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Joining of silicon carbide using MgO-Al_2O_3-SiO_2 filler

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Pressureless sintered SiC specimens were joined using MgO-Al_2O_3-SiO_2 (MAS) filler. MAS filler showed excellent behaviour of wetting on SiC substrate above 1480 °C, and the wettability was much influenced by the joining atmosphere. The joining was carried out at 1500 and 1600 °C for 30 min in Ar atmosphere. The flexural strength of the joined specimen showed 342–380 MPa up to 800 °C. However, the flexural strength of the joined specimen decreased to about 80 MPa at 900 °C due to softening of the joint interlayer. The results of the XRD and WDS showed that the reaction between SiC and the MAS filler produced the oxycarbide glass.

1. Introduction

Silicon carbide has been noticed for high temperature applications because of its excellent high temperature characteristics such as high strength, high toughness, good creep resistance and excellent thermal shock resistance. However, the applications of SiC have been prohibited by the difficulty and high cost of fabrication of ceramic parts of large or complex shape. This difficulty may be overcome by making huge and complicated ceramic products through joining of simple and small ceramic parts. Therefore, ceramic joining technique becomes increasingly important.

Many joining techniques have been developed for nonoxide ceramics including SiC [1–10]. Since SiC ceramics are, particularly, used in high temperature applications such as heat engine, heat exchanger, recuperator, etc., the strength of high temperatures and thermal shock resistance of the joined part and the reproducibility of the joining technique are very important. In this point of view, the brazing method seems to be most proper method for SiC/SiC joining. The brazing method shows good sealing features by formation of joint interlayer through solidification of liquid phase with low cost [5, 6].

In this study, MgO-Al_2O_3-SiO_2 (MAS) system was selected as the source of the filler material for brazing SiC ceramics. Most silicate glasses have been reported to exibit good wettability with SiC [11]. Moreover, some MAS glasses show a wetting angle less than 10° on SiC substrate [11]. It is also reported that some MAS compositions have nearly the same low thermal expansion coefficient as SiC itself and the reaction between MAS and SiC at elevated temperatures has the possibility of producing an oxycarbide glass which may exhibit high strength at high temperatures [12–15].

2. Experimental

2.1. Starting materials

SiC specimens used in this study were prepared from the pressureless sintered α-SiC billets (fabricated by Korean Tungsten Co., Korea) and the basic properties were measured as given in Table I. The starting powders used in this study to prepare the filler agent were MgO (99%, 0.5 μm, Junsei Chemical Co., Japan), Al_2O_3 (99.99%, 0.2 μm, AKP50, Sumitomo Chemical Co., Japan) and SiO_2 (99.9%, 0.8 μm, High Purity Chemical Co., Japan). All powders were calcined at 1000 °C before weighing; in particular, MgO, which easily forms $Mg(OH)_2$ through reaction with water vapor in the atmosphere was weighed as soon as calcined to prevent hydration. The composition of the joining filler was controlled to meet the thermal expansion coefficient of SiC.

2.2. Wetting behaviour of MgO-Al_2O_3-SiO_2 filler on SiC

To observe the wettability of the MAS joining filler on SiC, an MAS material was prepared from the starting powders, MgO, Al_2O_3 and SiO_2. MgO, Al_2O_3 and SiO_2 powders were mixed in weight percents of 15 : 25 : 60 in ethyl alcohol using a ball mill for 24 hours to produce a slurry. The slurry was dried and parched in an oven at 200 °C for 24 hours. The powder was pressed into 1 mm thick disk type specimens. SiC substrate was polished with a 10 μm-grained diamond polishing plate and cleaned ultrasonically in acetone for 15 min and again cleaned in ethyl alcohol for 5 min. The MAS disk was placed on the SiC substrate and heated at a heating rate of 5 °C/min up to the aimed temperatures over 1350 °C to 1530 °C in Ar atmosphere, holding 30 min at each temperature. The heat treatment was conducted

TABLE I Properties of SiC specimen

Manufacturer	Korea Tungsten Co.
Density	3.15 g/cm^3
Thermal conductivity	0.15 cal/cm.S. °C
Thermal expansion coefficient	4.5×10^{-6}/°C
Flexural strength	370 MPa
Hardness	2500 GPa

in both a graphite furnace and an alumina tube furnace. X-ray diffractometer (XRD) analysis was performed to observe the phase of the wetted layer on SiC substrate after cooling.

2.3. Thermal expansion behaviour of MgO-Al_2O_3-SiO_2 glass and SiC

Thermal expansion behaviour of the MAS glass (MgO : Al_2O_3 : $SiO_2 = 15 : 25 : 60$) and SiC was observed using a dilatometer (402EP, Netzsch, Germany) to confirm whether the thermal expansion mismatch between the MAS filler and SiC might be overcome. The MAS filler and SiC specimens of $3 \times 4 \times 50$ mm were prepared for measurement of thermal expansion behaviour with heating rate of 10 °C/min in Ar atmosphere.

To prepare the MAS glass, the mixture of MgO, Al_2O_3 and SiO_2 of the composition of MgO : Al_2O_3 : $SiO_2 = 15 : 25 : 60$ wt % was melted in a Pt crucible at 1600 °C for 30 min and quenched to room temperature. The cooled glass specimen was annealed at 600 °C for 2 hours and cut into the desired size of $3 \times 4 \times 50$ mm using a precise cutting machine (Isomet, Buhler, U.S.A.).

2.4. Joining of SiC/SiC with MAS filler

A large SiC billet was cut into rectangular specimens of $15 \times 25 \times 20$ mm. The 15×25 mm faces of SiC to be contacted with MAS filler were polished with 10 μm-grained diamond polishing plate and cleaned ultrasonically in acetone for 15 min and cleaned again in ethyl alcohol for 5 min. The prepared MAS joining powder was pressed into sheets of about 1 mm thickness to be inserted between two polished SiC specimens before heating in the graphite vacuum furnace at both 1500 and 1600 °C for 30 min. No load was applied to the specimen for joining except for the load of the specimen itself. Throughout heating of the specimen from room temperature to 1000 °C, a vacuum of 10^{-5} torr was maintained. Ar gas was introduced into the furnace chamber at 1000 °C and the temperature was held for 30 min to stabilize the Ar atmosphere in the furnace chamber, followed by continuous heating up to 1500 and 1600 °C with the heating rate of 15 °C/min in Ar atmosphere. The specimens were heat-treated at 1500 and 1600 °C for 30 min and the specimens were cooled down to room temperature with the cooling rate of 100 °C/min. The joined specimens were cut into the standard bar type specimens of $3 \times 4 \times 35$ mm for the measurement of flexural strength using a precise cutting/grinding machine (MX-833, Maruto, Japan).

2.5. Characterization

The joint interlayer of the joined SiC/SiC specimen was observed with FE-SEM (Field Emission SEM, S-4200, Hitachi, Japan) and an optical microscope(ML-MET, Meiji, Japan). Line scanning quantitative analysis of Si, C, Al, Mg elements across the joint interlayer was performed using the electron probe microanalyzer (EPMA) and the wavelength dispersive spectrometer (WDS, JXA-8600, Jeol, Japan).

Room and high temperature flexural strength was measured with three point flexure system (Instron 6505, Instron Co., U.S.A.). The strength was measured with the span of 30 mm and the crosshead speed of 0.5 mm/min. The fracture surfaces of the specimens were observed with FE-SEM and an optical microscope.

3. Results and discussion

3.1. Wettability of MAS filler on SiC

The wetting behaviour of MAS filler on SiC was observed and the results are given in Table II. As can be seen in Table II, MAS filler was nearly spread on SiC when heated in the alumina tube furnace above 1480 °C. However, the wetting angle was about 45 degrees when the specimen was heated in the graphite furnace. The difference is probably due to the effects of carbon oxide gases produced through the reaction of the graphite heating element with the oxygen existing as an impurity in Ar atmosphere. The gaseous species like carbon oxide may change the wetting behaviour of the filler on the substrate by influencing the surface tension of gas-liquid and gas-solid interfaces which determines the wetting angle. Therefore, it can be found that the wettability of the MAS filler on SiC is much influenced by the gaseous atmosphere. Therefore, the MAS filler was fully melted but partially wetted on SiC in the graphite furnace above 1480 °C, as can be seen in Table II.

XRD analysis on the MAS-coated SiC substrates showed no crystalline peak but showed only the typical

TABLE II Wetting behaviour of MgO-Al_2O_3-SiO_2 filler on SiC substrate

Furnace	1350 °C	1400 °C	1430 °C	1450 °C	1480 °C	1500 °C	1530 °C
In an Alumina tube furnace	×	×	×	△	○	○	○
In a Graphite furnace	×	×	×	△	□	□	

× : not melted
△ : partially melted
□ : fully melted, but partially wetted contact angle ($\theta \leq 45$)
○ : perfect wetted (spreading) contact angle ($\theta \fallingdotseq 0$)

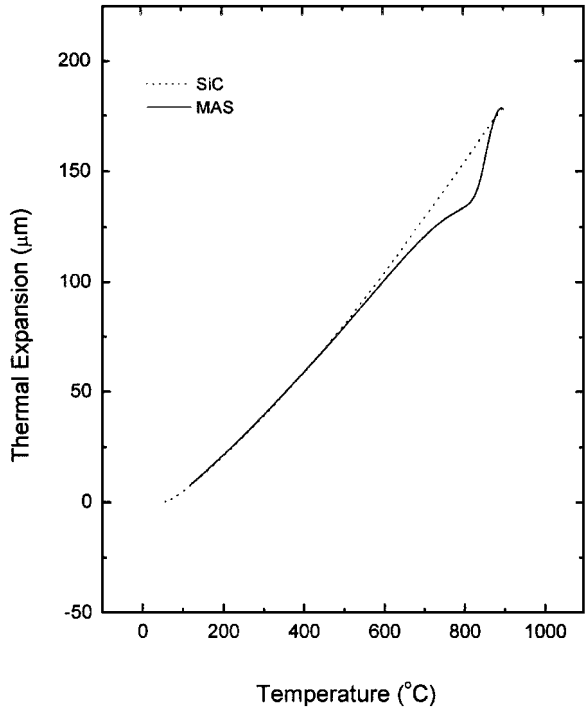


Figure 1 Thermal expansion behaviour of SiC and MAS specimens.

halo pattern in the range of 20–40 degrees, implying that the joint interlayer might be a glass phase.

3.2. Thermal expansion behaviour of SiC and MAS filler

Thermal expansion behaviour of the MAS filler and SiC is shown in Fig. 1. The thermal expansion behaviour of the MAS filler is congruent with that of SiC up to 700 °C. The MAS filler represents the typical thermal expansion behaviour of the glass in the temperature range of 700 to 900 °C. The glass transition temperature can be observed at about 800 °C and rapid softening point can be observed at 900 °C in Fig. 1. It can be expected that the critical strength degradation of the joined SiC/SiC specimen may occur at 900 °C by softening of the formed glass.

3.3. Observation of the joint interlayer

Fig. 2 shows the microstructure of a cross section of the joint SiC/SiC interlayer brazed at both 1500 and 1600 °C for 30 min with the MAS filler. The thickness of the MAS interlayer after joining can be observed

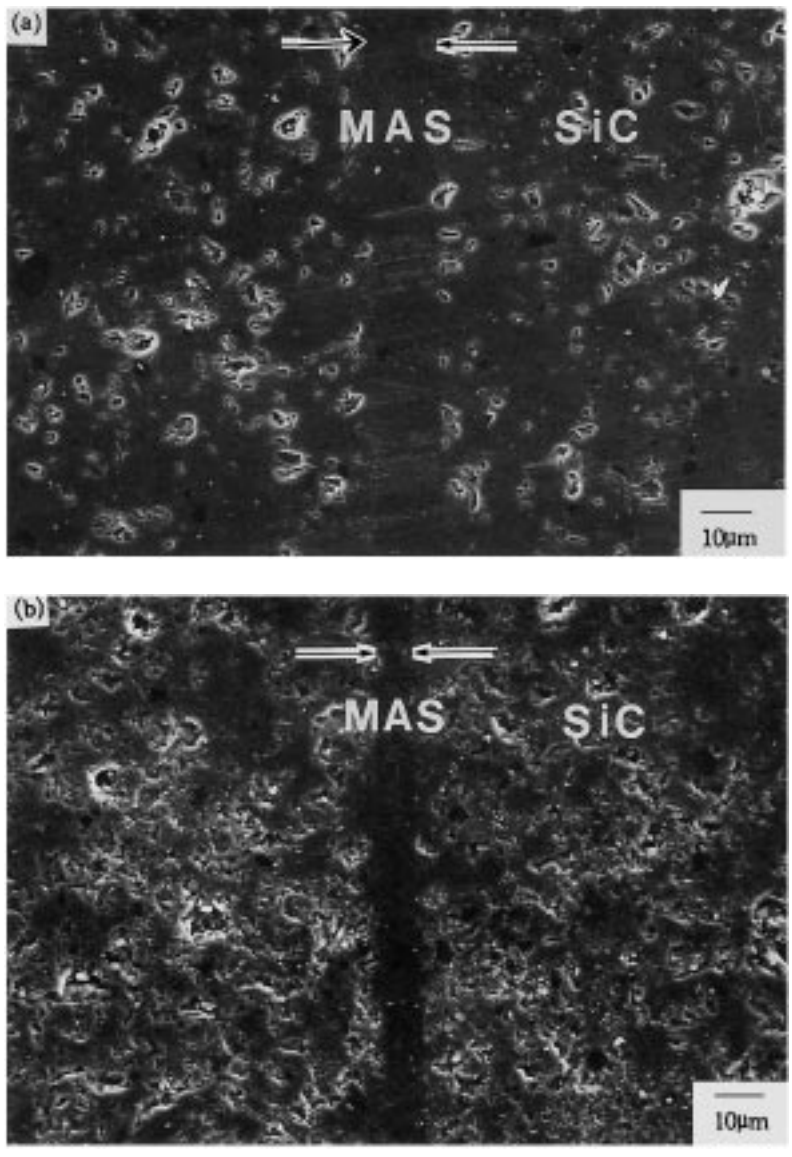


Figure 2 SEM images of the cross section of the specimen joined at (a) 1500 °C and (b) 1600 °C.

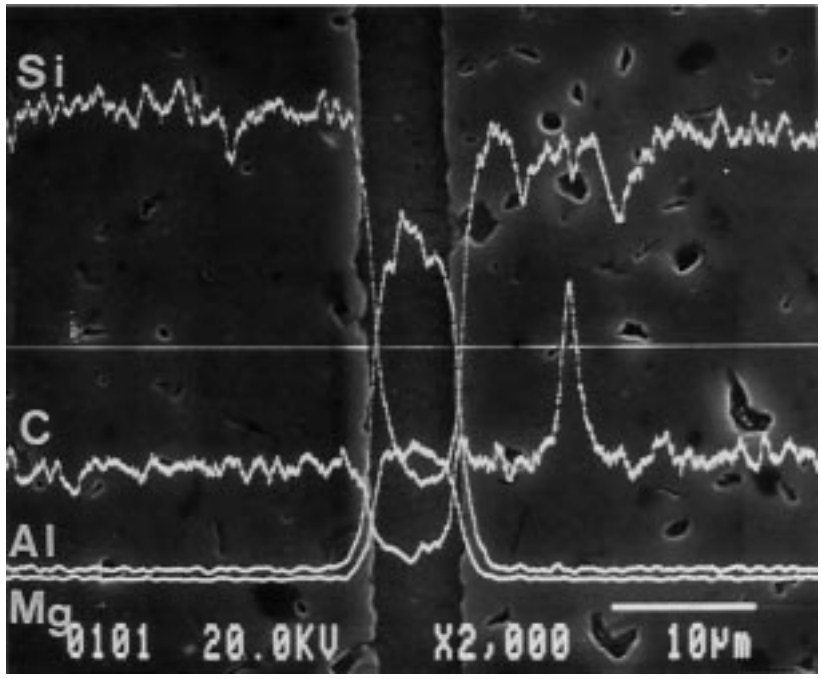


Figure 3 EPMA line scanning analysis of Si, C, Al, Mg elements across the specimen joined at 1600 °C.

to be about 10 and 5 μm for the joining temperatures 1500 and 1600 °C, respectively, in Fig. 2. The colour of the joint interlayer was black and no crack was observed throughout the entire joint interlayer by SEM, as can be seen in Fig. 2. The fact that no crack was observed means that no severe thermal expansion mismatch occurred between SiC and the MAS filler during the joining process. This also means that the thermal expansion coefficient of the oxycarbide glass, which might have been produced in the joint interlayer by the reaction of the MAS filler and SiC matrix during the joining process, is in accord with that of SiC matrix.

Fig. 3 shows the result of EPMA line scanning across the SiC/interlayer/SiC specimen. The concentration profiles of the elements Mg and Al are higher in the joint interlayer. On the other hand, the concentration profiles of the elements Si and C are higher in SiC matrix. However, a small fraction of Si, C element is found in the joint interlayer and Mg, Al element is found in the SiC matrix by the interdiffusion of the elements of MAS and SiC through the boundaries during the joining process.

Table III shows the result of WDS analysis for the joint interlayer. The measured values are the atomic percents except for oxygen atom in the joint interlayer.

TABLE III WDS analysis for the joint interlayer

Elements	Molar ratio (Excluding O atom)	Molar ratio[a] (Including O atom)
Si	53.2	29.0
C	25.1	13.7
Al	11.4	6.2
Mg	10.3	5.6
O		45.5

[a]Calculated values.

These values are the averages of the values analyzed at 5 random points in the layer. The calculated values including oxygen have been obtained by assuming that the metal ions Si, Mg, Al are stoichiometric with oxygen ion. It is assumed from the data given in Table III that 13.7 mol % of carbon quantity diffused into the joint interlayer. The XRD analysis in Section 3.1 confirmed the wetted layer on SiC substrate to be a glass phase. Consequently, the joint interlayer, which was produced by the reaction of MAS filler and SiC matrix in the joint interlayer at 1500 and 1600 °C during joining process and contains 13.7 mol % of carbon, is considered to be an oxycarbide glass which has been reported to have good strength and stability at high temperatures.

3.4. Flexural strength of the joined specimen

The flexural strength of the joined specimen was measured as a function of temperature as shown in Fig. 4. Flexural strength of the joined specimen shows 342–380 MPa up to 800 °C. However, the strength decreases critically to 80 MPa at 900 °C.

The thermal expansion behaviour of MAS is congruent with that of SiC up to 700 °C as can be seen in Fig. 1, however, the typical thermal expansion behaviour of the glass was observed for MAS at 800 °C, which is assumed to be the glass transition temperature of the MAS filler. The softening point was observed at about 900 °C, which agrees well with the critical degradation of the strength of the joined specimen at 900 °C as can be seen in Fig. 4.

Fig. 5 shows the fracture surface of the joined SiC specimen wherein the fracture origin can be observed. The fracture origin is located in the glass phase region, but the crack propagates into the SiC matrix as can be seen in Fig. 5. This means that even though the crack

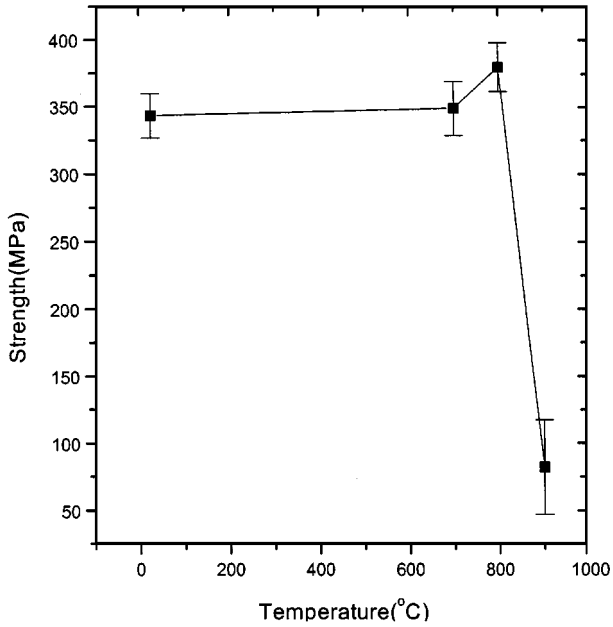


Figure 4 Flexural strength of the specimen joined at 1500 °C as a function of temperature.

initiates in the joint interlayer, it propagates into the SiC matrix, which can be confirmed by the side view of the fractured specimen as shown in Fig. 6. This implies that the strength of the joint interlayer is not lower than that of SiC matrix.

Fig. 7 shows the fracture surface of the specimen fractured at 800 °C wherein the fracture origin can be observed in SiC matrix. The glass transition begins around this temperature as can be seen in Fig. 1 and the strength increase may be due to the thermal stress relaxation or crack healing of the joint interlayer at 800 °C, resulting in fracture of SiC matrix rather than interlayer of the joined specimen as can be seen in Fig. 7.

Fig. 8 shows the fracture surface of the fractured specimen at 900 °C. Many craters including small grains, which can be observed in Fig. 8a, are assumed to be the result of nucleation and crystallization of crystallites from MAS glass during cooling after melting at 900 °C as can be expected from Fig. 1. The flexural strength decreases to 80 MPa at 900 °C by softening due to melting of the joint interlayer. The side view

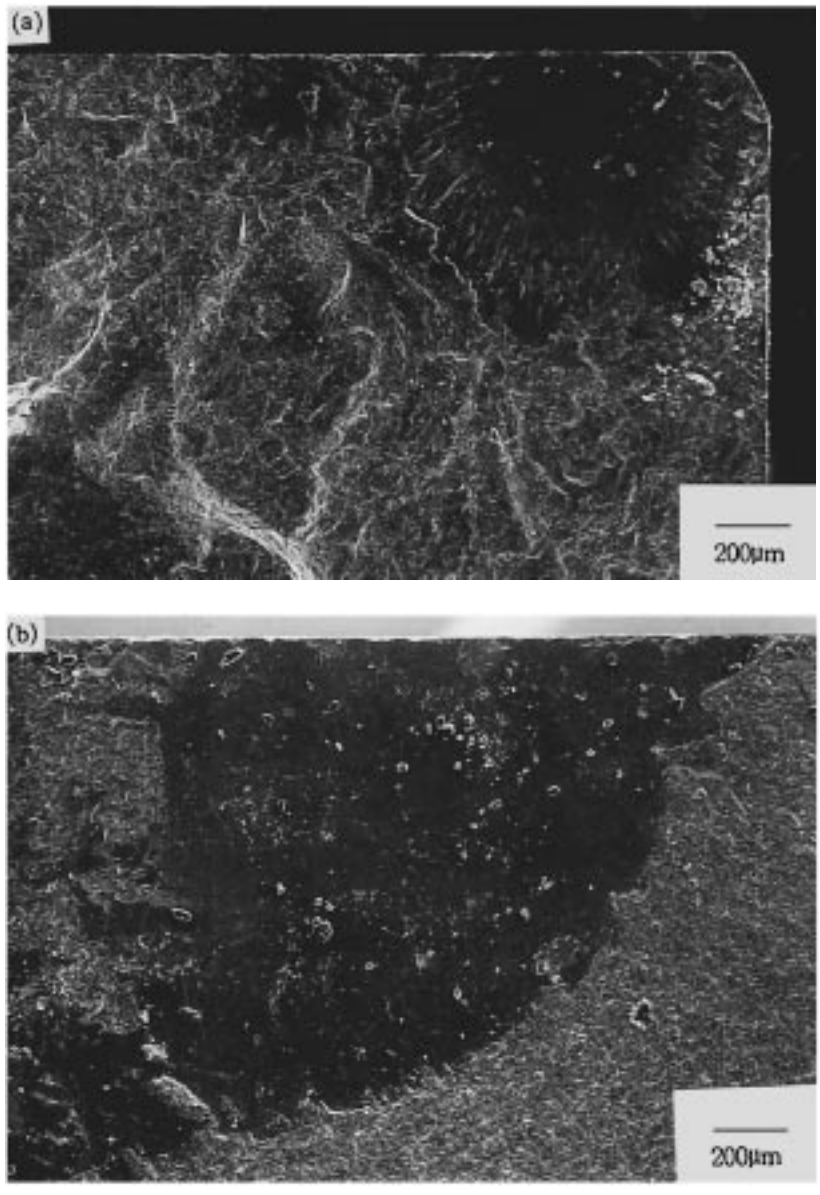


Figure 5 SEM images of the fracture surfaces of the specimen joined at (a) 1500 °C and (b) 1600 °C and fractured at room temperature.

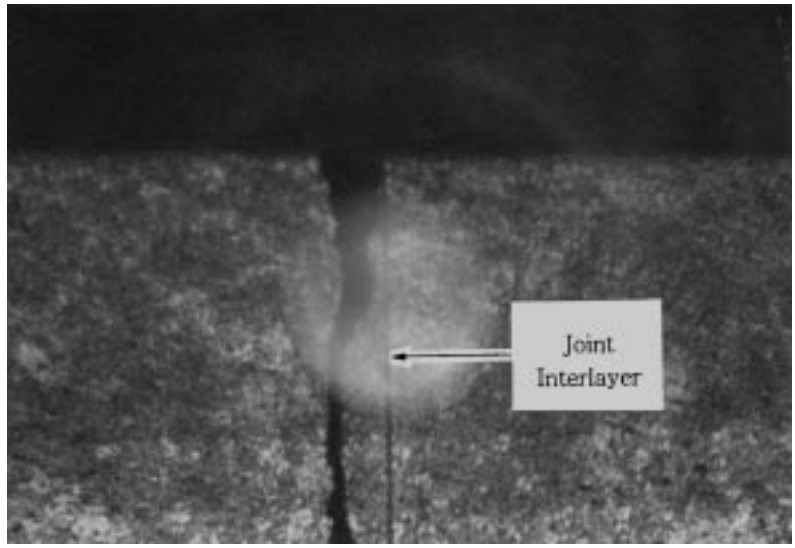
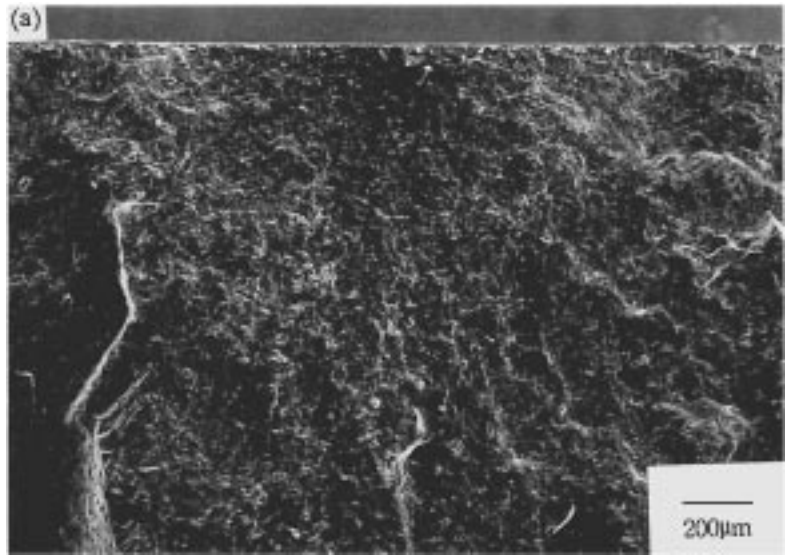


Figure 6 Optical microphotograph of the side view of the fractured specimen which was joined at 1500 °C and fractured at room temperature.



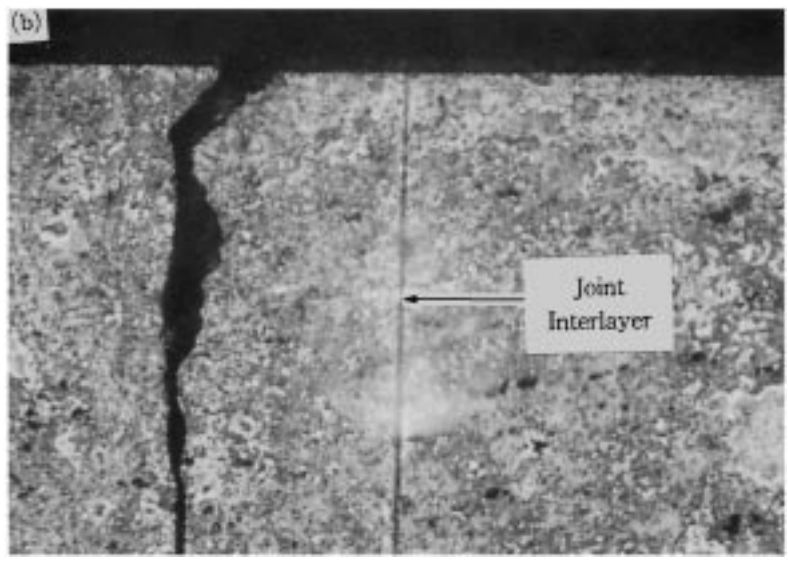


Figure 7 Microphotographs of the specimen joined at 1500 °C and fractured at 800 °C. (a) SEM image of the fracture surface and (b) Optical microscopic image of the side view of the fractured specimen.

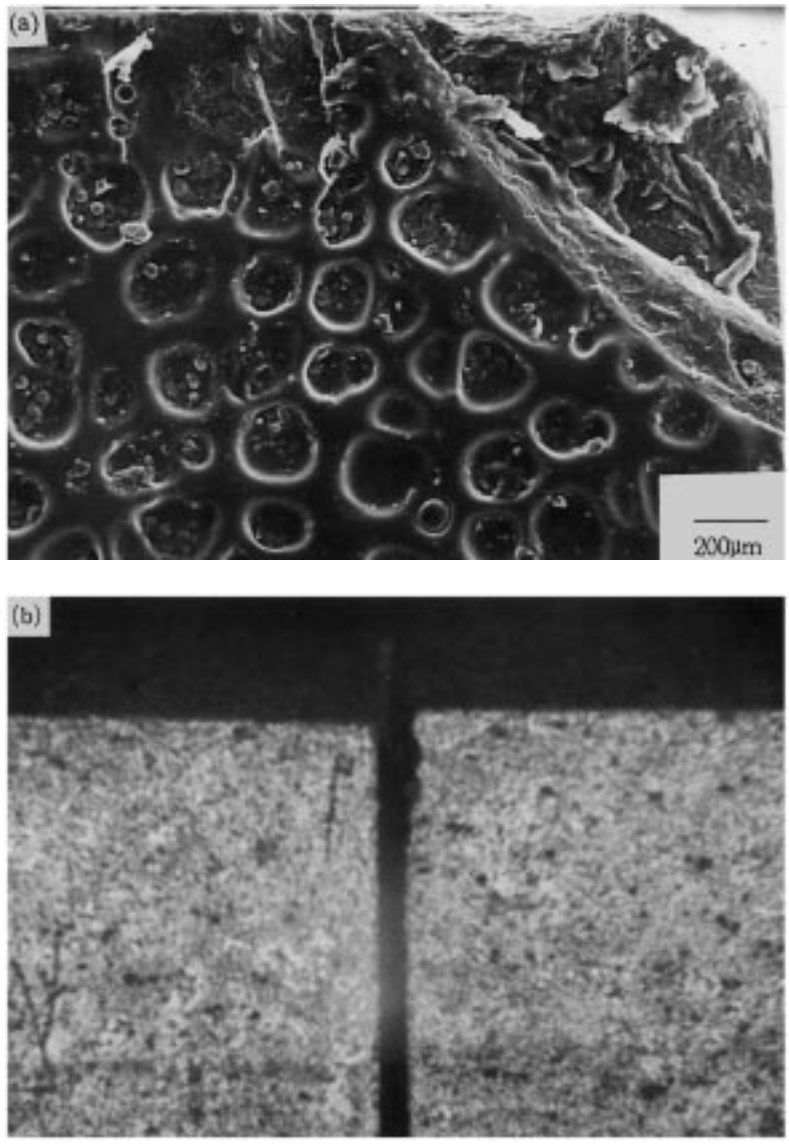


Figure 8 Microphotographs of the specimen joined at 1500 °C and fractured at 900 °C. (a) SEM image of the fracture surface and (b) Optical microscopic image of the side view of the fractured specimen.

of the fractured specimen shows that the crack propagates along the joint interlayer according to the failure of the joint interlayer by the softening of joint interlayer oxycarbide glass at 900 °C as can be seen in Fig. 8b.

4. Conclusions

From the study of joining SiC ceramics using MgO-Al_2O_3-SiO_2 filler, the results can be summarized as follows:

1. MgO-Al_2O_3-SiO_2 filler wets satisfactorily on SiC substrate above 1480 °C and the wetting behaviour of MAS filler on SiC is influenced by the joining atmosphere.

2. Dense and strong joint interlayer is produced by the reaction of the MAS filler with SiC matrix. The produced joint interlayer is assumed to be the oxycarbide glass which has high strength and high temperature stability.

3. Thermal expansion behaviour of the MAS filler is almost the same with that of SiC matrixt up to 800 °C, hence, the joined specimen shows the strength of 342–380 MPa, which is almost the same with that of as-received SiC specimen up to 800 °C. However, the strength decreases to 80 MPa at 900 °C due to the softening of joint interlayer at 900 °C.

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