

Effect of Zirconia Content on the Oxidation Behavior of Silicon Carbide/Zirconia/Mullite Composites

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The oxidation of hot-pressed SiC-particle (SiC_p)/zirconia (ZrO₂)/mullite composites with various ZrO₂ contents, exposed in air isothermally at 1000° and 1200°C for up to 500 h, was investigated; an emphasis was placed on the effects of the ZrO₂ content on the oxidation behavior. A clear critical volume fraction of ZrO₂ existed for exposures at either 1000° or 1200°C: the oxidation rate increased dramatically at ZrO₂ contents of >20 vol%. The sharp transition in the oxidation rate due to the variation of ZrO₂ content could be explained by the percolation theory, when applied to the oxygen diffusivity in a randomly distributed two-phase medium. Morphologically, the composites with ZrO₂ contents greater than the critical value showed a large oxidation zone, whereas the composites with ZrO₂ contents less than the critical value revealed a much-thinner oxidation zone. The results also indicated that the formation of zircon (ZrSiO₄) at 1200°C, through the reaction between ZrO₂ and the oxide product, could reduce the oxidation rate of the composite.

I. Introduction

CERAMICS are promising materials for making structural components for use at elevated temperatures. Specifically, mullite has been considered to be one of the best candidates, because of its good high-temperature strength, high creep resistance, good thermal-shock resistance, excellent chemical stability, and low theoretical density. However, the low fracture toughness (~2 MPa·m^{1/2}) has limited its use. One of the remedies is the incorporation of reinforcements. Partially stabilized zirconia (PSZ) and various forms of silicon carbide (SiC), such as particles, whiskers, and fibers, have shown their effectiveness in toughening mullite.^{1–5} Because mullite-matrix composites are considered for use in high-temperature environments, their oxidation behavior, as well as the ensuing degradation of their mechanical properties, is of great concern.

The oxidation of monolithic SiC has been subjected to investigation in the last few decades. Previous studies suggested that the inward diffusion of oxygen through the growing oxide layer was the rate-controlling step.^{6–11} Under such a condition, linear-parabolic oxidation kinetics were obeyed: the oxide thickness was initially proportional to time and then to the square root of time. The oxidation behavior of SiC-reinforced ceramic-matrix composites has also been investigated.^{12–24} Porter and Chokshi¹⁹ examined the oxidation behavior of an 18-vol%-SiC-whisker-reinforced alumina (Al₂O₃) composite at temperatures in the range of 1500°–1700°C. They reported that mullite formed because of interaction between the matrix and the oxidation product. In a study on the oxidation of SiC_p/Al₂O₃ and SiC_p/mullite composites at 1375°–1575°C, Luthra and Park¹⁶ found a parabolic rate behavior, and the parabolic rate constant increased as the SiC content in the composites increased. Two reaction products, i.e., mullite and an amorphous aluminosilicate, were observed in the oxidized SiC_p/Al₂O₃ composite, and some partially oxidized SiC particles were found between the reaction product layer and the unoxidized zone. Kriven *et al.*²⁰ found that SiC whisker (SiC_w)/Al₂O₃ composites had a faster oxidation rate than SiC_w/mullite composites, whereas Borom and co-workers^{13,14} emphasized that the oxidation behavior of SiC-reinforced alumina- or mullite-matrix composites was affected by the reaction of the oxidation product and matrix.

There were some studies on the oxidation behavior of zirconia-containing (ZrO₂-containing) composites as well. Backhaus-Ricoult¹⁸ stated that the microstructure of SiC-reinforced ZrO₂/Al₂O₃ composites after exposure in air could be characterized by three typical subscales: (i) a glassy aluminosilicate in the outermost surface; (ii) an intermediate white scale with Al₂O₃, ZrO₂, reaction products (mainly mullite), and large pores; and (iii) an inner black scale that contained zircon (ZrSiO₄), partially “dissolved” SiC whiskers, and carbon. Liu *et al.*²¹ claimed that the oxidation rate of a SiC_w/ZrO₂/mullite composite was faster than that of a SiC_w/mullite composite, because of the reduced crystallization rate in silica (SiO₂) by the existence of ZrO₂. Lin²² and Lin *et al.*^{23,24} found that the oxidation rate of some SiC_w/ZrO₂/mullite composites was much faster than that of a SiC_w/mullite composite, because of higher oxygen diffusion in ZrO₂, which provided a rapid transport route of oxygen in the ZrO₂-containing matrices. Therefore, addition of PSZ particles into the mullite matrix, as an effective toughening phase, could cause degradation of the oxidation resistance of the SiC_w/mullite composite. Oxidation versus depth behavior was studied for several composites, and oxidation modes were defined and quantified based on plots of

N. S. Jacobson—contributing editor

Manuscript No. 191493. Received May 15, 1997; approved December 8, 1997. Supported by the National Science Council of Taiwan under Grant No. NSC83-0405-E-009-006. Author AZ was supported by the U.S. Dept. of Energy, Materials Science Division, under Grant No. DE-FG02-91ER45439.
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oxide-layer thickness (around whiskers) versus depth.^{22–24} However, they studied only composites with ~30% ZrO₂ and did not elucidate the effect of ZrO₂ content on the oxidation behavior of SiC_w/ZrO₂/mullite composites.

In the present study, hot-pressed SiC_p/ZrO₂/mullite composites are exposed isothermally in air at 1000° and 1200°C. The purpose is to investigate the effect of the matrix composition, i.e., the variation of ZrO₂ content, on the oxidation behavior of SiC_p/ZrO₂/mullite composites. The effect of the formation of ZrSiO₄, as a result of the interaction between ZrO₂ and the oxidation product, on the oxidation rate is also investigated.

II. Experimental Procedure

Composites of SiC_p/mullite and SiC_p/ZrO₂/mullite, all of which contained 30 vol% of SiC particulates, were fabricated by hot pressing. The starting materials were commercial mullite powder (0.2 μm average particle size, KM-mullite, Kyoritsu Ceramic Materials Co., Nagoya, Japan), 3 mol% Y₂O₃ partially stabilized ZrO₂ (0.3 μm average particle size, Product No. TZ-3Y, Toyo Soda Mfg. Co., Tokyo, Japan), and SiC powder (7 μm average particle size, Cerac, Milwaukee, WI). Powder mixtures of desired composition were dispersed and homogenized by using an ultrasonic dispersing process (Model XL-2020, SONICATOR®, Heat Systems, Farmingdale, NY) with methanol as a medium. To form a stable suspension, the pH of each slurry was adjusted to 10 with ammonium hydroxide (NH₄OH). The slurry was partially dried on a hot plate under continuous stirring and oven-dried thereafter. The dried, crushed, and sieved powder mixtures were uniaxially pressed into disks 60 mm in diameter. The green compact was then coated with boron nitride (BN) and placed into a graphite die that was lined with graphite foil. The composites that contained various contents of ZrO₂ were hot-pressed at 1600°C in an argon atmosphere under a pressure of 30 MPa for 45 min. The designations, compositions, and hot-pressing conditions of the composites are listed in Table I. For the sake of convenience, the “zirconia + mullite” portion in each SiC_p/ZrO₂/mullite composite is called the “matrix,” even though this matrix itself is a composite. The matrix, either mullite or zirconia + mullite, has a content of 70 vol% in each composite, whereas the ZrO₂ content is expressed as a volume percentage of the matrix only, rather than a volume percentage of the entire composite (see footnotes in Table I).

The as-hot-pressed composites were ground and then cut into pieces with dimensions of 10 mm × 6 mm × 3 mm. All specimens were ground and polished with diamond paste and weighed before and after oxidation using a precision electronic balance (Model R200D, Satorius AG, Goettingen, Germany); the balance was accurate to 0.01 mg. Composite samples were exposed to air in a box furnace (Model 51333, Lindberg, Wauertown, WI) isothermally at 1000° and 1200°C for up to 500

h. Specimens were loaded into the furnace at room temperature, and then the furnace temperature was increased at a rate of 20°C/min until the set temperature was attained. One specimen for each composition was drawn from the furnace at various intervals to measure the weight change. Specimens drawn from the furnace were not reloaded for further oxidation, to avoid the formation of extended cracks due to thermal shock. The extent of oxidation was expressed by the weight change per unit surface area (called weight gain hereafter).

The major phases on the surfaces of the as-hot-pressed specimens and the exposed specimens were identified via X-ray diffractometry (XRD) (Model MXP18, Mac Science, Tokyo, Japan). The as-polished cross sections of oxidized specimens were observed by using polarized light microscopy (Model BH-2, Olympus, Tokyo, Japan) as well as by using a scanning electron microscopy (SEM) microscope (Model S-2500, Hitachi, Tokyo, Japan) that was equipped for energy-dispersive X-ray spectroscopy (EDS) (Kevex Instruments, Valencia, CA).

III. Results

Figure 1 shows the plots of weight gain versus time for various SiC_p/ZrO₂/mullite composites after exposure at 1000° and 1200°C, respectively. The weight gain increased as time increased for each composite at 1000° and 1200°C. The weight gains of the composites that contained <20 vol% ZrO₂ were significantly less than those of the composites that contained ≥30 vol% ZrO₂. Figure 2 shows the relationship between the weight gain and the volume fraction of ZrO₂ for exposure at 1000°C for 500 h and 1200°C for 500 h. This figure indicates that the weight gains for the composites that contained <20 vol% ZrO₂ were comparatively small, whereas the weight gain increased rapidly when the composites contained >20 vol% ZrO₂. It appeared that there was a critical volume fraction of ZrO₂ content required for rapid oxidation. In other words, the oxidation rate would be accelerated abruptly beyond this critical ZrO₂ content, whereas the weight gain remained fairly low below the critical value. It is also noted that the weight-gain curve for 1200°C slightly declined as the ZrO₂ content increased to >80 vol%.

Figure 3 shows the XRD spectrum of the surface of the as-hot-pressed MZY50/SiC composite, as well as the XRD spectra after exposure for 500 h at 1000° and 1200°C. The as-hot-pressed sample consisted of four major phases: mullite, monoclinic ZrO₂ (m-ZrO₂), tetragonal ZrO₂ (t-ZrO₂), and SiC (Fig. 3(a)). After exposure at 1000°C for 500 h, the matrix was rather stable; i.e., the interaction between the oxide product and the matrix was insignificant (Fig. 3(b)). No new crystalline phases were found. However, observations via transmission electron microscopy (TEM) in a previous study²² indicated that there was an amorphous SiO₂ layer around each of SiC particles located near the surface of the composite. As shown in

Table I. Designation, Compositions, and Hot-Pressing Conditions of Composites

Designation	Composition [†]	Hot-pressing conditions [‡]
MZY0/SiC	Mullite + 30 vol% SiC	1675°C/45 min
MZY5/SiC	(Mullite + 5 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY10/SiC	(Mullite + 10 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY15/SiC	(Mullite + 15 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY20/SiC	(Mullite + 20 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY25/SiC	(Mullite + 25 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY30/SiC	(Mullite + 30 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY40/SiC	(Mullite + 40 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY50/SiC	(Mullite + 50 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY60/SiC	(Mullite + 60 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY80/SiC	(Mullite + 80 vol% 3Y-PSZ) + 30 vol% SiC	1600°C/45 min
MZY100/SiC	3Y-PSZ + 30 vol% SiC	1600°C/45 min

[†]The volume percentage of the matrix in parentheses is 70% for each composite; the balance is SiC_p. The ZrO₂ content is based on the matrix itself; i.e., the amount (in vol%) of Y-PSZ = volume of Y-PSZ × 100/(volume of mullite + volume of Y-PSZ). [‡]All hot pressing was performed under a pressure of 30 MPa and under a 1 atm argon-gas atmosphere.

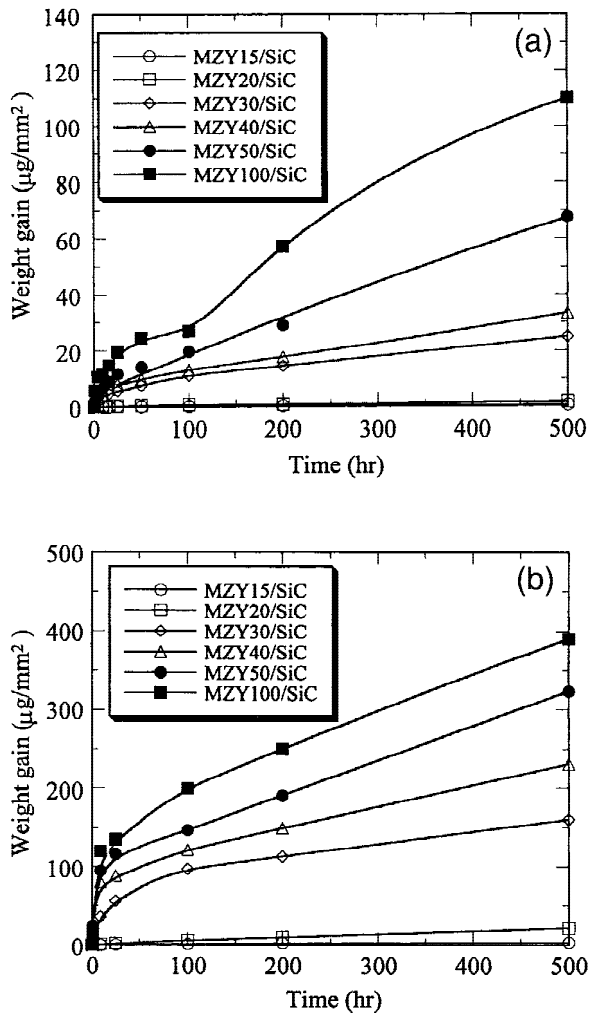


Fig. 1. Curves of weight gain versus time at (a) 1000° and (b) 1200°C for samples listed in Table I.

Fig. 3(c), after exposure at 1200°C for 500 h, some stronger diffracted peaks of cristobalite were identified, whereas $ZrSiO_4$ was also found (due to the interaction between SiO_2 and ZrO_2), which led to the reduction of the ZrO_2 peak intensities. Figure 4 shows the XRD spectra of composites with various ZrO_2 contents after exposure at 1200°C for 500 h. It is apparent that the relative intensity of the corresponding $ZrSiO_4$ peaks increased as the ZrO_2 content increased.

Figure 5 shows polarized-light optical micrographs of the MZY15/SiC composite (for 500 h), the MZY20/SiC composite (for 500 h), and the MZY50/SiC composite (for 25 h), all after exposure at 1200°C. The cross-sectional samples clearly exhibited a distinct layered structure; this layering was due to the different extent of oxidation at various depths, which caused a change in composition. Figure 5(a) reveals the cross section of the MZY15/SiC composite; it has two oxidized surfaces that are glued together, the interfaces of which are located at the center of the micrograph. The oxidation zone consists of an outer white scale and an inner black scale, whereas the gray region is the unoxidized substrate. Figure 5(b) demonstrates a two-layer structure for the MZY20/SiC composite; both the white and black scales are thicker than the corresponding scales in the MZY15/SiC composite (Fig. 5(a)). Figure 5(c) shows the MZY50/SiC composite after exposure at 1200°C for 25 h; this figure indicates much-thicker white and black regions (the unoxidized region is not shown). Figure 6 shows an SEM micrograph of the cross section of the MZY20/SiC composite after exposure at 1200°C for 500 h. The outermost surface of the composite is shown on the left. The bright particles are ZrO_2

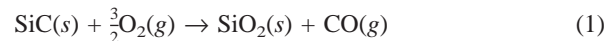
embedded in the mullite matrix (shown as the gray regions in the figure). Angular SiC particles were encompassed by a dark layer (indicated by the arrow). The dark layer was identified as being the oxidation product, SiO_2 . The variation of the oxidation of SiC particles with depth is also observed. There is a sharp change in the thickness of the SiO_2 layer at a depth of ~45 μm . The outer region ("A-B") corresponds to the white scale shown in Fig. 5(b), whereas the inner region ("B-C") corresponds to the black scale in Fig. 5(b).

Figures 7 and 8 demonstrate the effect of ZrO_2 content on the oxidation morphology of $SiC_p/ZrO_2/mullite$ composites. Figure 7 shows an SEM micrograph of the MZY15/SiC composite after exposure at 1200°C for 500 h, indicating that SiC particles at a depth beyond ~40 μm did not oxidize noticeably. That is, there was a small oxidation zone in the MZY15/SiC composite after exposure at 1200°C for 500 h. Figure 8 shows a series of micrographs for the MZY30/SiC composite at various depths after exposure at 1200°C for 25 h. The SiC particles were slightly oxidized, even at a depth of >600 μm , which indicates a much-larger oxidized depth than that of the MZY15/SiC composite exposed for 500 h.

IV. Discussion

For the sake of convenience in our discussion, two terms are first defined. First, the *silica layer* of an individual SiC particle in a SiC-containing composite means the layer of SiO_2 that is formed as a result of the oxidation reaction occurring on the surface of the SiC particle. When a SiC particle is partially oxidized, a silica layer will encompass it. Second, the *oxidation zone* of a SiC-containing composite after exposure in an oxidizing environment is defined as the zone from the outermost surface of the composite to the depth where no oxidation of the incorporated SiC particles can be detected.

The inward diffusion of oxygen from the atmosphere causes the oxidation of SiC particles within the oxidation zone, which results in weight gain, because of the formation of SiO_2 , according to the reaction



where most of the gaseous product CO was believed to diffuse all the way out to the surface. Thus, the atomic-weight difference between the SiC and SiO_2 was the reason for the weight gain during oxidation, and the extent of oxidation could be represented by the weight gain of each sample. In contrast, no weight gain was detected in the oxidation test of mullite and $ZrO_2/mullite$ composites,²² which indicates that the inward diffusion of oxygen was negligible in the composites that contained no SiC.

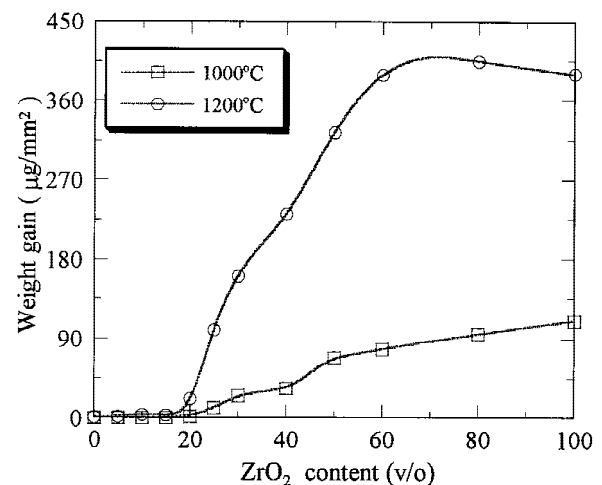


Fig. 2. Curves of weight gain versus ZrO_2 content at 1000° and 1200°C for 500 h.

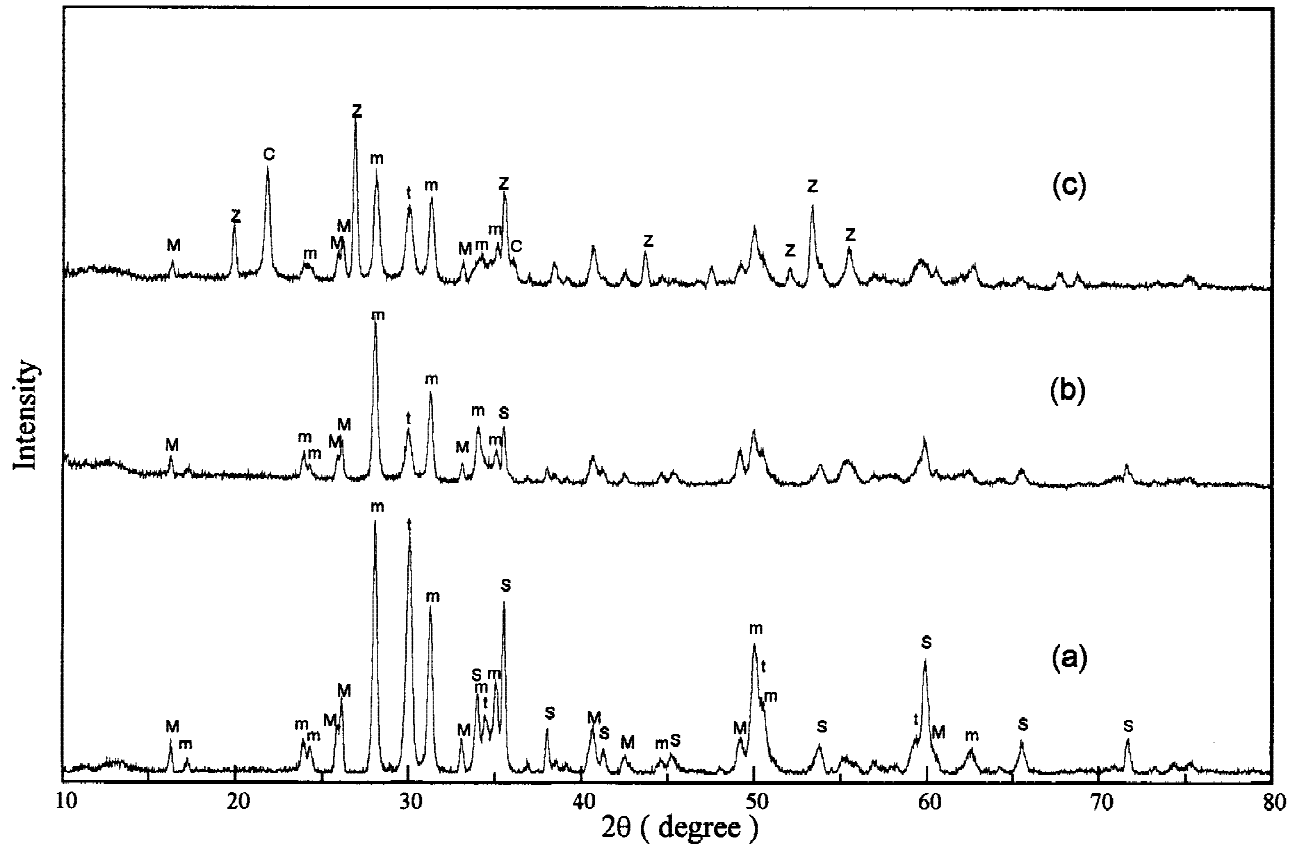


Fig. 3. XRD spectra of the MZY50/SiC composite (as hot-pressed (spectrum “(a)”), after exposure at 1000°C for 500 h (spectrum “(b)”), and after exposure at 1200°C for 500 h (spectrum “(c)”). (M = mullite, Z = zircon, C = cristobalite, m = m-ZrO₂, t = t-ZrO₂, and S = SiC.)

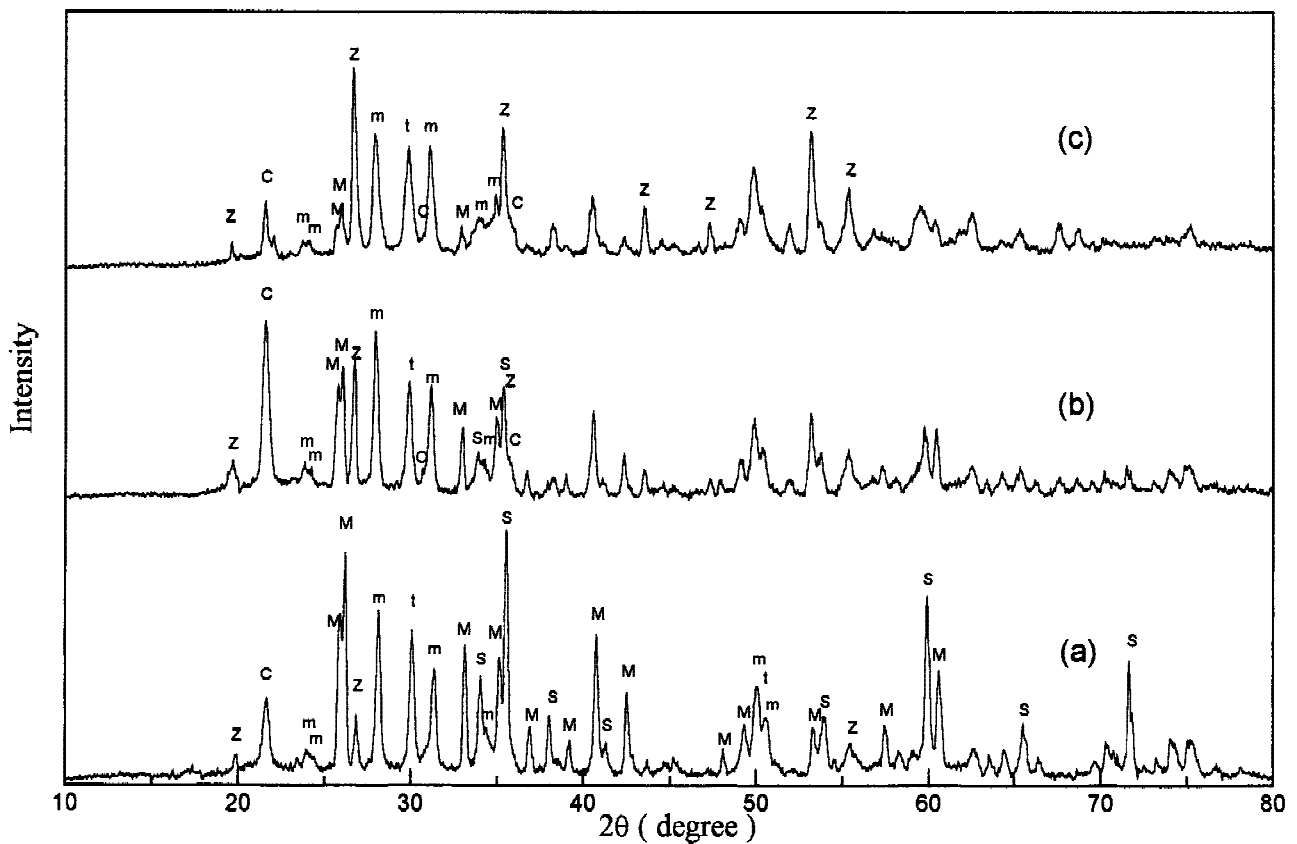


Fig. 4. XRD spectra of the MZY15/SiC (spectrum “(a)”), MZY25/SiC (spectrum “(b)”), and MZY50/SiC (spectrum “(c)”) composites, all after exposure at 1200°C for 500 h. (M = mullite, Z = zircon, C = cristobalite, m = m-ZrO₂, t = t-ZrO₂, and S = SiC.)

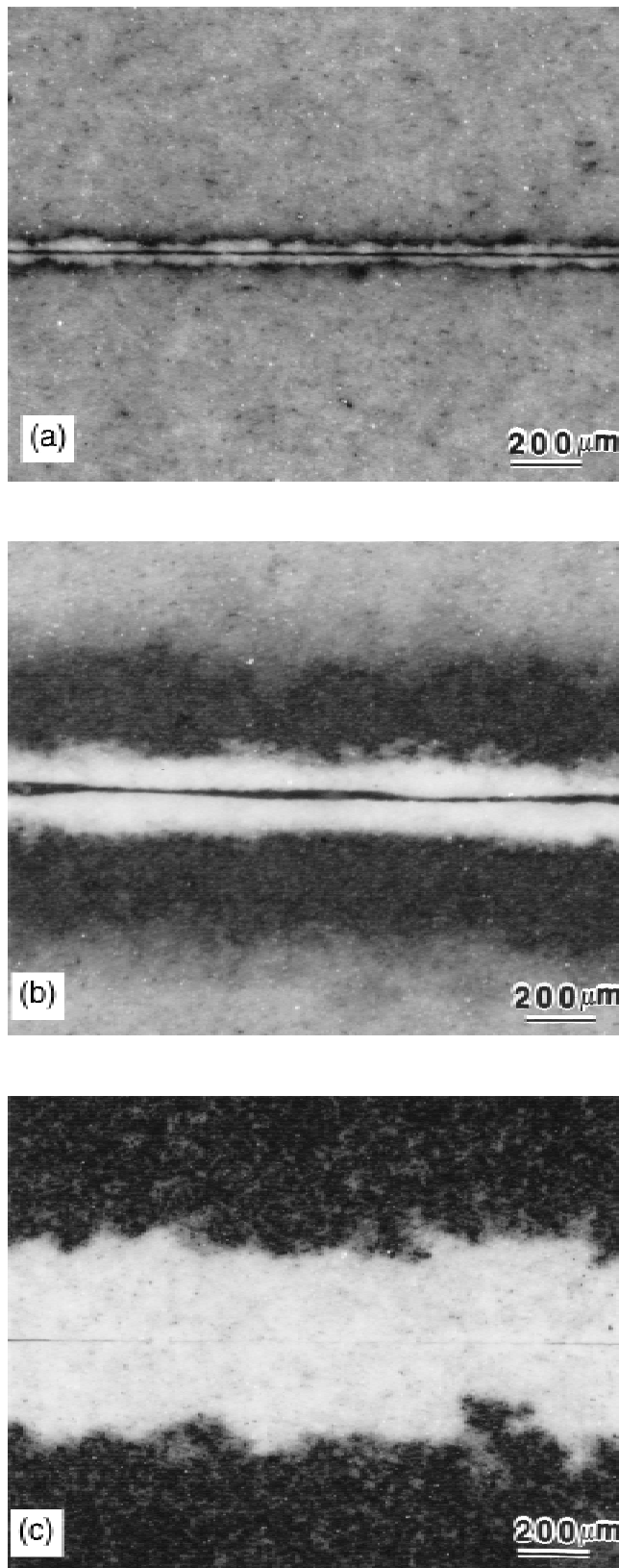


Fig. 5. Polarized-light optical micrographs of the (a) MZY15/SiC (500 h/1200°C), (b) MZY20/SiC (500 h/1200°C), and (c) MZY50/SiC (25 h/1200°C) composites.

As shown in Figs. 1 and 2, the weight gain abruptly increased when the amount of incorporated ZrO_2 was above a certain volume fraction. There appeared to be a threshold value of ~ 20 vol% ZrO_2 for the oxidation rate of $\text{SiC}_p/\text{ZrO}_2/\text{mullite}$ composites. A plausible explanation for this phenomenon can

be based on the percolation theory.^{25–27} It applies to a wide variety of transport phenomena, including diffusivity and thermal or electric conductivity. In a two-phase system, when one phase has a very high diffusivity of a species compared to that of the other phase, there exists a critical volume fraction, or percolation threshold (f_c), of the high-diffusivity phase. Percolation occurs beyond this threshold, and the diffusivity of the particular species in the composite has the order of magnitude of the high diffusivity. In other words, for a binary composite with $D_2 \gg D_1$, percolation theory predicts that D_m has the approximate order of D_1 if $f < f_c$ and has the approximate order of D_2 if $f > f_c$ (where D_1 and D_2 are the diffusivities of a certain species in the two phases, D_m is the diffusivity of that species in the composite, and f is the volume fraction of the second phase).

Because oxygen diffusivity in ZrO_2 is much higher than that in mullite (Table II) and using mullite and ZrO_2 as the first and second phases, respectively, the relationships of oxygen diffusivity in $\text{ZrO}_2/\text{mullite}$ matrices would be

$$D_{\text{matrix}}^{\text{O}} \approx \text{order of } D_{\text{zirconia}}^{\text{O}} \quad (\text{if } f > f_c) \quad (2a)$$

$$D_{\text{matrix}}^{\text{O}} \approx \text{order of } D_{\text{mullite}}^{\text{O}} \quad (\text{if } f < f_c) \quad (2b)$$

where the superscript denotes the diffusing species (oxygen). Note that the $\text{ZrO}_2/\text{mullite}$ assembly is called the “matrix,” because it serves as a matrix for the SiC_p . From the results shown in Figs. 1 and 2, $f_c \approx 20$ vol% ZrO_2 . The oxygen diffusivity in a matrix with >20 vol% ZrO_2 should be very close to that in ZrO_2 , which leads to a rapid increase in the oxidation rate of SiC particles. On the other hand, the diffusivities in matrices with $f < f_c$ should be of the same order as that of mullite (which is very low); thus, SiC particles were better protected by these matrices.

In addition to the sharp transition at f_c , the weight gain of $\text{SiC}_p/\text{ZrO}_2/\text{mullite}$ composites also increased as the ZrO_2 content increased, either when $f < f_c$ or when $f > f_c$. For the oxidation of an “individual” SiC particle in $\text{SiC}_p/\text{ZrO}_2/\text{mullite}$ composites, the inward diffusion of oxygen will proceed via the following serial steps: (i) oxygen diffuses through the ZrO_2 -containing matrix to the surface of SiC, where the oxidation reaction occurs; and (ii) as the silica layer is formed, oxygen must further diffuse through it to arrive at the interface of the silica layer and the unoxidized SiC core. That is, the inward diffusion of oxygen may be controlled by either diffusion through the ZrO_2 -containing matrix or diffusion through the silica layer, depending on which one is slower. It is easy to compare the diffusivities of oxygen in SiO_2 , ZrO_2 , and mullite (Table II). At 1000°C, the diffusivity in ZrO_2 is between 10^{-9} and 10^{-5} cm^2/s ; this value is dependent on crystal structure, additives, and the stoichiometry.^{28,29} At the same temperature, the diffusivity in amorphous silica is much lower (10^{-13} – 10^{-12} cm^2/s).^{30,31} The diffusivity in mullite is unknown. It was suggested by Cherkasoy *et al.*³² (quoted by Luthra and Park¹⁶) to be similar to that in Al_2O_3 , which, in turn, is between 10^{-20} and 10^{-18} cm^2/s (based on reports quoted by Luthra and Park¹⁶). Oxygen diffusion in Al_2O_3 , and possibly in mullite, being extremely slow in the bulk, is mainly through grain boundaries and, therefore, is strongly dependent on the microstructure. However, it may be safe to generally state that oxygen diffusivity in SiO_2 is very small compared to that in ZrO_2 but is very large compared to that in mullite. Therefore, if $f < f_c$ (e.g., the MZY15/SiC composite), the oxygen diffusivity in the matrix is much lower than that in the silica layer and, thus, the oxidation rate is likely to be controlled by the oxygen diffusion in the matrix. More accurately, the controlling step is determined by the lowest reciprocal diffusion impedance, or diffusivity (D) divided by the corresponding thickness. Most of the oxygen will be consumed continuously by the oxidizing SiC particles at or near the surface until they are completely oxidized, which results in a shallow oxidation zone. Because the oxygen diffusivity slowly increases as the ZrO_2 content increases in the range of $f < f_c$, according to the effective medium theory,^{33,34}

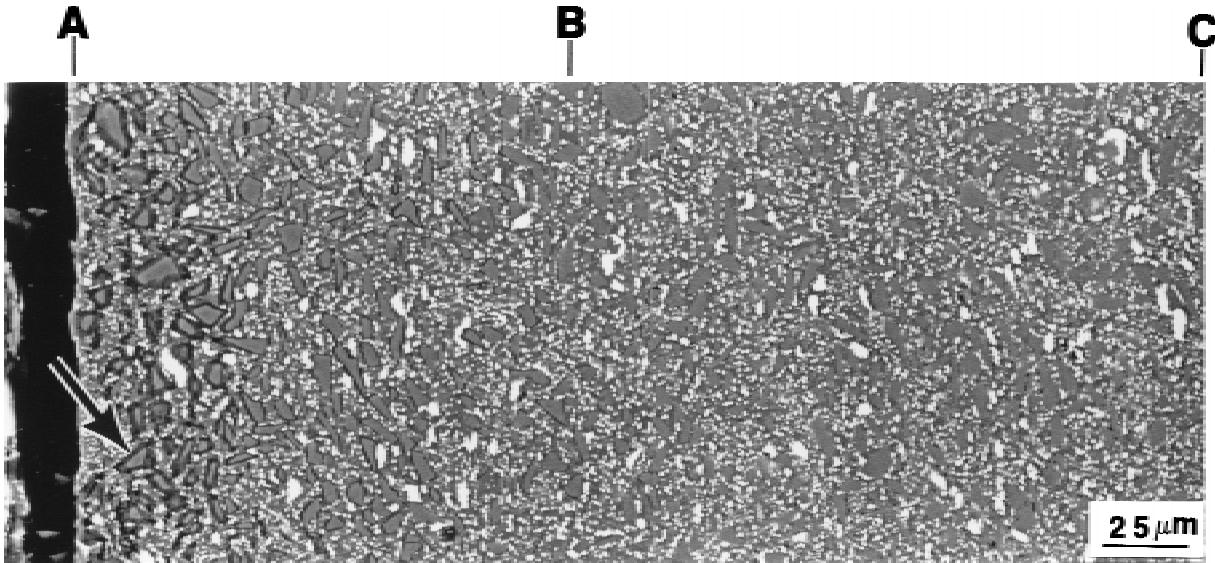


Fig. 6. SEM micrograph of a cross section of the MZY20/SiC composite after exposure at 1200°C for 500 h, revealing a variation of the oxidation of SiC particles with depth: region “A–B” corresponds to the white layer in Fig. 5(b), and region “B–C” corresponds to the black layer in Fig. 5(b).

it is inferred that the oxidation rate will also slowly increase as the ZrO_2 content increases. This observation is consistent with the result as shown in Fig. 2. The oxidation mechanism and morphology, as described previously for the composites with ZrO_2 contents less than the threshold value, are illustrated schematically in Fig. 9(a). However, when $f > f_c$, as it is in the MZY30/SiC composite, the oxidation of SiC particles at various depths will proceed in parallel. Because the oxygen diffusivity in the matrix now becomes much faster than that in the silica layer around SiC, the oxygen will pass over partially oxidized SiC particles and continuously diffuse into the inner region, leading to the oxidation of more SiC particles and, thus, a deep oxidation zone. The oxidation mechanism and morphol-

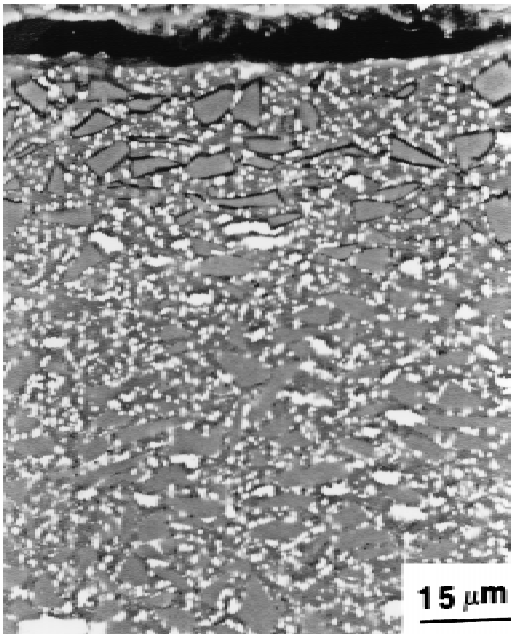


Fig. 7. SEM micrograph of a cross section of the MZY15/SiC composite after exposure at 1200°C for 500 h, showing a small oxidation zone.

ogy for the composites with ZrO_2 contents greater than the threshold value are illustrated schematically in Fig. 9(b).

For the SiC_p/ZrO_2 /mullite composites, the zircon ($ZrSiO_4$) phase was formed in samples exposed at 1200°C but not at 1000°C. The reaction proceeded according to the equation



The mullite phase in the matrix was very stable and did not react with SiC or ZrO_2 .²² However, at higher temperatures, such as 1200°C, the oxidation product (SiO_2) would react with ZrO_2 to form $ZrSiO_4$, thus modifying the composition of the matrix. In other words, the formation of $ZrSiO_4$ would cause the consumption of ZrO_2 at the expense of SiO_2 . The oxygen diffusivity in $ZrSiO_4$ is probably much slower than that in ZrO_2 . For example, the formation of a $ZrSiO_4$ layer effectively stopped the increase in weight gain during the oxidation of a silicon oxynitride–zirconia ($Si_2N_2O-ZrO_2$) composite.³⁵ Therefore, the substitution of ZrO_2 by $ZrSiO_4$ will slow the oxygen diffusion in the matrix, which leads to a decrease in the oxidation rate. The fact that the weight gain at 1200°C did not increase (or even slightly decrease) when the ZrO_2 content was >80 vol% (Fig. 2) may be attributed to the fact that more $ZrSiO_4$ formed at higher ZrO_2 contents, as determined by XRD (Fig. 4).

V. Summary

An evident critical volume fraction of ~20 vol% ZrO_2 existed in the SiC_p/ZrO_2 /mullite composites after exposure in air isothermally at 1000° and 1200°C. The oxidation rate was much more rapid beyond this threshold. The dramatic change in oxidation rate due to the variation of ZrO_2 content can be well explained by percolation theory. The ZrO_2 content also had a strong influence on the oxidation morphology. The composites with ZrO_2 contents less than the threshold value showed a small oxidation zone, whereas the composites with ZrO_2 contents greater than the threshold value showed a large oxidation zone and a smooth variation of silica-layer thickness of SiC at various depths. In addition, the formation of $ZrSiO_4$, as a result of the interaction between the matrix and the oxide product, would lead to a reduction of the oxidation rate.

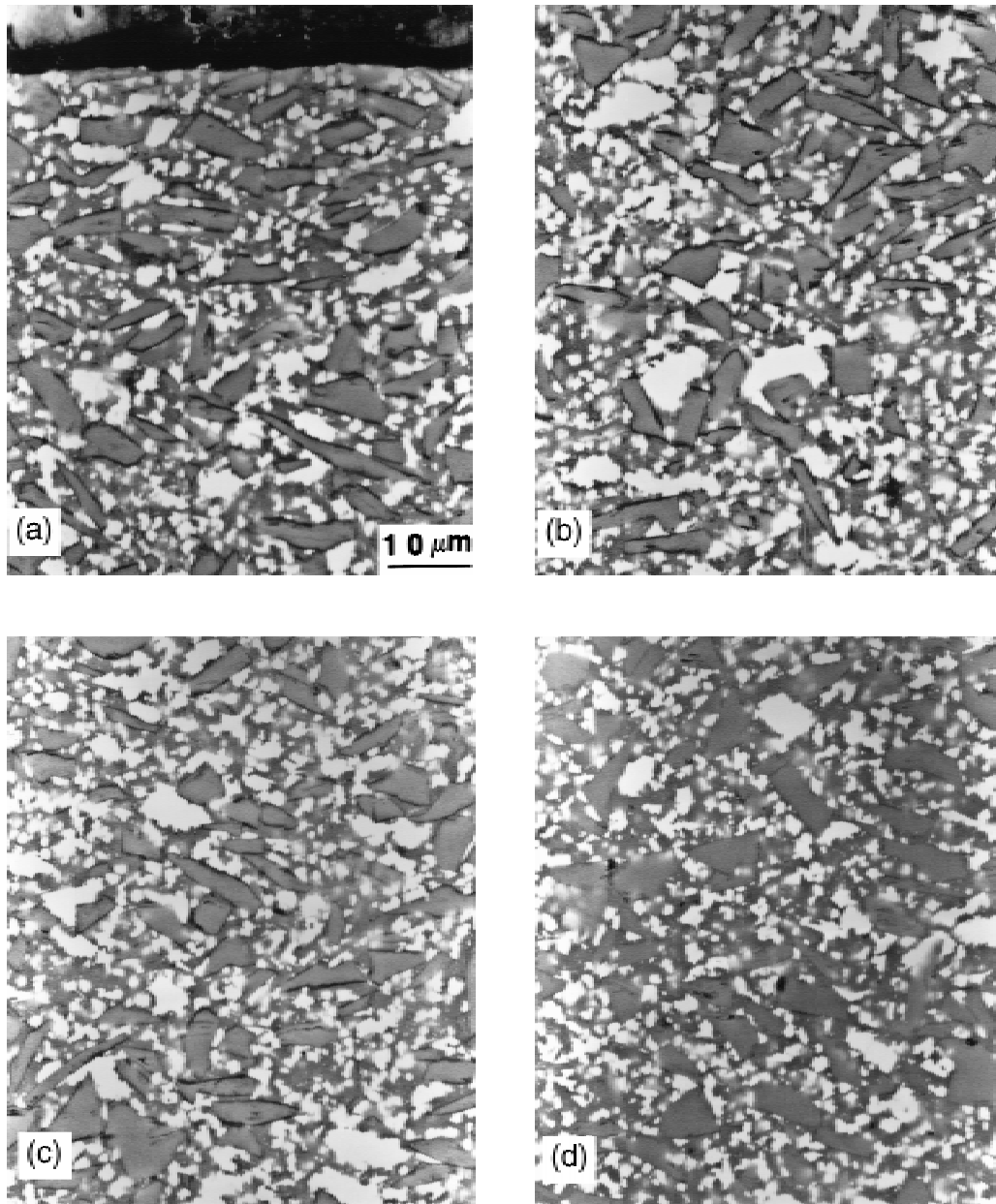


Fig. 8. SEM micrographs of a cross section of the MZY30/SiC composite after exposure at 1200°C for 25 h, showing a large oxidation zone (from the outermost surface to a depth of (a) 60 μm (bottom of the micrograph), (b) 130 μm (bottom of the micrograph), (c) 250 μm (bottom of the micrograph), and (d) 670 μm (bottom of the micrograph)).

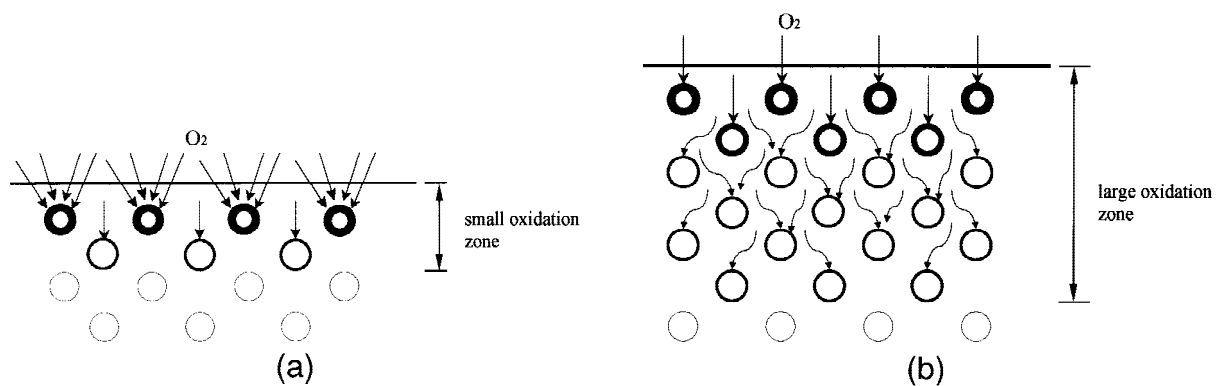


Fig. 9. Two distinct mechanisms for the oxidation of SiC/ZrO₂/mullite composites are shown. When $f < f_c$, the oxygen diffusivity in the matrix is much lower than that in the silica layer, so that most of the oxygen will be consumed continuously by the SiC particles located near the surface (Fig. 9(a)); a small oxidation zone is obtained. When $f > f_c$, the oxygen diffusivity in the silica layer is much lower than that in the matrix, so that oxygen will pass over the partially oxidized SiC particles and enter into the inner region, causing more SiC particles to be oxidized (Fig. 9(b)); a large oxidation zone is obtained.

Table II. Oxygen Diffusivities in Mullite, Zirconia, and Silica

Material	Diffusivity (cm ² /s)	Temperature (°C)	Reference
Mullite	~10 ⁻¹⁹	1000	Estimated [†]
Zirconia	~10 ⁻⁹	1000	Dou et al. ²⁸ and Kofstad ²⁹
Silica	~10 ⁻¹³	1000	Norton ³⁰ and Lamkin et al. ³¹

[†]See text.

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