon, Al ₂ O ₃
	SiC	1900	10	SiC, silicon, Al_2O_3
	SiC	1950	5	SiC, silicon, Al_2O_3



Fig. 3. Equilibrium total vapor pressures of several reaction schemes between SiC and SiO_2 .

silicon-saturated extreme, where the silicon activity is 1.13,14 In the case of calculations for Fig. 4, the activity of silicon is specified to be 1, because possible carbon impurity from raw materials has been removed and silicon has been observed in our experiments. The gas composition is important and also is depicted in Fig. 4 in the SiO:CO ratio of partial pressure (P_{SiO} : P_{CO}). The total pressure is >101 kPa at ~1810°C, so that, above this temperature, an extensive reaction proceeds under an external pressure of 101 kPa. (Actually, the involved reactions are all endothermic, and the temperature is the invariant point where the three condensed phases coexist at the gas-phase pressure of 101 kPa, so that the reaction is almost completed at the temperature.) Therefore, the gas-phase composition is approximately 2SiO(g) + CO(g) at temperature, as shown in Fig. 4. The near equilibrium reaction, therefore, must proceed without violating the ratio and equilibrium of the overall system. Therefore, the reaction is approximated by

$$2\operatorname{SiC}(s) + 3\operatorname{SiO}_2(l) \longrightarrow \operatorname{Si}(l) + 4\operatorname{SiO}(g) + 2\operatorname{CO}(g)$$
(4)

which is the only reaction scheme that meets the necessary conditions. When a higher external pressure is applied, the net reaction proceeds at higher temperature, according to a different reaction scheme (with lower $P_{\rm SiO}$: $P_{\rm CO}$).

Reaction (4) was used to reanalyze the present experimental results. For experiment A, excess SiO_2 was supplied compared with that of reaction (4), which then reacted with the produced silicon to form gaseous SiO by reaction (3), leading to the total reaction (1). For experiments B and C, the weight losses according to reaction (4) were calculated to be 56 and 89 wt%, respectively, which were in close agreement with the experimental results of 55 and 91 wt%, respectively. These results also indicated that the reactions in our experiments occurred as a near-equilibrium process.

Using the assumed activity of SiO_2 in mullite to be that of the concentration as before, a similar calculation was conducted for the reaction between SiC and mullite. The result indicated that a



Fig. 4. Equilibrium total pressure and gas composition of $SiC-SiO_2$ system (the activity of silicon is specified to be 1 for the calculations).

reaction occurred at ~1840°C, only a little higher than that for pure SiO₂, which was well within experimental uncertainty. Because of this marginal stability of mullite with SiC, a minor mullite phase should have been observed in the experiments at 1830° and 1850°C.

(3) Infiltration of Mullite into the SiC Preform

To suppress the reaction described above, a load was applied to the BN lid to force the system to remained closed. The gas pressure inside was obtained from Fig. 4, and a sufficiently higher load than this was applied. The experimental details and the results are shown in Table IV. As shown in Table IV, mullite could be successfully infiltrated into a porous SiC preform under such conditions, and only small bubbles were identified in the melted infiltrant. The XRD analysis of the obtained composite indicated no phase presence other than SiC and mullite. The calculation indicated that only 0.36 wt% of the total SiO₂ was consumed because of the reactions with SiC to form gaseous SiO and CO. The amount of formed silicon was too little to be detected using XRD.

If mullite melted nonhomogeneously to form solid Al_2O_3 precipitates and liquid aluminosilicate, as the phase diagram indicates,¹⁵ the aluminosilicate melt must have infiltrated into the SiC preform, resulting in a SiC–aluminosilicate composite. The present result appeared to imply that mullite melted homogeneously under the present conditions. Therefore, the melt was presumably metastable.

As was expected from the low viscosity of the molten mullite $(<0.2 \text{ Pa} \text{ s})^{15}$ and its good wettability, almost full infiltration was achieved within 10 min for the present preform dimensions (13 mm × 10 mm × 6 mm). Figure 5 shows the microstructure of the composite obtained by infiltration at 1900°C. The absence of fine SiC grains indicated that dissolution–reprecipitation of SiC through molten mullite occurred to form a coarser SiC network. This indicated that sintering shrinkage occurred after infiltration

Table III. Experiments A, B, and C and Their Results[†]

	Experiment A	Experiment B	Experiment C
Mole ratio of SiC:SiO ₂	1:2	2:1	2:3
Weight of sample before reaction (g)	1.00	0.88	1.30
Weight of sample after reaction (g)	0.01	0.40	0.12
Weight lost of sample (g)	0.99	0.48	1.18
Percent of weight lost of sample			
Observed	99	55	91
Calculated from reactions (3) and (4)	100	56	89
Phase composition of sample	Silicon	Silicon SiC	Silicon

[†]Raw materials were mixtures of SiC and SiO₂ powders and the reaction condition was a 10 min hold at 1900°C.

Table IV.Mullite Formation and SiC Infiltration Using $Al_2O_3 + SiO_2$ Powder as the Raw Materials in aClosed System

Preform	Loading (kg)	Temperature (°C)	Time (min)	XRD results
SiC	8	1900	10	Mullite
	8	1900	10	SiC, mullite



Fig. 5. Microstructure of SiC-mullite composite fabricated by melt infiltration at 1900°C.

when the finer SiC powders were used in the preform preparation. The composite was almost fully dense, having a relative density of \sim 97%.

IV. Conclusions

The preparation of the SiC–mullite composite by melt infiltration was investigated. When the $Al_2O_3 + SiO_2$ powder mixture contained 31 wt% SiO_2 , mullite could be obtained over a wide temperature range from 1830° to 1900°C, when a BN crucible with a lid was used, which prevented the possible gaseous reaction with the carbonaceous environment. At 1950°C, gas evolution was observed inside the crucible because of mullite decomposition and

Acknowledgments

The authors thank the National Institute of Advanced Industrial Science and Technology (AIST), Kyushu Center, for the performance of the experiments. The authors are also grateful to Dr. N. S. Jacobson for his suggestion on the thermodynamic calculations and analyses of the paper.

References

¹J. H. She, J. K. Guo, and D. L. Jiang, "Hot Isostatic Pressing of α-Silicon Carbide Ceramics," *Ceram. Int.*, **19** [5] 347–51 (1993).

²P. Popper and D. Davies, "The Preparation and Properties of Self-Bonded Silicon Carbide," *Powder Metall.*, **8**, 113–27 (1961).

³I. A. Aksay, D. M. Dabbs, and M. Sarikaya, "Mullite for Structural, Electronic, and Optical Applications," *J. Am. Ceram. Soc.*, **74** [10] 2343–58 (1991).

⁴M. I. Osendi, "Oxidation Behavior of Mullite–SiC Composites," J. Mater. Sci., 25, 3561–65 (1990).

⁵H. R. Rezaie, W. M. Rainforth, and W. E. Lee, "Fabrication and Mechanical Properties of SiC-Platelet-Reinforced Mullite-Matrix Composites," *J. Eur. Ceram. Soc.*, **19** [9] 1777–87 (1999).

⁶K. G. K. Warrier and G. M. Anilkumar, "Densification of Mullite–SiC Nanocomposite Sol–Gel Precursors by Pressureless Sintering," *Mater. Chem. Phys.*, **67** [1–3] 263–66 (2001).

⁷W. B. Hillig, "Melt Infiltration Approach to Ceramic-Matrix Composites," J. Am. Ceram. Soc., **71** [2] C-96–C-99 (1988).

⁸M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables, 3rd Ed.," *J. Phys. Chem. Ref. Data*, **14** [Suppl. 1] (American Chemical Society, New York) (1985).

⁹P. D. Miller, J. G. Lee, and I. B. Cutler, "The Reduction of Silica with Carbon and Silicon Carbide," *J. Am. Ceram. Soc.*, **62** [3–4] 147–49 (1979).

¹⁰D. H. Filsinger and D. B. Bourrie, "Silica to Silicon: Key Carbothermic Reactions and Kinetics," J. Am. Ceram. Soc., **73** [6] 1726–32 (1990).

¹¹N. S. Jacobson and E. J. Opila, "Thermodynamics of Si-C-O System," *Metall. Trans. A.*, **24** [A] 1212–14 (1993).

¹²(a)F. Danes, E. Saint-Aman, and L. Coudurier, "The Si-C-O System," J. Mater. Sci., 28, 489–95 (1993). (b)*ibid.*, 28, 6524–30 (1993).

¹³N. S. Jacobson, K. N. Lee, and D. S. Fox, "Reactions of Silicon Carbide and Silicon(IV) Oxide at Elevated Temperatures," *J. Am. Ceram. Soc.*, **75** [6] 1603–11 (1992).

¹⁴N. S. Jacobson and R. A. Rapp, "Thermochemical Degradation Mechanisms for the Reinforced Carbon/Carbon Panels on the Space Shuttle," Technical Memorandum 106793, NASA, Washington, DC, 1995.

¹⁵Z. Xiao and B. S. Mitchell, "Mullite Decomposition Kinetics and Melt Stabilization in the Temperature Range 1900°–2000°C," *J. Am. Ceram. Soc.*, **83** [4] 761–67 (2000).