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Oxidation behaviour of SiC-platelets and particulates-reinforced Al_2O_3/ZrO_2 matrix composites

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The oxidation behavior of hot-pressed SiC-platelets and particulates-reinforced Al_2O_3/ZrO_2 composites has been studied in an electric furnace at atmospheric pressure at different temperatures. The mass gain as a result of transformation of SiC into SiO_2 is described as a function of oxidation temperature, time and type of SiC. The mass gain up to 1100°C was low, but increased strongly at 1350°C. The oxidation process follows a parabolic rate at all oxidation temperatures. Oxidation of composites containing SiC-particulates is higher than the corresponding one containing SiC-platelets. The activation energy, obtained in the present investigation, was 297–333 kj/mol. Diffusion of oxygen and carbon monoxide through the matrix and oxide products appeared to be the rate controlling process. The reaction products were aluminosilicate glass phase and mullite as indicated by SEM and EDX. *© 2003 Kluwer Academic Publishers*

1. Introduction

Silicon carbide as a technical ceramic has been recognized and considered as an important and promising candidate material for use in high temperature structural ceramic components in applications including heat engines, heat exchanger, wear-resistant components and in advanced engines. This is due to its unique combination of properties, such as excellent oxidation resistance, strength retention at high temperature, high wear resistance, high thermal conductivity and good thermal-shock resistance.

The potential rate controlling mechanisms of SiC oxidation consist of (a) inward diffusion of oxygen, (b) outward diffusion of CO through the SiO_2 scale, and (c) interfacial reaction control at the SiO_2/SiC interface [1]. In general, it has been found that below 1350°C, the activation energies for oxidation of SiC are similar to those corresponding to pure Si [1]. However, above 1350°C, increasing the activation energies are found which in turn indicate a combination of inward ionic oxygen transport plus molecular oxygen diffusion [2].

There are two basic problems in describing the oxidation behaviour of non-oxide particle-reinforced oxide matrix composites using conventional methods (mass gain/area or oxide layer thickness vs. time): The surface area of the specimen is not the true area of oxidizing surfaces, and (2) the oxidized layer may contain incompletely oxidized particles. To meaningfully characterize the oxidation behaviour of non-oxide particles/oxide matrix composites, two modes were proposed [3]. Mode I is defined as the case where oxygen can react with the whole particle before it diffuse further into the matrix, forming a layer of "crust" with completely oxidized particles. Mode II is the case where oxygen can deeply penetrate into the matrix before all particles in the outer region are completely oxidized.

The oxidation behaviour of SiC whiskers or particulates as reinforcements in oxide-matrix composites has been investigated [4–7]. The oxidation resistance of silicon carbide-containing composites is influenced by the matrix constituent because of possible interactions between the silica and the matrix [8–11]. Kriven *et al.* [12] reported that the room-temperature flexural strength of SiC whisker (SiC_w) reinforced alumina decreased dramatically after exposure at temperatures above 1000°C, while the mullite SiC_w composites did not show any significant degradation even after exposure at up to 1200°C. This difference was attributed to the higher oxidation rate of SiC whiskers in the alumina matrix compared to that in the mullite matrix. Becher and Tiegs [13] suggested that the temperature dependence of the mechanical properties in the Al_2O_3/SiC composites was related to the oxidation of SiC whiskers and the subsequent reaction of the silica with the alumina matrix, especially at temperatures above 1100°C. Recently ZrO_2 particles were added to a SiC whiskers-reinforced oxide matrix, significantly improving the room-temperature fracture toughness. However, addition of zirconia could be a problem regarding the oxidation resistance because oxygen can be readily transported in zirconia.

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TABLE I Characteristics of starting powder

	Alumina	3 mol%-Y_2O_3 zirconia	α-SiC platelets	α-SiC particulates
Crystal structure	Corundum (α-Al_2O_3) hexagonal	Tetragonal and monoclinic ZrO_2	Hexagonal polytypes	Hexagonal polytypes
Fired density (g/cm^3)	3.97	5.99	3.22	3.18
Surface area (m^2/g)	14.10	15.00	0.11	0.30
Purity (%)	99.90	99.90	99.90	99.90
Impurities content	Fe 6 ppm	Y_2O_3 5.090%		
	SiO_2 4 ppm	SiO_2 0.009%		
	CaO 1 ppm	Na_2O 0.018%		
	MgO 1 ppm	Al_2O_3 <0.005%	–	–
	K_2O 1 ppm	Fe_2O_3 0.002%		
		L.I.O 3.530%		

The purpose of the present study is to ascertain the high-temperature (1000, 1100, and 1350°C) oxidation behaviour of SiC-platelets and particulates-reinforced Al_2O_3/ZrO_2 matrix composites containing 10 wt% α-SiC through kinetics and analysis of reaction products.

2. Experimental procedure

The material employed in this work consisted of submicron α-alumina and 3 mol% yttria-stabilized zirconia powders as matrix, in addition to two fine SiC powders as reinforcing materials; namely, platelets and particulates types. Table I summarizes physical and chemical characteristics of these materials.

Oxidation studies were conducted on the following hot-pressed composites: 80 wt% Al_2O_3 + 10 wt% stabilized ZrO_2 + 10 wt% SiC platelet sintered at 1500 and 1700°C (Specimens A1 and A2, respectively) and 80 wt% Al_2O_3 + 10 wt% stabilized ZrO_2 + 10 wt% SiC particulate sintered at 1500 and 1700°C (Specimens B1 and B2, respectively). Details on the preparation of powder, mixing, hot-pressing, microstructure and mechanical properties of the specimens are reported elsewhere [14].

Sintered specimens were cut into bars 4*4*30 mm for oxidation test. Test-specimens were heat-treated in a kiln in static air at 1000, 1100, 1350°C for 100 hours. Mass changes were systematically measured in a highly sensitive microbalance as a function of time and temperature. The reaction products were characterized using scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDX). The thickness of the reaction product was determined on scanning electron micrographs of the specimen cross section.

3. Results and discussion

3.1. Oxidation kinetics

The oxidation resistivity curves of the studied composites at different temperatures are shown in Fig. 1a to c. From these figures, it is clear that the mass gain per unit area up to 1100°C was low, but increased strongly at about 1350°C. These results strongly differs from the oxidation behavior of pure silicon carbide or of pure silicon nitride above 1100°C as was described by Billy [15]. This author and others [8, 16–19] reported

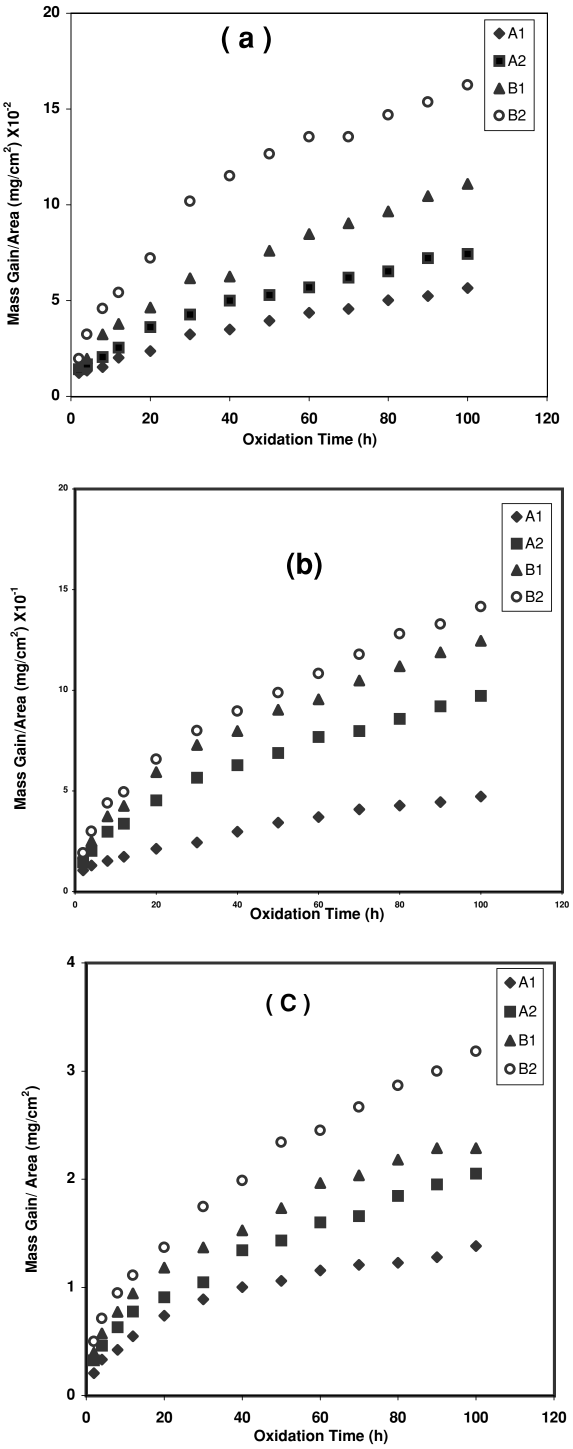

Figure 1 Oxidation resistivity of the investigated SiC-Al_2O_3-ZrO_2 composites in air at (a) 1000°C, (b) 1100°C and (c) 1350°C.

decreasing oxidation rates with increase of temperature in the range 1100–1500°C, attributed to the crystallization of the protective surface SiO_2 layer which occurs above 1100°C and is promoted at higher temperatures. This is not clearly the case in our study. At high temperatures, the oxidation products of SiC in the studied composites form new phases with the matrix, which reduce the oxidation resistance by increasing oxygen permeability.

The evaluation of the oxidation process in Al_2O_3-SiC composites was outlined [20] as follows:

(a) Reaction of SiC particles on the specimens surface with oxygen to form a thin layer of silica, which has a very low permeability to oxygen.

(b) While the oxidation of SiC particles is continuing, the so-formed silica reacts with alumina producing mullite or aluminosilicate liquid through which oxygen permeability are much higher. The overall oxidation of alumina-silicon carbide composites is complex, and is influenced not only by the amount of oxidizable phase, but also by the alumina content in the produced layer and by the presence of impurities in the matrix; depending on the combination of these features, a protective or non-protective scale can result.

(c) The oxidation product grows with a two-layered structure: a non-protective porous and buckled layer in contact with the unreacted material, which acts as a fast path for oxygen to the reaction interface, and an external protective layer whose composition and morphology controls the diffusion of oxygen and the escape of carbon monoxide.

The mass gain versus time curves at all temperatures approximate the classical parabolic behaviour (Fig. 2), being represented by the equation

$$(\Delta M)^2 = K_p t$$

where ΔM is the mass gain in time t, and K_p is the parabolic rate coefficient. The higher rates of oxidation of the composites sintered at 1700°C in comparison with these sintered at 1500°C—for the same type of SiC (platelets or particulates)- can be attributed to their high values of apparent porosity (Table II). On the other hand, the composites containing SiC-particulates showed higher rates of oxidation in comparison with these containing SiC-platelets. This result can be discussed in term of its high surface area (Table I).

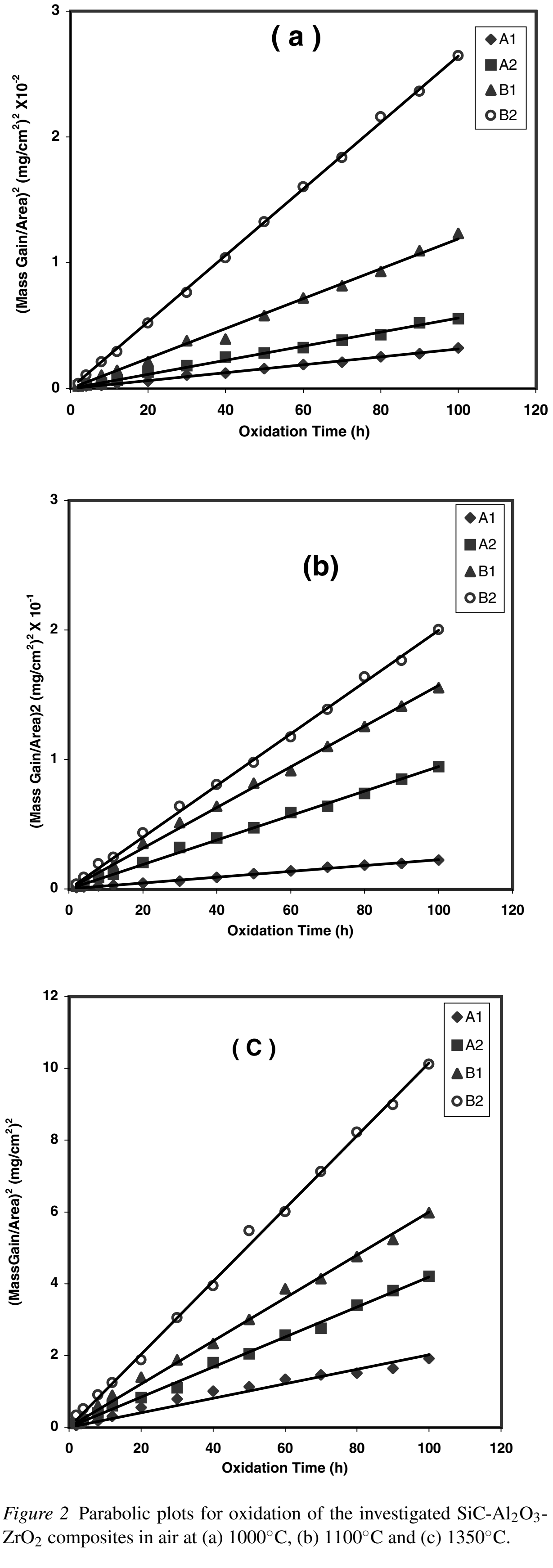

Figure 2 Parabolic plots for oxidation of the investigated SiC-Al_2O_3-ZrO_2 composites in air at (a) 1000°C, (b) 1100°C and (c) 1350°C.

A comparison between the experimental data and those of hot-pressed SiC, SiC-reinforced Al_2O_3 without ZrO_2 or SiC_w-reinforced Al_2O_3/ZrO_2 showed that the parabolic oxidation rate coefficients of the invesigated composites were around one to three orders of magnitude higher than that of the hot-pressed SiC ceramic found in the literature [4, 21, 22] as shown in Table III. Alumina, in fact, has been observed to increase the diffusion of oxygen to the interface: oxidation rates of pure SiC are enhanced by a factor of 10–20 in comparison with these for SiC contained in either alumina or mullite matrices [9]. Moreover, the presence in the oxide product of alumina together with an amount of silica lower than the stoichiometric one necessary to form mullite can result in the creation of either a metastable eutictic or immesible non-equilibrium aluminosilicate liquid. This influences oxygen permeability through the oxidation product. The gaseous diffusion through the liquid phase will be fast and the oxidation rate is accelerated.

TABLE II Densification parameters of the investigated composites before and after oxidation at 1350°C for 100 h in air

Sample	Before oxidation		After oxidation	
	Bulk density (g/cm^3)	Apparent porosity (%)	Bulk density (g/cm^3)	Apparent porosity (%)
A1	4.06	0.36	4.01	0.86
A2	4.07	0.61	3.98	1.43
B1	4.09	0.76	3.96	1.89
B2	4.04	0.95	3.92	2.33

TABLE III Oxidation data for the studied SiC-platelets and particulates-reinforced Al_2O_3/ZrO_2 composites in comparison with literature data on oxidation of SiC, Al_2O_3 containing SiC and SiC_w-reinforced Al_2O_3/ZrO_2 composites in air

Author and Reference	Materials	Oxidation temp. (°C)	Oxidation time (h)	Mass gain/area (mg/cm^2)	Oxidation rate Constant (mg^2/cm$^{-4}\cdot$s^{-1})
	A1	1000	70	0.582	
			100	0.679	8.611×10^{-9}
		1100	70	0.691	
			100	0.796	6.389×10^{-8}
		1350	70	1.208	
			100	1.659	5.833×10^{-6}
	A2	1000	70	0.620	
			100	0.744	1.555×10^{-8}
		1100	70	0.798	
			100	0.972	2.639×10^{-7}
		1350	70	1.659	
			100	2.051	1.164×10^{-5}
	B1	1000	70	0.903	
			100	1.110	3.305×10^{-8}
		1100	70	1.049	
			100	1.246	4.361×10^{-7}
		1350	70	2.035	
			100	2.444	1.664×10^{-5}
	B2	1000	70	1.168	
			100	1.411	7.333×10^{-8}
		1100	70	1.178	
			100	1.415	7.333×10^{-6}
		1350	70	2.972	
			100	3.746	2.819×10^{-5}
Schlichting and	HP-SiC +0.5 Al	1200	25		1.778×10^{-8}
Kriegesmann [21]		1400	25		6.944×10^{-8}
Luthra and Park [22]	Al_2O_3 + 20 vol% SiC_w	1375^a	72		2.778×10^{-6}
	Al_2O_3 + 30 vol% SiC_w	1375^a	72		6.389×10^{-6}
Wang *et al.* [4]	61 wt% Al_2O_3 + 31 wt%	1200	70	0.16	1.186×10^{-6}
	SiC_w + 8 wt% ZrO_2	1350	70	0.80	2.511×10^{-6}
	75 wt% Al_2O_3 + 17 wt%	1150	70	0.10	5.528×10^{-8}
	SiC_w + 8 wt% ZrO_2 +	1200	70	0.25	2.575×10^{-7}
	0.3 wt% SiO_2	1350	70	1.07	4.555×10^{-6}
	71 wt% Al_2O_3 + 17 wt%	1100	70	0.23	4.667×10^{-7}
	SiC_w + 12 wt% ZrO_2 +	1200	100	0.77	1.411×10^{-6}
	1.0 wt% (SiO_2 +MgO)	1350	70	1.52	9.500×10^{-6}

[a] In oxygen.

In addition, the probability of damage of the protecting SiO_2 film is enhanced with increased alumina content because the alumina, which exists near to SiC particles, can take part in the reaction [23]. This is perhaps another reason for the high oxidation rates found.

The results also confirm that the oxidation resistivity of the investigated composites of comparable values in comparison with the work of Wang *et al.* [4]. Liu *et al.* [24] reported that the oxidation rates for the SiC_w-reinforced mullite composite were slightly lower than for that without ZrO_2. ZrO_2 retards the crystallization of the oxide film and decreases the viscosity of the liquid phase formed during the oxidation, which may be responsible for the higher oxidation rate of the ZrO_2-containing material.

The parabolic rate coefficients as a function of temperature is given in Fig. 3 using the Arrhenius equation

$$K_p = C \exp(-Q/RT)$$

Where Q is the activation energy, R the gas constant and T the absolute temperature. An activation energy of 333 kj/mol for A1, 331 kj/mol for A2, 312 kj/mol for B1 and 297 kj/mol for B2 is obtained. Activation energies of 120–350 kj/mol have been reported by various authors [2, 25, 26] to describe the oxidation of SiC

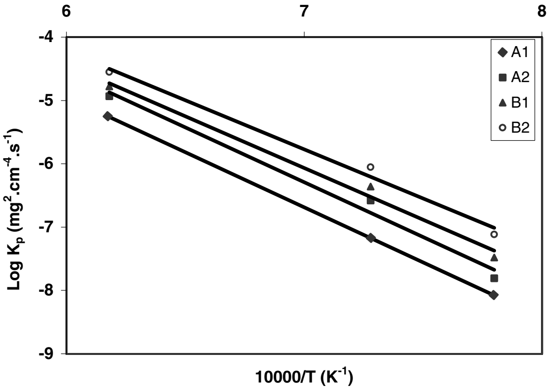

Figure 3 Parabolic rate coefficients for oxidation of SiC-reinforced Al_2O_3/ZrO_2 composites in air as a function of temperature.

at temperatures below 1500°C. The reported activation energy in this regime (120–350) agrees very well with the energy required for molecular oxygen permeation in fused silica. However, high values of activation energy in the range 364–548 kj/mol have also been reported by Singhal [27] and Costello and Tressler [28] for HP-SiC which were attributed to the diffusion of CO through the oxide layer. Moreover, Luthra and Park [22] calculated activation energies for the oxygen diffusion through alumina and mullite to be 330–460 kj/mol. In view of these results, the oxidation process of the investigated composites may be considered to be under a mixed-oxygen and carbon monoxide diffusion controlled.

The effect of the used oxidation time (100 h) at 1350°C on the density quality of the composites is shown in Table II. From the table, it is obvious that slight decrease in bulk density and slight increase in apparent porosity were recorded. The calculated decrease in density quality is assumed to be due to a combination of oxidation of SiC into silica, formation of mullite–through the reaction of alumina matrix with the liberated silica—which accompanied by volume expansion, and formation of gas pores through CO gas escapes during oxidation. It has been concluded that the oxidation of SiC to SiO_2 is accompanied by an increase in the volume of a unit cell of the molecular lattice of approximately 100%.

3.2. Microstructure observations

In order to investigate the morphological evolution of the oxidation reaction products using SEM and EDX, specimen B2-which showed the lowest oxidation resistivity—was chosen for this. The surface morphology of the oxide film formed on specimen B2 after oxidation in air at 1350°C was shown in Fig. 4. The figure showed that the surface of the specimen was covered with a layer of glassy phase and pores: the reaction product is a continuous aluminosilicate glass phase, which contains needle-like crystals of mullite. The spectra of EDX-point analysis confirmed the existence of SiO_2-rich aluminosilicate glassy phase and mullite as shown in Fig. 5a and b, respectively. Large peaks of Al and Si are observed in the needle-like crystals, whereas a large peak of Si and a small trace of Al are observed in the glassy phase layer. Comparing the morphologies between Fig. 6a and b, the results clearly showed that the thickness of the oxidized layer increased from specimen A2-containing SiC-platelets- to specimen B2 containing SiC-particulates. This finding confirm the results of oxidation kinetics.

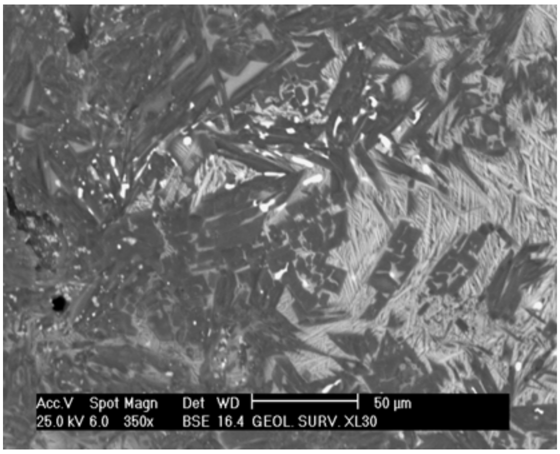

Figure 4 Scanning electron micrograph of surface of specimen B2 oxidized at 1350°C for 100 h in air.

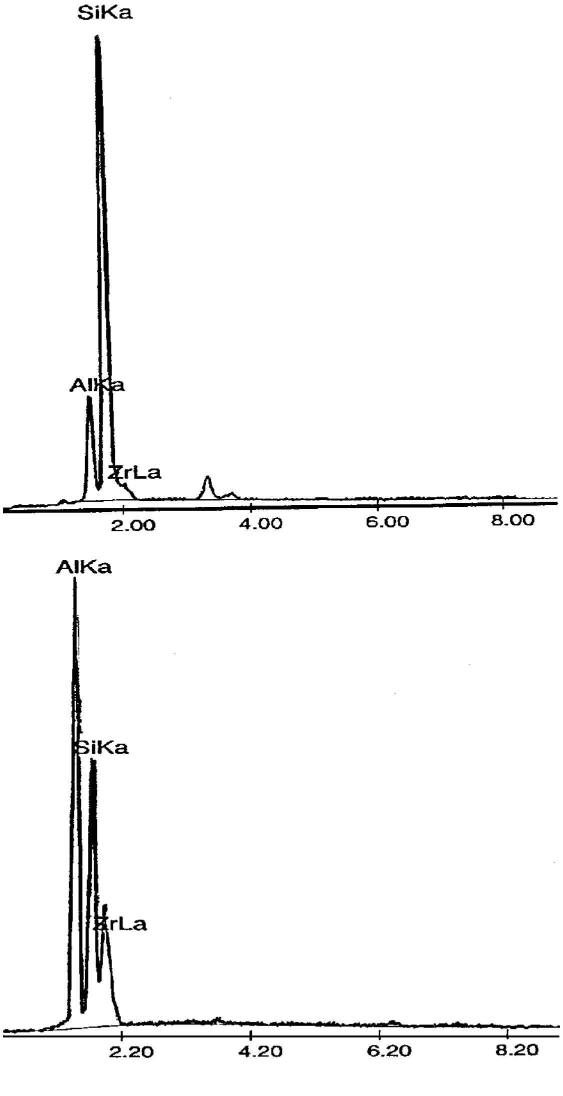

Figure 5 Energy dispersive X-ray analyses of (a) surface oxide layer and (b) needle-like crystals of specimen B2 after oxidation at 1350°C for 100 h in air.

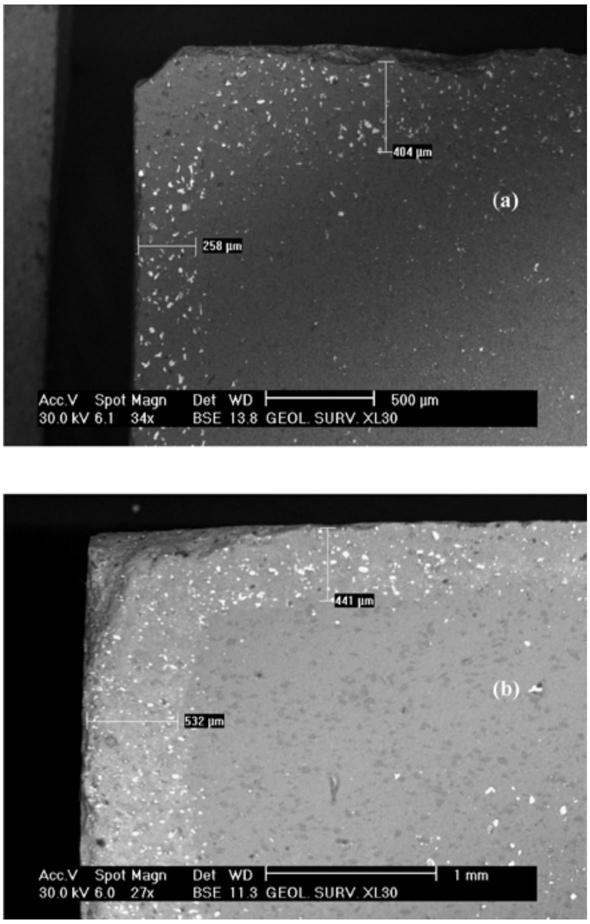

Figure 6 Cross section of specimens (a) A2 and (b) B2 oxidized at 1350°C for 100 h in air.

4. Conclusion

The oxidation behaviour of hot-pressed SiC-Platelets and particulates-reinforced Al_2O_3/ZrO_2 composites—sintered at 1500 and 1700°C—containing 10 wt% SiC has been tested at 1000, 1100, and 1350°C for oxidation time up to 100 h. The mass gain- as a results of transformation of SiC into SiO_2- up to 1100°C was low, but increased strongly at 1350°C. The oxidation process follows a parabolic rate low at all oxidation temperatures indicating that the oxidation process is controlled by oxidant diffusion. Also the results revealed that, the oxidation of composites containing SiC-particulates is higher than the corresponding one containing SiC-platelets.

The experimental data confirmed that these composites have a lower thermal stability than hot- pressed SiC and SiC-reinforced Al_2O_3 without ZrO_2. The activation energy was 297–333 kj/mol. Diffusion of oxygen and carbon monoxide through the matrix and oxide products appeared to be the rate-controlling step. The scanning electron microscope and the spectra of EDX-point analysis indicating the existence of mullite and SiO_2- rich aluminosilicate galss phase in the oxide layer after oxidation at 1350°C for 100 h. The investigated composites showed little decrease in density quality after oxidation.

References

1. K. MOTZFELD, *Acta Chem. Scand.* **18** (1964) 1596.
2. T. NARUSHIMA, T. GOTO and T. HIRARI, *J. Amer. Ceram. Soc.* **72** (1989) 1386.
3. C. C. LIN, PhD thesis, University of Illinois at Urbana-Champaign, 1991.
4. P. WANG, G. GRATHWOHL, F. PORZ and F. THÜMMLER, *Powder Metallurgy International* **23** (1991) 370.
5. G. URRETAVIZCAYA, A. L. CAVALIERI and J. M. PORTO LOPEZ, *Ceram. Int.* **21** (1995) 97.
6. CHIEN-CHEN LIN, *J. Amer. Ceram. Soc.* **82** (1999) 2833.
7. M. ISABEL NIETO *et al.*, *J. Ceram. Soc. Jpn.* **100** (1992) 459.
8. R. E. TRESSLER, in "Corrosion of Advanced Ceramics," edited by G. Nickel, NATO ASI Series (Kluwer Academic, 1994) p. 3.
9. M. P. BOROM, M. K. BRUN and L. E. SZALA, in Ceram. Eng. Sci. Proc. (The American Ceramic Society, Westerville, Ohio, 1987) Vol 8, p. 654.
10. K. LUTHRA, in Ceram. Eng. Sci. Proc. (The American Ceramic Society, Westerville, Ohio, 1987) Vol. 8, p. 649.
11. R. A. MARRA and D. J. BRAY, in Ceram. Eng. Sci. Proc. (The American Ceramic Society, Westerville, Ohio, 1986) Vol. 7, p. 945.
12. W. M. KRIVEN, in "Tailoring Multiphase and Composite Ceramics," edited by R. E. Tressler *et al.* (Plenum Press, New York, 1986) p. 223.
13. P. F. BECHER, T. N. TIEGS, *J. Amer. Ceram. Soc.* **70** (1987) 651.
14. S. K. H. IBRAHIM, PhD thesis, Fakultät für Bergbau, Hütten Wesen und Geowissenschaften der Rheinisch-Westfälischen Technischen Hochschube Aachen, 2000.
15. M. BILLY, *Mater. Sci. Eng.* **88** (1987) 53.
16. M. A. LAMKIN, F. L. FILEY and R. J. FORDHAM, *J. Eur. Ceram. Soc.* **10** (1992) 347.
17. E. OPILA, *J. Amer. Ceram. Soc.* **78** (1995) 1107.
18. K. L. LUTHRA, *ibid.* **74** (1991) 1095.
19. D. S. FOX, *ibid.* **81** (1998) 945.
20. D. SCITI and A. BELLOSI, *J. Mater. Sci.* **33** (1998) 3823.
21. J. SCHLICHTING and J. KRIEGESMANN, *Ber. DKG* **56** (1979) 72.
22. K. L. LUTHRA, H. D. PARK, *J. Amer. Ceram. Soc.* **73** (1990) 1014.
23. S. S. SINGHAL and F. F. LANGE, *ibid.* **58** (1975) 433.
24. H. Y. LIU, K. L. WEISSKOPF, M. J. HOFMANN, G. PETZOW, *J. Euro. Ceram. Soc.* **5** (1989) 123.
25. Z. ZHENG, R. E. TRESSLER and K. E. SPEAR, *J. Electrochem. Soc.* **137** (1990) 854.
26. J. A. COSTELLO and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **69** (1986) 67.
27. S. C SINGHAL , *J. Mater. Sci.* **11** (1976) 1246.
28. J. A. COSTELLO and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **64** (1981) 327.

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