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Fracture strength of melt-infiltrated SiC-mullite composite

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The fracture strength of a melt-infiltrated SiC-mullite composite was measured from room temperature to 1500°C using a three-point bending test. The strength under argon at atmospheric pressure was not high. Mullite decomposition was found to be severe even at 1100°C in a reducing atmosphere, thus significantly degrading its strength. The strength in air, where the decomposition was suppressed, was moderately high and retained up to 1100°C. The composite revealed typical brittle failure up to the highest investigated temperature of 1500°C, with an indication of failure by slow crack growth at high temperature. © *2004 Kluwer Academic Publishers*

1. Introduction

SiC-based composites have been considered as potential materials for applications at high temperature, attracting a great deal of attention in the past two decades [1]. Mullite ($3Al_2O_3 \cdot 2SiO_2$) is one of the important ceramic materials and has been used for a wide range of purposes [2]. Mullite has a close thermal expansion match and good chemical compatibility with SiC. Thus, there have been reported many studies on the SiC-mullite composites [3, 4]. The composites can be fabricated through various processes, such as normal pressureless sintering and hot-pressing. Melt infiltration is an alternative to these conventional methods with notable advantage of fabrication of essentially fully dense composites of complex shapes with good geometric and dimensional fidelity. The process has been tried in a previous study, and dense SiC-mullite composite has been successfully obtained in a short time with little dimensional change [5]. The fracture strength of the composite, however, is yet to investigate. There seems to be no relevant reports in the literature to date. The present study, therefore, has been conducted to evaluate the fracture strength of the composite both at room temperature and at high temperature.

2. Experimental procedure

The SiC-mullite composite was fabricated by melt infiltration process. Details of the fabrication process were reported elsewhere [5], so they were only briefly introduced here. As an infiltrant, a powder mixture of high purity commercial Al_2O_3 (99.5% pure, Sumitomo Chemicals, Japan, average particle size of ∼0.6 μm) and SiO_2 (99.5% pure, Mitsuwa-Kagaku, Japan, average particle size of ∼5 μm) was prepared by wet ball milling in ethyl alcohol for 2 h, followed by drying in an oven at 90°C. A series of infiltrants with the Al_2O_3 content of 69, 72, 75, and 80 wt% around the stoichiometric mullite (Al_2O_3 content of ∼72 wt%) were prepared and tested. Each of them will be referred to as 69%-Al_2O_3, etc. in this report. A SiC powder compact with a relative density of 50% approximately was press-molded in a die from high purity commercial SiC powder (99% pure, Showa-Denko, Japan, average particle size ∼5 μm), and served as the preform. The infiltration process was performed in an induction furnace under argon at atmospheric pressure. Typically, the SiC preform with dimensions of $13 \times 10 \times 6$ mm^3 together with the infiltrant were placed in a boron nitride (BN) crucible with a lid and heated from 1000°C up to the temperature above the melting point of mullite (∼1830°C) in 5 min, held for 10 min, followed by cooling to 1000°C in 5 min and then naturally to room temperature. The crystalline phases of the so-formed composite were determined using an X-ray diffractometer (XRD). The microstructure of the composite was characterized using a scanning electron microscope (SEM).

The fracture strength of the SiC-mullite composite was measured from room temperature to 1500°C using a three-point bending test with an outer span of 8 mm and a crosshead speed of 0.07 mm/min. Rectangular bars were cut from the infiltrated compact and ground to the nominal dimensions of 1.8 mm × 2.5 mm × 12 mm. The tensile face was carefully polished with 1 μm diamond paste, followed by slightly chamfering the edges. The specimen was held at the testing temperature for 5 min before bending to achieve temperature stability in the system. After failure, the specimen was

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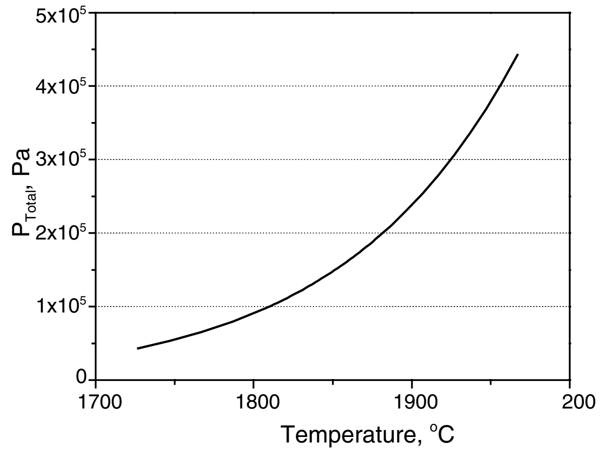

Figure 1 Equilibrium total vapor pressure as a function of temperature for SiC-SiO_2 system (the activity of silicon is specified to be one for the calculations).

rapidly cooled. At least five effective specimens were tested to determine the strength for each condition. The fracture surface after failure was examined using SEM.

3. Results and discussion

3.1. Material synthesis

Mullite could be easily synthesized by melting a powder mixture of Al_2O_3 and SiO_2 in a BN crucible with a lid in a temperature range from 1830 to 1925°C. When infiltrated into porous SiC preform, mullite significantly reacted with SiC to form gaseous SiO and CO even at the lowest investigated temperature of 1830°C, consuming SiO_2 and leaving Al_2O_3 and Si phases in the sample. Fig. 1 shows the equilibrium total vapor pressure as a function of temperature for SiC-SiO_2 system, revealing an equilibrium total pressure over 101 kPa at the temperature of ~1810°C. For the system of SiC and molten mullite, thermodynamic calculations indicate that the equilibrium total vapor pressure exceeds 101 kPa above at ~1850°C. Thus, a gas pressurizing was necessary for a successful fabrication of the SiC-mullite composite. The system was maintained closed by applying an outside load on the BN lid. As a result, the atmosphere for the infiltration was actually at a pressure over 101 kPa around 1900°C (thermodynamic calculation indicates ~142 kPa). The SiC-mullite composite therefore was successfully obtained by melt infiltration. Fig. 2A shows the typical microstructure of the 69%-Al_2O_3 composite, revealing a skeleton structure of SiC in the matrix of mullite. Besides phases of SiC and mullite, some amount of defects of voids and glass phase of aluminosilicate were also present in the microstructure of the composite. The presence of the glass phase would be attributed to the Al_2O_3 content in the infiltrant slightly less than that of the single mullite phase formation (~72 wt%). Accordingly, infiltrants with a higher Al_2O_3 content (72 and 75 wt%) were tried. The amount of the glassy phases, therefore, notably decreased as shown in Fig. 2B. The complete removal, however, was not achieved even for the highest Al_2O_3 content (80 wt%), where excess Al_2O_3 was found present on the surface of the sample after infiltration with 80%-Al_2O_3 infiltrant. This can be well understood by considering the Al_2O_3-SiO_2 phase diagram. According to the most recognized phase diagram of the Al_2O_3-SiO_2 system of Aksay and Pask [6], mullite has a non-stoichiometric composition range of Al_2O_3 from 70 to 76 wt%, and melts incongruently, which might be the reason why the glassy phase could not be completely removed in the present study. The microstructures of the 72%-, 75%-, and 80%-Al_2O_3 composites were almost identical. The density of the composite was determined to be 3.10 g/cm^3 using Archimedes principle, so that the composite was quite dense (relative density of ~97% for 75%-Al_2O_3).

3.2. Fracture strength in argon

The Fracture strength of the SiC-mullite composite was measured under argon at atmospheric pressure and the obtained data were summarized in Table I. Fig. 3 shows the result for the 69%-Al_2O_3 composite. The symbols in Fig. 3 represent the mean values obtained from 5 effective tests, while the total ranges of the individual strength data are given by error bars. The room temperature strength is not high (274 MPa). The strength decreases substantially at high temperatures, which has been tentatively ascribed to the presence of the glassy phases. Since the microstructures of the 72%-, 75%-, and 80%-Al_2O_3 composites were almost identical, further fracture strength evaluation was mainly done

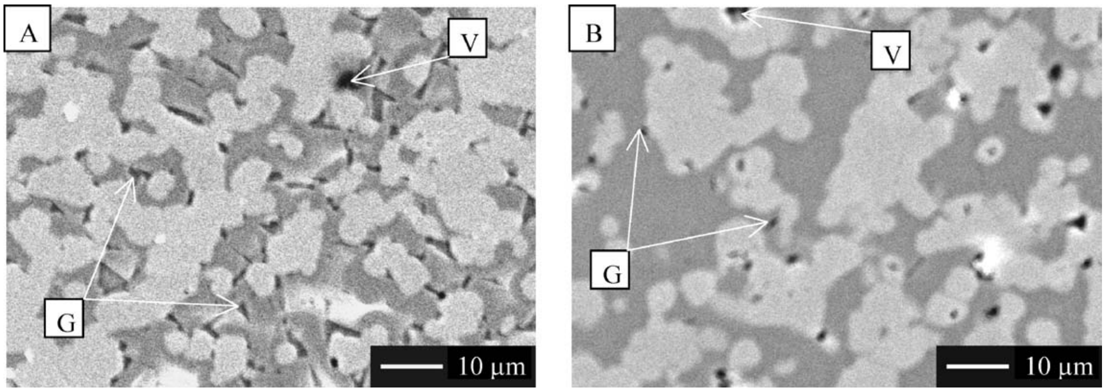

Figure 2 Microstructure of SiC-mullite composite (A: 69%-Al_2O_3; B: 75%-Al_2O_3). White phase: SiC; Dark phase: mullite; G: glass of aluminosilicate; V: void.

TABLE I The fracture strength of SiC-mullite composite

Loading rate (MPa/S)	Composite	Temperature °(C)	Atmosphere	Fracture strength[a] (MPa)	Weibull modulus (m)	Regression coefficient (R)
2	69%-Al_2O_3	25	In argon	274 (75)	9.9	0.9493
		1100		226 (22)	29.5	0.9224
		1300		142 (42)	9.6	0.9907
		1500		48 (45)	2.8	0.9553
	75%-Al_2O_3	25	In argon	351 (53)	19.4	0.9522
		1100		241 (67)	9.8	0.9838
		1300		149 (16)	25.5	0.9829
		1500		97 (21)	13.7	0.9209
	75%-Al_2O_3	25	In air	351 (53)	19.4	0.9522
		1100		350 (70)	12.5	0.9390
		1300		240 (29)	24.0	0.9644
		1500		161 (42)	11.6	0.9896
0.2[b]	75%-Al_2O_3	1300	In air	207 (54)	12.1	0.9742

[a] The fracture strengths are mean values of five effective strength data while the maximum span of all the individual strength data are given in parenthesis.

[b] The calculated crack velocity exponent (*n*) from different loading rate is 15.

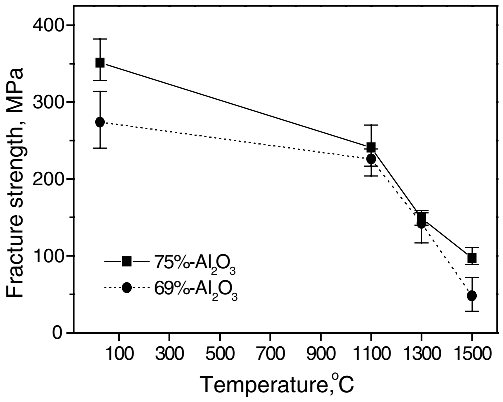

Figure 3 Fracture strength of SiC-mullite composite in argon (The symbols represent mean values of five effective strength data while the total ranges of the individual strength data are given by error bars).

using the 75%-Al_2O_3 composites and the results were also shown in Fig. 3. The room temperature strength of the 75%-Al_2O_3 composite was higher (351 MPa) than that of the 69%-Al_2O_3 composite. This could be attributed to the higher density and fewer defects of the former. Namely, the Al_2O_3 content in the infiltrant had a subtle but discernible influence on the infiltration behavior, and denser composites were obtained for the Al_2O_3 content of greater than 72%. The high temperature strength, however, showed only a slight improvement over that of 69%-Al_2O_3, indicating that the glassy phases are not the primary cause of high temperature strength degradation.

3.3. Mullite decomposition in argon and in air

The color of the specimen after the strength measurement changed slightly from gray to white-gray, indicating some surface modification and scale formation of the specimen during high temperature. Thus, room temperature strength measurements were intended on the 75%-Al_2O_3 specimen after heat treatment at 1500°C. Fig. 4 shows the results. The symbols in Fig. 4 represent the mean values obtained from 5 effective tests, while the total ranges of the individual strength data are given by error bars. As seen from Fig. 4, heat treatment at 1500°C for 15 min could substantially weaken the composite, endowing the composite with room temperature facture strength of almost half of that of no heat treatment. Short heat treatment of 3 min could only increase the strength a little. Carefully removal of the surface layer after 3 min heat treatment at 1500°C, however, was found to restore the original room temperature strength of more than 80%. Thus, surface modification as well as scale formation of the specimen during strength measurements at high temperature was proposed to be responsible for the weak high temperature fracture strength of the SiC-mullite composite.

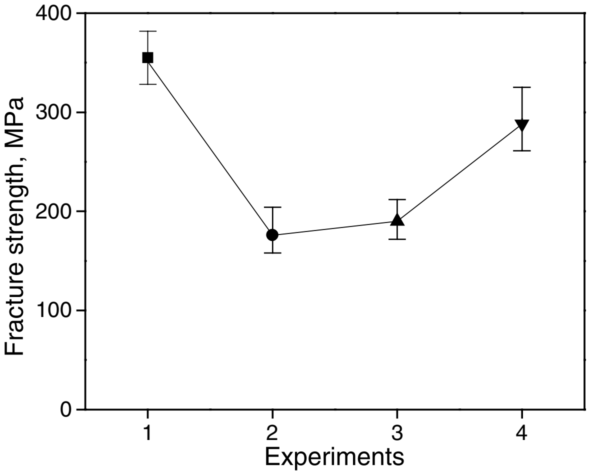

Figure 4 Room-temperature fracture strength of SiC-mullite composite after heat treatment at 1500°C (The symbols represent mean values of five effective strength data while the total ranges of the individual strength data are given by error bars. The specimens are not heat treated in (■), heat treated at 1500°C for 15 min in (●), heat treated at 1500°C for 3 min in (▲), and heat treated at 1500°C for 3 min and then carefully ground away the scale before measurements in (▼). The line shows the tendency of the fracture strength after different heat treatments).

In the present study, the most possible cause for the surface modification of the specimen at high temperatures was mullite decomposition, which was presumably occurring in our system and responsible for the low high temperature strength of the composite. Based

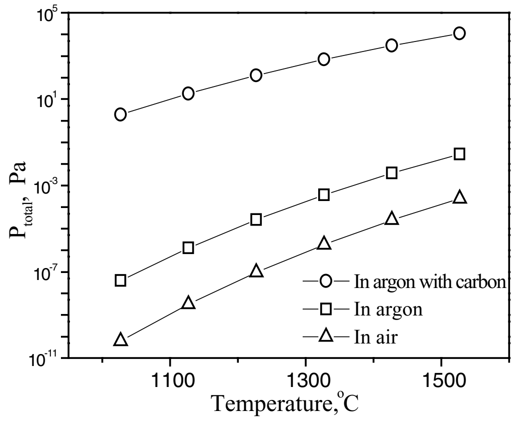

Figure 5 Total vapor pressures (P_{total}) for mullite decomposition in different conditions.

on the thermodynamic calculations, Fig. 5 shows the equilibrium total vapor pressure of mullite (P_{total}) as a function of temperature in different conditions at high temperatures. Under argon at atmospheric pressure, the P_{total} is not high. With a presence of carbon, the P_{total}, however, shows almost six orders of magnitude of increase, indicating an extensive decomposition of mullite at this condition. In the present study, the strength was measured in an open system under argon at atmospheric pressure, and carbon was used as a heating element, resulting in a reducing environment. Carbon could react with mullite through gas transmissions, leading to decomposition of mullite. The proposed reactions were as follows:

$$3Al_2O_3 \cdot 2SiO_2(s) \rightarrow 3Al_2O_3(s) + 2SiO(g) + O_2(g), \quad \text{(Mullite decomposition)} \quad (1)$$

$$2C(s) + O_2(g) \rightarrow 2CO(g), \quad (O_2\ \text{consumption}) \quad (2)$$

$$2C(s) + SiO(g) \rightarrow SiC(s) + CO(g), \quad \text{(SiO consumption)} \quad (3)$$

where overall reaction would be kinematically rate-controlled by the transport of gaseous species, so that it would be slow at lower temperatures. Fig. 5 also shows P_{total} under air at atmospheric pressure. The P_{total} in air is almost three orders of magnitude lower than that in argon and much lower than that in argon with carbon presence, indicating mullite decomposition under this condition having been suppressed dramatically. The strength measured in air, therefore, would be expectedly much better than that in argon with carbon presence.

3.4. Fracture strength in air

Based on the results of thermodynamic calculations above, the fracture strength of the composite was again measured in air. The results are shown in Table I and Fig. 6. The symbols in Fig. 6 represent the mean values obtained from 5 effective tests, while the total ranges of the individual strength data are given by the error bars. As seen in Fig. 6, the high temperature fracture strength in air is apparently higher than that in argon. The average value at 1100°C was 350 MPa, which is almost the same as that at room temperature. At temperatures of 1300 and 1500°C, the strength in air was also much higher than that in argon, though it significantly decreased. The specimen showed almost the same color before and after failure, indicating that the mullite decomposition had been efficiently suppressed. Crack healing, which may be a concern for the measurements in air, was presumably not extensive in the present case, since, as will be discussed later, slow crack growth was the dominant failure mode at high temperatures.

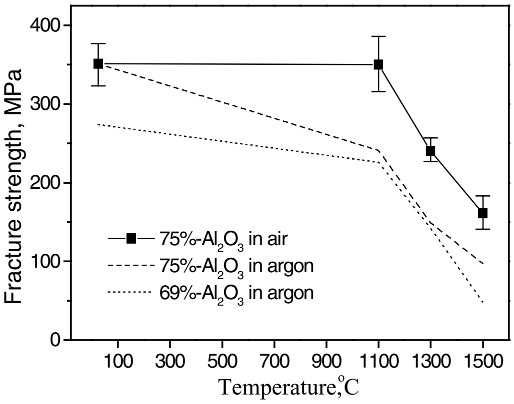

Figure 6 Fracture strength of SiC-mullite composite in air (The symbols represent mean values of five effective strength data while the total ranges of the individual strength data are given by error bars. The fracture strengths of the 69%-Al_2O_3 and 75%-Al_2O_3 composites in argon are also plotted in this figure for comparison).

Although only five effective specimens were tested at each temperature due to the high cost and much time consumption during the specimen productions, we would also like to show our Weibull analysis on all of the obtained strength data based on the two-parameter Weibull equation [7]:

$$P_f = 1 - \exp(-(\sigma/\sigma_0)^m) \quad (4)$$

where P_f was the probability of failure of a specimen, σ the fracture strength, σ_0 a normalizing stress, and m

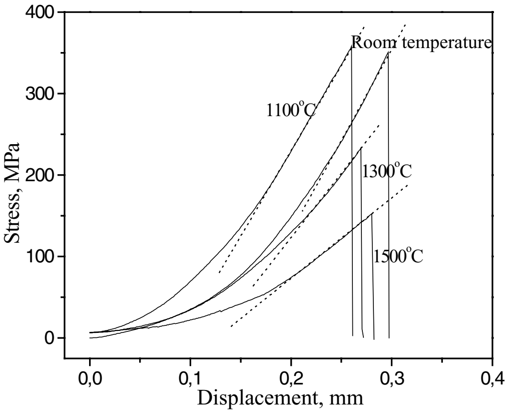

Figure 7 Typical stress-displacement curves of SiC-mullite composite at different temperatures in air (Dash lines indicate the quite linear parts of the curves where no plastic deformations occur during measurements. The non-linear parts at the beginning of the curves were proposed to be due to the testing devices).

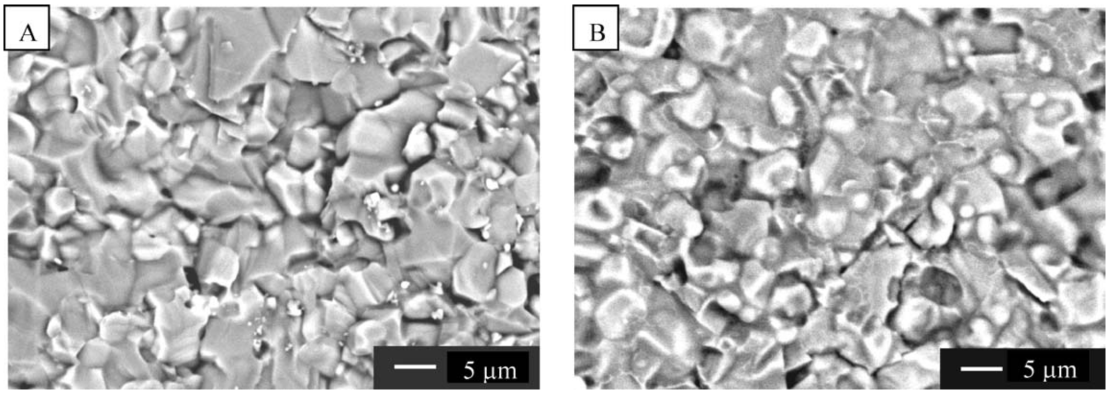

Figure 8 Fracture surfaces of SiC-mullite composite after failure in air at (A) room temperature and (B) 1500°C.

the Weibull modulus. The results were summarized in Table I. It has been pointed out that a value of Weibull modulus that exceeds 10 indicates a good material [8]. Most of the *m* values in Table I are close to or greater than 10, indicating good reliability of the data. However, we could not well believe such indication since the *m* values in Table I are quite discrepancy at different temperature and some of the regression coefficient values, *R*, are not satisfactory. These could be contributed to the fact that only very small amount of specimens were used for tests. Another interesting thing shown in Table I is that for 75%-Al_2O_3 composite similar *m* values were obtained in argon and in air at the same temperature. The reason was not clear.

Fig. 7 shows typical stress-displacement curves of the SiC-mullite composite in air. The curves were strongly non-linear during the beginning and then quite linear until failure (as shown by dash lines in Fig. 7). The non-linear displacements were proposed to be due to the testing devices. The quite linear displacements close to failure, however, strongly indicates that the composite was linearly elastic up to 1500°C and almost no plastic deformations could be observed until failure. The fracture surface, as shown in Fig. 8A and B, has a little indication of debonding at the SiC-mullite interface at high temperature. Thus, the fracture mode was typical brittle fracture from room temperature to 1500°C, where cracks originated either at the machining flaws or voids, then rapidly propagated and destroyed the material. The failure of the composite was presumably governed by slow crack growth (SCG), which is known to be operative in the fracture of ceramic materials [9–11]. The strength measurement with a slower loading rate was accordingly conducted at 1300°C in air, and the results are listed in Table I. The slower loading rate led to a definite decrease in strength, and the crack velocity exponent (*n*) was tentatively calculated to be ~15, though the data points were not sufficient. The exponent is comparable to that of hot-pressed SiC in air at 1400°C (*n* value of ~21) [9], indicating a fact that the composite suffers from slow crack growth at high temperature similar to other polycrystalline materials. However, further investigations are definitely necessary to confirm and elucidate the detailed SCG mechanism for the present composite.

In comparison with the composites made by other processes, the room temperature strength of the present composite was moderately high, though a much higher strength was actually reported by some novel processes [12, 13].

4. Conclusions

The fracture strength of the melt-infiltrated SiC-mullite composite was investigated from room temperature to 1500°C using a three-point bending test. Under argon at atmospheric pressure, the measured bending strength was low even at 1100°C. Mullite decomposition on the surface of the specimen due to the reducing environment was proposed to be responsible for the low strength. The strength in air, in which mullite decomposition was suppressed, was moderately high, and the room temperature strength was retained up to 1100°C. The composite revealed typical brittle failure due to slow crack growth.

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