

論文

Oxidation Behavior of Al_2O_3 -SiC Composites

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 Al_2O_3 -SiC 복합재료의 산화거동

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ABSTRACT

Oxidation studies were conducted on Al_2O_3 -SiC composites at 1375–1575°C in O_2 . The composites were prepared by hot pressing mixtures of Al_2O_3 and SiC powders. The reaction products contained alumina, mullite, an alumino-silicate liquid, and gas bubbles. The parabolic rate constants were about 3 orders of magnitude higher than those expected for the oxidation of SiC particles alone. Higher rates are caused by higher oxygen permeabilities through the reaction products than through pure silica. Our results suggest that oxygen permeabilities are comparable in three condensed phases observed in the reaction products.

1. Introduction

Ceramics are becoming increasingly important as high-temperature structural materials because their potential use temperatures are higher than those of metals. Although brittleness is a major limiting factor for many applications, this limitation can be alleviated by using ceramics in the form of composites. However, very few materials are currently available as fibers or whiskers for reinforcement of composites. The most temperature-resistant ceramic fiber/whisker material available is

silicon carbide. Alumina is good matrix candidates because of his excellent high-temperature stability and because of his low oxygen permeabilities. Therefore, considerable work is being performed on SiC-fiber/whisker-reinforced composites in alumina matrix[1-4]. Most of the work in the literature, however, is related to mechanical properties.

Silicon carbide has excellent resistance to high-temperature oxidation because it forms a protective film of silica. However, the oxidation of SiC-reinforced composites might be influenced by the matrix constituent because of possible interaction of

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the silica with the matrix. The purpose of the present study was to understand the mechanism of oxidation of Al_2O_3 -SiC composites.

2. Experimental Procedure

Raw materials for Al_2O_3 -SiC composites were 1 to 4 μm SiC particles (Lonza Inc.), 0.3 μm alumina (Adolf Meller Co.). Powder mixtures of desired composition were homogenized, in batches of 0.1 kg, by ball milling for 8h using alumina balls and isopropanol as a dispersing agent. The ball-milled powders were dried at room temperature, and subsequently pressed into pellets 31.6mm in diameter. The pellets were hot pressed at 1650°C for 10min using a pressure of 18MPa. The hot-pressed samples attained a density of at least 99% of theoretical value.

Silicon carbide particles were well dispersed in the matrix in the hot-pressed samples, as shown in the microstructures in Fig. 1.

Oxidation studies were conducted on hot pressed samples of Al_2O_3 -SiC composites in flowing oxygen. The sample weight was continuously monitored using a Cahn 1000 microbalance to an accuracy of 0.01mg. The sample temperature was measured using a Pt-6% Rh/Pt-30% Rh thermocouple placed near the sample in the hot zone of the reaction tube. The gases entered at the bottom of the reaction tube after passing through a single-bore alumina tube, and were exhausted at the top and passed through a bubbler.

The reaction products formed during oxidation were characterized using x-ray diffraction, optical microscopy, electron microprobe analysis, and scanning electron microscopy. To protect the edges of the oxidized sample during sectioning and polishing, a thick metallic coating was used on the surface. The coating was obtained either by sputtering a 5 μm film of titanium or by electroplating

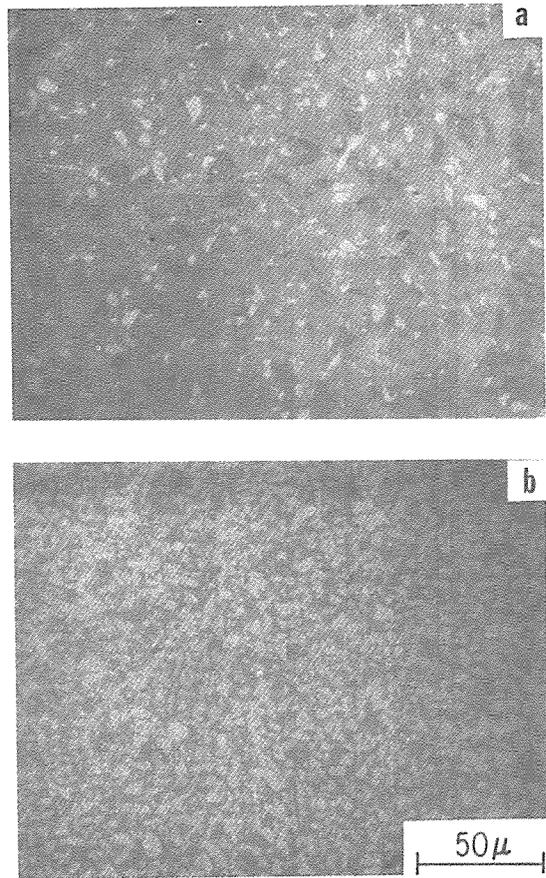


Fig. 1 Optical micrographs of hot-pressed samples of (a) Al_2O_3 -8%SiC and (b) Al_2O_3 -50%SiC. The brighter phase is SiC.

15 μ -thick nickel. The reaction product layer thickness on the samples was measured using optical microscopy equipped with scale.

3. Results

3-1. Reaction Rates

Oxidation studies were conducted at 1375 to 1575 °C on Al_2O_3 matrix composites containing 8, 20, 30, and 50% SiC. All of the experiments were

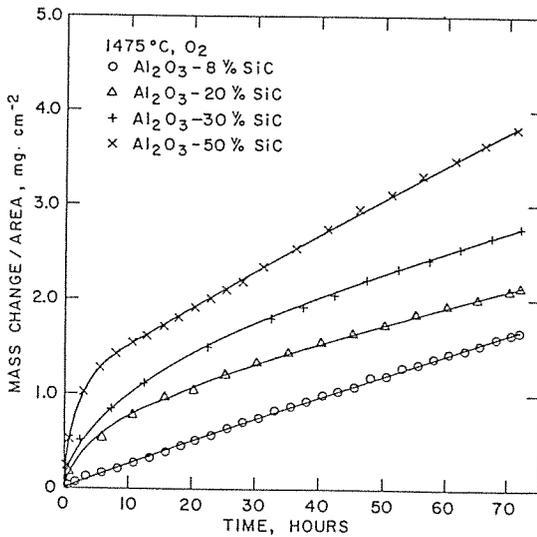


Fig. 2 Typical plots of (mass gain/area) vs. time for oxidation of Al_2O_3 -SiC composites

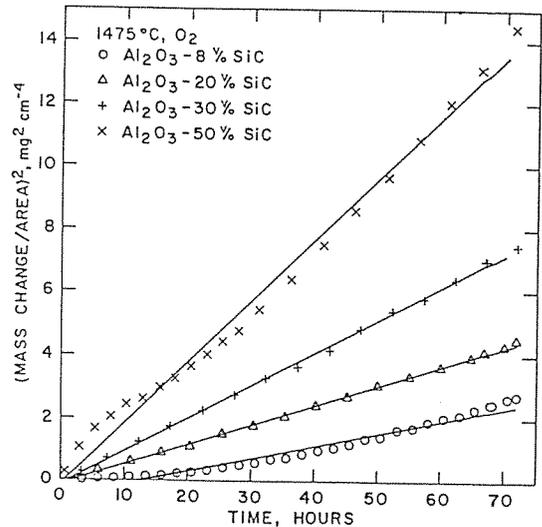


Fig. 3 Typical plots of (mass gain/area)² vs. time for oxidation of Al_2O_3 -SiC composites.

Table 1. Thickness of Reaction Product Layer (μm) Formed in 72 Hours

Temp. ($^{\circ}\text{C}$)	Al_2O_3 -8%SiC	Al_2O_3 -20%SiC	Al_2O_3 -30%SiC	Al_2O_3 -50%SiC	SiC ^a
1375	31 ± 11	30 ± 9	35 ± 13	31 ± 10	1.7
1475	122 ± 29	84 ± 18	82 ± 25	90 ± 33	2.2
1575	195 ± 21	185 ± 22	175 ± 35	188 ± 76	2.6

Table 3. Activation Energies of Oxidation of Composites

Composition	Activation Energy (kJ/mole)	
	Based on K_p	Base on K_m
Al_2O_3 -8%SiC	478 ± 21	422 ± 80
Al_2O_3 -20%SiC	473 ± 15	434 ± 3
Al_2O_3 -30%SiC	411 ± 18	364 ± 8
Al_2O_3 -50%SiC	441 ± 23	472 ± 10

Table 2. Parabolic Rate Constant (K_m) For Oxidation of SiC-Containing Composites

Composite Composition	$K_m, \text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1} \times 10^{10}$		
	1375 $^{\circ}\text{C}$	1475 $^{\circ}\text{C}$	1575 $^{\circ}\text{C}$
	O_2	O_2	O_2
Al_2O_3 -8%SiC	1.1	12.3	24.7
Al_2O_3 -20%SiC	2.8	17.2	83.4
Al_2O_3 -30%SiC	6.4	27.5	113.7
Al_2O_3 -50%SiC	7.2	54.8	303.5

conducted for a period of 72h. Fig. 2 shows typical mass gain results for Al_2O_3 -SiC composites. The mass gain after 72h, indicative of an average reaction rate, increases with the SiC content of the composite. Except possibly for the Al_2O_3 -8% SiC composite, for which the reaction rate appears to stay essentially constant, all compositions exhibit a continuous decrease in reaction rate with time. Fig. 3 shows typical plots of the mass gain squared versus time. The results can be fitted reasonably

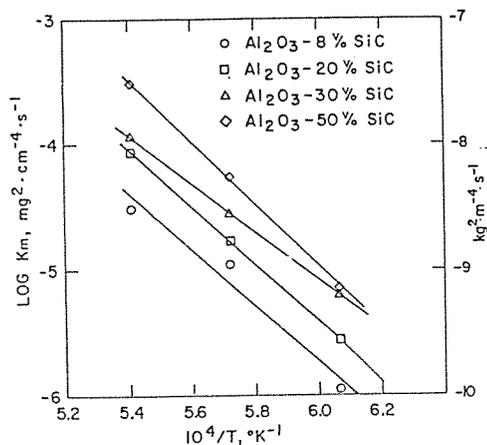


Fig. 4 Plots of $\log K_m$ as a function of $1/T$ for oxidation of Al_2O_3 -SiC composites. Activation energies calculated from the slopes of the straight lines are given in Table 3.

well to straight lines, which indicates that the oxidation process follows a parabolic rate law. The observed deviation from the parabolic law are believed to be related to the formation of CO gas bubbles and to the formation of a liquid whose composition changes with time and thickness.

The above results indicate that the reaction follows a parabolic rate law on the mass gain basis. Assuming a parabolic rate law, the parabolic rate constant K_p , expressed in the units of $\text{m}^2\text{-s}^{-1}$, can be obtained from the thickness of the reaction product. Table 1 gives the results of the measurements of the reaction product layer thickness on the samples used in our study. Table 1 also gives the expected thickness of SiO_2 on pure SiC particles from the literature[5,6]. The observed thickness on Al_2O_3 -SiC are factors of ~ 20 to 100 higher than those on SiC. Since K_p is proportional to the square of the thickness, K_p values are about three orders of magnitude higher than those of SiC.

The results in Fig. 3 indicate that the parabolic

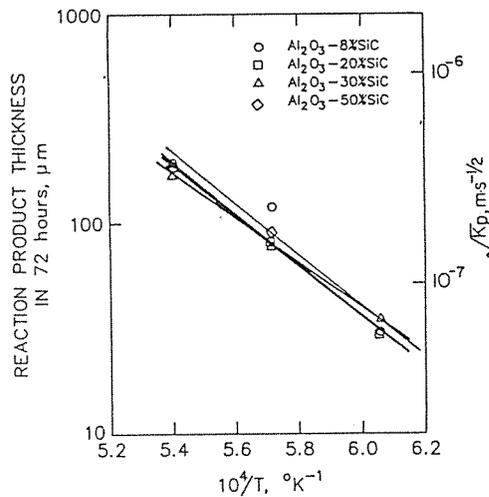


Fig. 5 Plots of reaction product layer thickness as a function of $1/T$ for Al_2O_3 -SiC composites oxidized for 72h in oxygen. Activation energies calculated from the slopes of the straight lines are given in Table 3.

rate constants, expressed on a mass gain basis (K_m), increase with the concentration of SiC in the composite. On the other hand, thickness values in Table 1, and thus the K_p values, are essentially independent of the composition of the Al_2O_3 -SiC composite. This difference between K_m and K_p arises because the volume of the reaction product per unit mass gain is a function of the composition. It decreases with an increase in the volume fraction of SiC.

Activation energies(Q) of oxidation can be obtained from the parabolic rate constants based on mass gain(K_m) or thickness of the reaction product layer after 72h. Table 2 gives a summary of the parabolic rate constants(K_m) and the thickness of the reaction product layer as a function of $1/T$ are shown in Fig. 4 and 5, respectively. The activation energies calculated from these plots are given in Table 3. The activation energies of Al_2O_3 -30%

SiC composite have low value with comparison of other compositions. Since another experiment is not conducted, there is not any specific explanation of this behavior. However, there does not appear to be any specific dependence of the activation energy on the composite composition. The activation energies are of the order of 450kJ/mole.

3-2. Characterization of the Reaction Product

The phases present in the reaction product depend on the composition of the composite. Equilibrium phases in the reaction product can be obtained by considering the phase diagram information. On oxidation, the composites used in our study would contain SiO₂ and Al₂O₃ in various proportions. The Al₂O₃-SiO₂ stable phase diagram shows only three phases: alumina, silica, and mullite.

Table 4. X-ray Diffraction Data of Oxidized Composites

Composition	1375°C	1475°C	1575°C
Al ₂ O ₃ -8%SiC	A	A+M	A+M
Al ₂ O ₃ -20%SiC	M+A+S	M+A+S	M+A
Al ₂ O ₃ -30%SiC	M+A+S	M+A+S	M+A+S
Al ₂ O ₃ -50%SiC	M+A+S	M+A+S	M+S

A=Al₂O₃

M=mullite

S=alumino-silicate glass

If the reaction product does not contain any unoxidized SiC particles, the reaction products contain alumina and mullite for Al₂O₃-SiC composites containing up to 24.4% SiC. For higher concentrations of SiC in Al₂O₃-SiC composites, the reaction products should be mullite and silica. Our x-ray diffraction

results (Table 4) were only in partial agreement with this. For alumina matrix composites containing 8 and 20% SiC, the reaction product showed alumina and mullite, as expected, but an amorphous glassy phase was also observed at 20% SiC sample. For alumina-matrix composites containing 30 and 50% SiC, the reaction product showed traces of alumina, in addition to the expected mullite and an amorphous phase. The amorphous phase was subsequently identified by microprobe analysis to be an alumino-silicate glass. These results show that the reaction products are not in thermodynamic equilibrium.

The surfaces of reaction products indicated that gas bubbles had formed during oxidation. Fig. 6 shows typical photomicrographs of the surfaces of samples. In general, the bubbles increased with the amount of SiC in the composite and with temperature. The bubbles observed on 8% SiC samples were very small and could not be observed at the magnification of Fig. 6.

Cross sections of the reaction products formed during oxidation indicated all of the above three phases. Typical optical micrographs of the reaction products formed during oxidation are shown in Fig. 7. Silicon carbide particles were not detected in the reaction product, suggesting that the SiC particles had completely oxidized. Quantitative characterization of the amorphous alumino-silicate phase was performed using the microprobe analysis. It was observed to contain 4 to 27 mol% alumina.

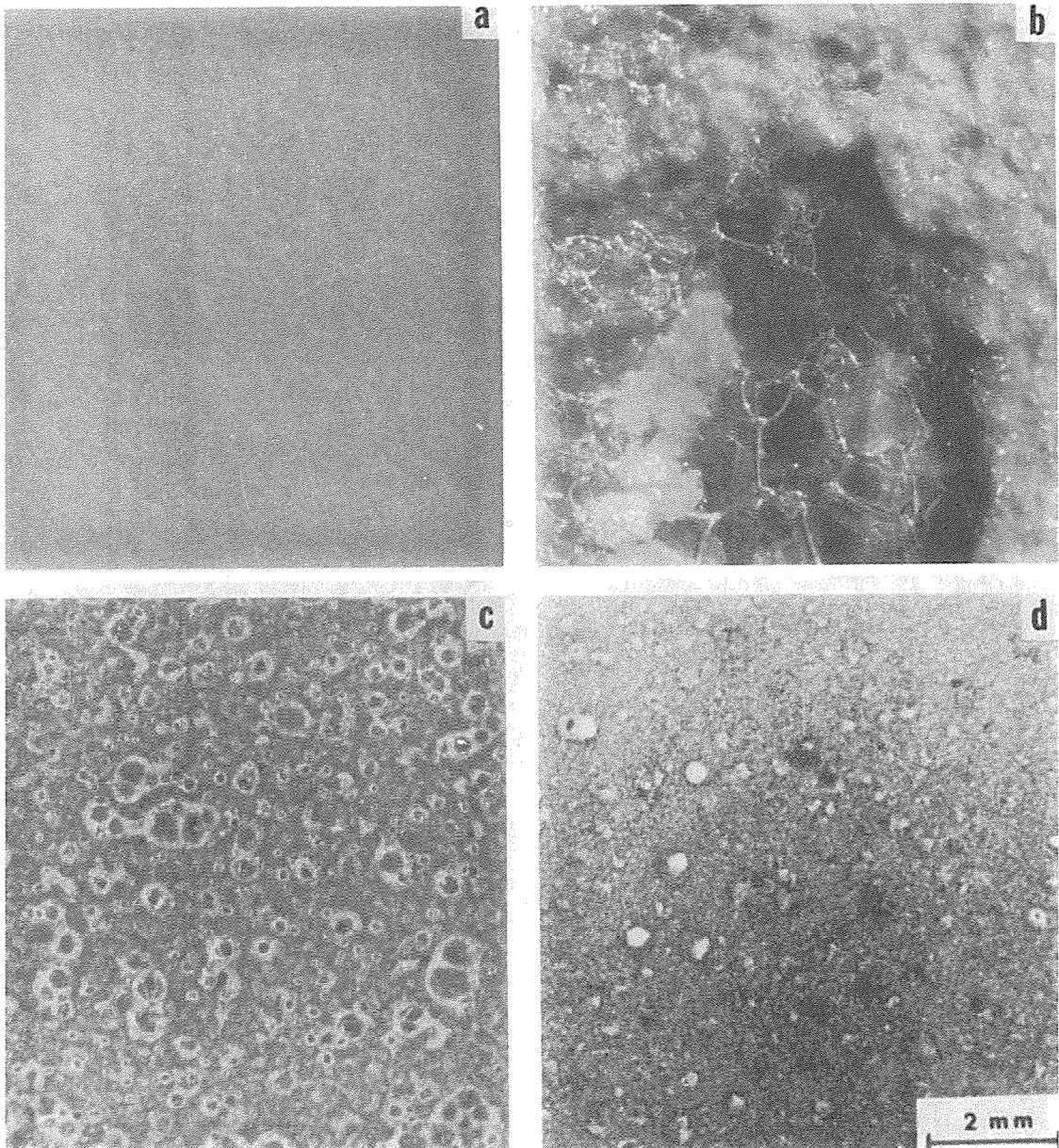
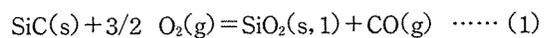


Fig. 6 Macrophotographs of the surfaces of Al_2O_3 -SiC composites exposed for 72h in oxygen : (a) Al_2O_3 -8%SiC at 1575°C ; (b), (c) and (d) Al_2O_3 -50%SiC at 1575 , 1475 , and 1375°C , respectively.

4. Discussion

4-1. Reaction Mechanism

When an alumina-SiC composite is exposed to an oxidizing environment, SiC will oxidize. The oxidation reaction of SiC can be expressed as



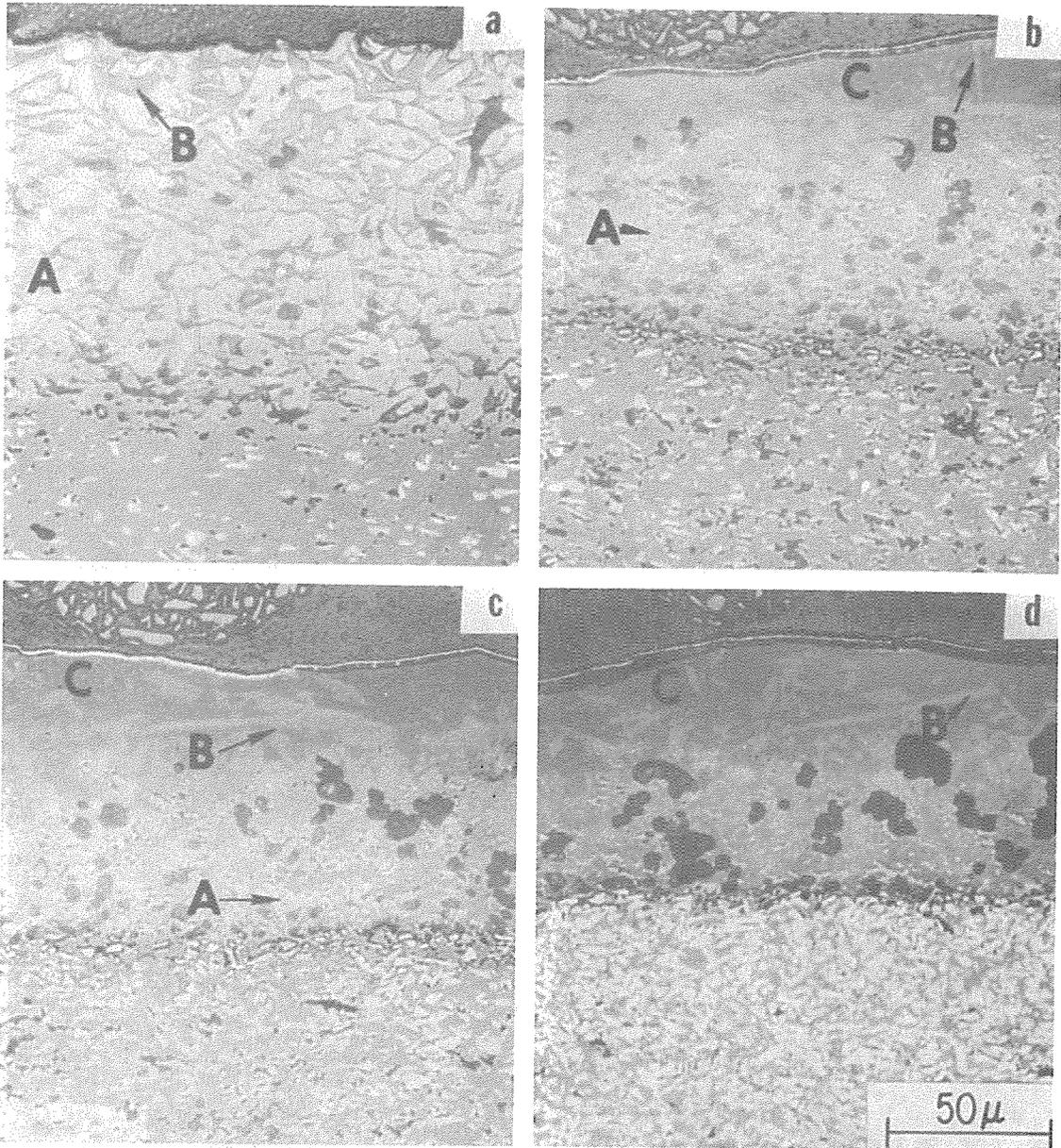


Fig. 7 Optical micrographs of the cross sections of the reaction product layer formed on Al_2O_3 -SiC composites oxidized for 72h at 1475°C : (a) 8% SiC, (2) 20% SiC, (c) 30% SiC, and (d) 50% SiC. Phases: A—alumina, B—mullite, and C—alumino-silicate liquid.

Oxidation can occur either by inward diffusion of oxygen through the oxide or by outward diffusion of aluminum or silicon. Kerans and Hermes[7] have recently proposed that the oxidation of SiC

in magnesium aluminate matrix occurs by the outward diffusion of cations. We believe that in the present case oxidation occurs by the inward diffusion of oxygen.

The formation of bubbles in our experiments indicates that the CO pressure at the interface between the composite and the reaction product is greater than 1 bar. This can happen only if the permeability of CO through the reaction product is comparable to or lower than that of oxygen[8]. In either case, the reaction rates would be similar to those expected for an oxygen diffusion limited scenario. The reaction rate can, therefore, be considered to be O_2 and outward diffusion of CO.

The proposed sequence of reaction steps is as follows. On exposure to an oxidizing environment, oxygen diffuses in through the oxide, oxidizing SiC. This is observed in Fig. 7, in which the reaction products do not contain SiC particle. While pure silica forms during the oxidation of SiC, here the oxidation product is proposed to be mullite and/or an alumino-silicate liquid, which is observed in Fig. 7. Oxygen permeabilities through alumina, mullite, and an alumino-silicate liquid are expected to be much greater than that through fused silica(see next section). Therefore, the rate of oxidation of an SiC particle in an alumina containing matrix is very fast compared with that of an SiC particle exposed directly to oxygen. The morphology of the oxidation product would be influenced by the volume change associated with oxidation. When the reaction product contains a solid as well as a liquid product, as in the present situation, the volume expansion can be easily accommodated by squeezing out of the liquid phase. This is consistent with our observations in Fig. 7, in which the fraction of the liquid phase in the reaction product is larger toward the gas/oxide interface. However, for Al_2O_3 -8% SiC composite shown in Fig. 7(a), the amorphous phase was not detected by microprobe analysis. This is consistent with theoretical consideration, in which the reaction products should contain alumina and mullite on Al_2O_3 -8% SiC composite.

4-2. Reaction Rate-Limiting Steps

The rate constants for the oxidation of Al_2O_3 -SiC composites can be calculated from the oxygen diffusivity data, assuming that CO formation does not destroy the integrity of the reaction product. If the reaction product is a multiphase mixture, as in the present case, oxygen diffusion will occur through the oxide phase that transports oxygen most rapidly or along the interfaces between the phases. Although diffusivity data are available for alumina and fused silica, no such data are available for mullite and alumino-silicate glass, and for interface diffusion. Therefore, we can not quantitatively predict the reaction rate constants in all cases.

The reaction rate would be limited by oxygen diffusion through any of the three oxides transporting oxygen rapidly beneath the reaction product. If the reaction rate is limited by oxygen diffusion through alumina, K_p for Al_2O_3 -20% SiC should be a factor of 10 lower than that for Al_2O_3 -8% SiC. Our observed values are similar for the two. This might be caused by oxygen diffusion through mullite, which is a major phase for Al_2O_3 -20% SiC composite. This further suggests that oxygen permeability through mullite should be of the same order of magnitude as for alumina.

If the reaction rate is limited by oxygen diffusion through mullite, for Al_2O_3 -SiC composites containing up to 24.4% SiC, K_p should be independent of the volume fraction of SiC, which is consistent with our observations. For higher concentrations of SiC, K_p should decrease with an increase in the volume fraction of SiC, and the rate for 50% SiC composite should be 0.45 times that for 30% SiC. This is inconsistent with our observations: the observed rates for 50% SiC and 30% SiC composites are comparable. This suggests that diffusion through alumino-silicate liquid is enhancing

the rate for 50% SiC over that expected for diffusion through mullite alone.

Finally, let us consider diffusion through aluminosilicate liquid. This is important for Al_2O_3 -SiC composites containing greater than 24.4% SiC. In all of these cases, the predominant reaction products are mullite and aluminosilicate liquid. The above results indicate that diffusion through aluminosilicate must also be influencing the rate. For Al_2O_3 -SiC composites, the reaction rate should increase with the amount of SiC, and the rate constant for 50% SiC composite should be about a factor of ~ 2.7 higher than for 30% SiC composite. This is inconsistent with our observations. These considerations indicate that our results cannot be completely explained by assuming oxygen diffusion through aluminosilicate glass. Therefore, this is not the rate-limiting step either, even though oxygen diffusion through the liquid is influencing the reaction rate.

These results indicate that for Al_2O_3 -8% SiC oxygen diffusion occurs primarily through alumina. For Al_2O_3 -20% SiC, oxygen diffuses through a thin aluminosilicate liquid at the external surface, followed by diffusion through mullite and alumina. For all other composites, oxygen diffuses through the aluminosilicate liquid and mullite.

5. Summary and Conclusions

1) Oxidation studies were conducted at 1375, 1475 and 1575°C on Al_2O_3 -SiC composites containing 8, 20, 30, and 50vol% SiC. The reaction products contained combinations of alumina, mullite, and a nonequilibrium aluminosilicate liquid. Crystalline silica, expected from the stable phase diagram, was never observed.

2) The observed parabolic rate constants increased with the volume fraction of SiC, when expressed on the basis of mass gain (i.e., in the units

of $\text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$). However, when expressed on the basis of the thickness of the reaction product layer (i.e., in the units of $\text{m}^2 \cdot \text{s}^{-1}$), they were essentially independent of the composite composition. The parabolic rate constants were about three orders of magnitude higher than those reported for the oxidation of SiC particles in the literature. The activation energies of oxidation were of the order of 450 to 500 kJ/mole.

3) Bubbles, presumably containing carbon monoxide, were observed in the reaction product. The reaction rates are mixed controlled, influenced both by the inward diffusion of O_2 as well as by the outward diffusion of CO. However, the rates are of the same order as those expected for the oxygen diffusion limited scenario. Our observed results further indicate that oxygen permeabilities through the three reaction products (alumina, mullite, and aluminosilicate liquid) are comparable.

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