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Oxidation Behavior of Particulate and Fibrous Silicon Carbide

D. W. McKee & P. A. Siemers

Metallurgy Laboratory, General Electric Corporate Research and Development,
Schenectady, New York 12301, USA

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ABSTRACT

The oxidation behavior of particulate, whisker and fibrous forms of silicon carbide to be used as reinforcements in ceramic matrix composites has been studied in flowing air. Oxidation rates below 1200°C obeyed a parabolic rate law but at higher temperatures the kinetics were controlled by the formation of a viscous silica glass which resulted in bonding between the particles and loss of surface area.

1 INTRODUCTION

Particulate and fibrous forms of silicon carbide have been evaluated as reinforcements in ceramic matrix composites designed for aerospace applications at very high temperatures.[1,2] Such materials, when used as structural components in advanced engines, will be required to withstand temperatures in excess of 1500°C in an oxidizing (air) environment for long periods of time. Silicon carbide in monolithic or bonded form is highly resistant to oxidation, as evidenced by its use in furnace elements to temperatures of 1600°C. In this case a coherent film of silica is formed on the surface which limits further oxidation. However as the rate of oxidation depends on the surface area of the material,[3] particulate and fibrous forms of silicon carbide will oxidize much more readily than the dense material.

The oxidation behavior of a variety of powdered and polycrystalline forms of silicon carbide has been reported, with large variations in the

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observed kinetics of the oxidation process.[4–7] For single crystal material, Costello and Tressler[8] have shown that the $(000\bar{1})$ C face of the SiC platelets is an order of magnitude more reactive towards oxygen at 1200°C than the (0001) Si face, and there is evidence[9,10] that impurities such as Mg and Al can markedly affect the oxidation kinetics. The silica scale formed has generally been found to be amorphous up to 1500°C.[5,11] In the present study the oxidation behavior of several forms of silicon carbide particles, including polycrystals, spheres, fibers and whiskers were investigated in flowing air at temperatures in the range 1000–1600°C.

2 MATERIALS

Particulate and fibrous silicon carbide samples were obtained from a number of different sources. Table 1 lists these materials, their initial surface areas (as determined by the BET method using nitrogen adsorption at -195°C) and crystallographic data. Apart from the (Arco) whiskers and the (General Electric) spheres, which were almost pure beta material (3C, cubic), the other particulate materials were mixtures of alpha (4H, 6H hexagonal, 15R rhombohedral) and beta forms.

Beta silicon carbon fiber of 30 μm diameter was obtained from Avco Specialty Materials Inc. This material was made by chemical vapor deposition of silicon onto a 37 μm diameter graphite filament. The outer surface of these fibers was subsequently coated by the vendor with a 2 μm layer of carbon-rich silicon carbide.

3 PROCEDURE

Measurements of oxidation kinetics in dry flowing air (200 ml/min) at 1 atm (0·1 MPa) were carried out in a Netzsch Thermal Analyzer STA 409 controlled atmosphere thermobalance (Netzsch Inc., Lionville, Pennsylvania), which recorded weight changes as functions of time and temperature. Oxidation data were obtained isothermally at temperatures in the range 1000–1600°C using sample weights of 100 mg. In the case of the 30 μm fibers, chopped pieces of known length were placed in 8 mm diameter alumina crucibles which were mounted in the thermobalance. The accuracy of the weight change measurements was $\pm 0{\cdot}1$ mg. The surface appearance of the various materials before and after oxidation in the thermobalance was observed in the scanning electron microscope and qualitative analyses of the surface composition were made with the electron microprobe.

TABLE 1
Characteristics of Silicon Carbide Materials

Material type and source		*Surface area* (m^2/g)	*Crystal structure d (exp)A(polytype)*				
			2·61 (6H)	*2·57 (4H, 15R)*	*2·51 (6H, 3C 15R)*	*2·36 (4H, 6H)*	*2·32 (15R)*
			Relative X-ray line intensity (experimental) (I(exp))				
2–5 μm Lonza[a]	Carbogran	2·1	31	8	100	32	2
0·8 μm Starck[b]	A10	13·5	27	9	100	24	3
Submicron GE[c]	CD627	11·0	29	6	100	28	—
Spheres GE[c]	(−140 + 320 mesh)	4·8	—	—	100	4	—
Whiskers	Arco[d]	2·5	—	—	100	—	—
β-Fibers 30 μm (SCS-6)	Avco[e]	0·01					

[a] Lonza Inc, Fairlawn, NJ.
[b] HC Starck, FRG.
[c] General Electric Co., Schenectady, NY.
[d] Arco (Atlantic Richfield Corp.), Grier, SC.
[e] Avco Speciality Materials, Inc., Lowell, MA.

4 RESULTS AND DISCUSSION

4.1 Silicon carbide powders and whiskers

Oxidation data in flowing dry air for two powdered silicon carbide materials are shown in Figs 1 and 2, and for SiC whiskers in Fig. 3. In each case the percent weight gain of 100 mg samples and the percent conversion to SiO_2 at

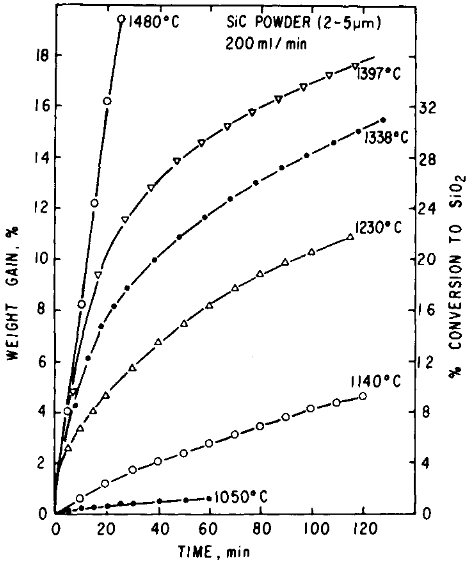


Fig. 1. Oxidation of SiC powder (Lonza, 2–5 μm) in flowing dry air. Weight gain and total conversion to SiO_2 versus time at various temperatures.

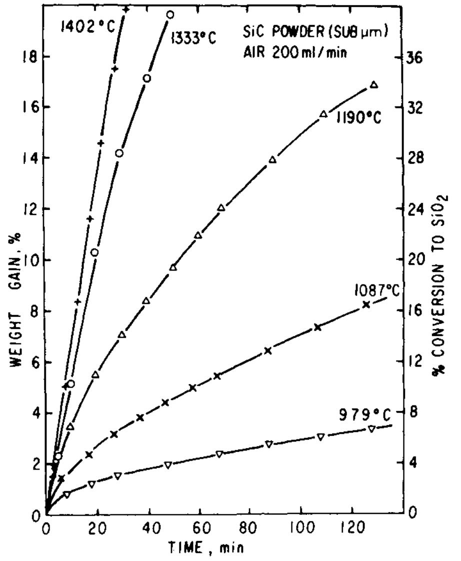


Fig. 2. Oxidation of SiC powder (G.E., sub-micrometer) in flowing dry air. Weight gain and total conversion to SiO_2 versus time at various temperatures.

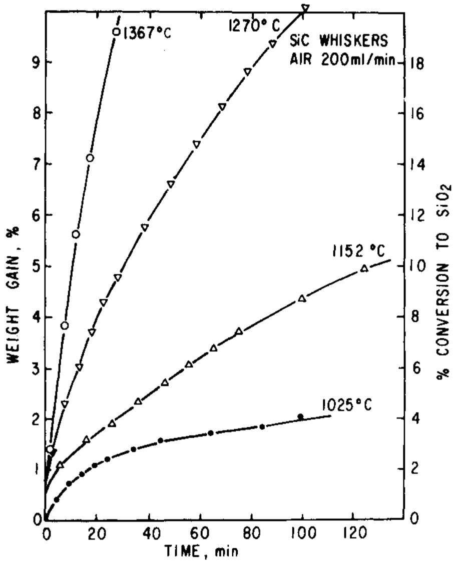


Fig. 3. Oxidation of SiC whiskers (Arco) in flowing dry air. Weight gain and total conversion to SiO_2 versus time at various temperatures.

various temperatures are plotted as a function of time. At temperatures below about 1400°C the weight gain curves for these materials obeyed parabolic kinetics, as expected for a process whose rate is controlled by diffusion through a growing oxide layer.[12] Typical parabolic plots for a powdered SiC sample are shown in Fig. 4, the data being plotted according to the relation,

$$\frac{(\Delta W)^2}{W_0} = kt$$

where ΔW is weight change, W_0 is initial weight, k is a constant and t is time.

In general, although the parabolic law was accurately obeyed for all the materials studied for oxidation periods of several hours at temperatures of 1000–1100°C, at higher temperatures the duration of applicability of the parabolic law became progressively shorter. Figure 5 shows a plot of the initial parabolic rate constant for oxidation at 1200°C as a function of the BET initial surface area for the various materials studied. It is apparent that a linear correlation exists between surface area and reactivity to oxygen, in spite of the widely different morphologies of the silicon carbide materials.

At temperatures above about 1400°C a change in the oxidation pattern of these particulate and fibrous materials was observed. As shown in Fig. 6, at these high temperatures although the initial oxidation rate was very rapid, the process became self-limiting after increasingly shorter periods of time and the weight gain reached a constant value which was often less than that observed at lower temperatures. This rapid truncation of the oxidation

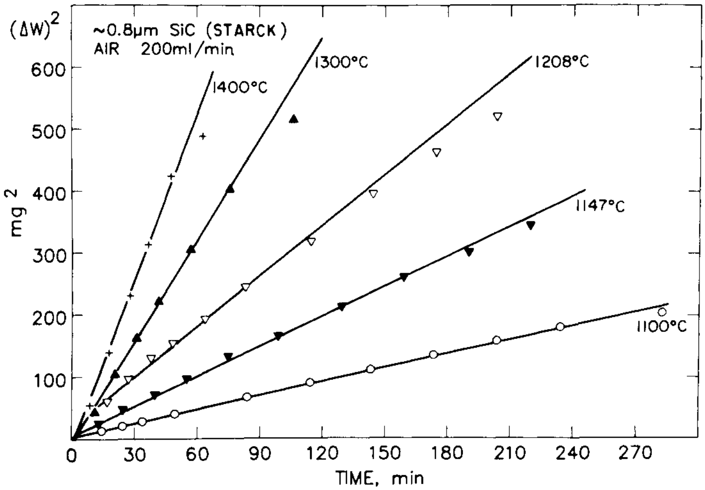


Fig. 4. Parabolic plots for oxidation of SiC powder (Starck 0·8 μm) in flowing dry air. (Weight Gain)^2 versus time at various temperatures.

process was observed for all the materials examined, as shown in Fig. 7, which summarizes oxidation data obtained in flowing air at 1500°C. In each case, after a short exposure to air at 1500°C, the conversion of SiC to SiO_2 reached a limiting value which varied from material to material.

This abrupt change in oxidation mechanism at temperatures above 1400°C is illustrated clearly by the Arrhenius plots shown in Figs 8–10, in which the log of the initial oxidation rate is plotted against reciprocal

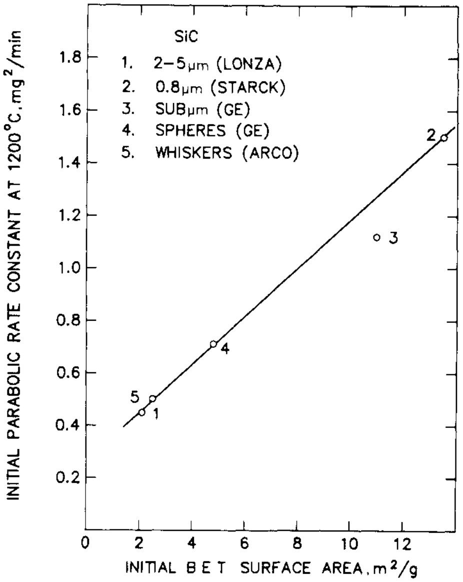


Fig. 5. Initial parabolic rate constants for oxidation of SiC particulates and whiskers at 1200°C in flowing air as a function of initial surface area.

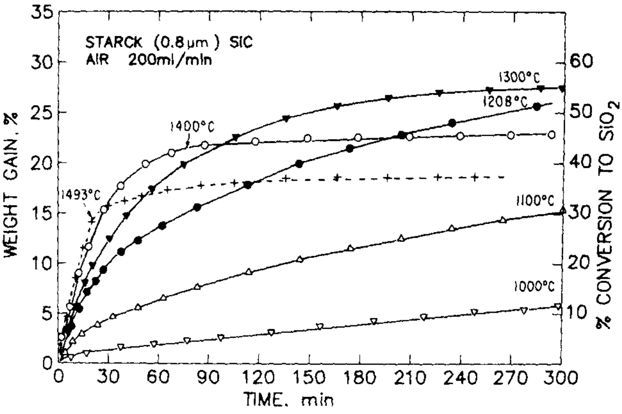


Fig. 6. Oxidation of SiC powder (Starck 0·8 µm) in flowing dry air. Weight gain and total conversion to SiO_2 versus time at various temperatures up to 1500°C.

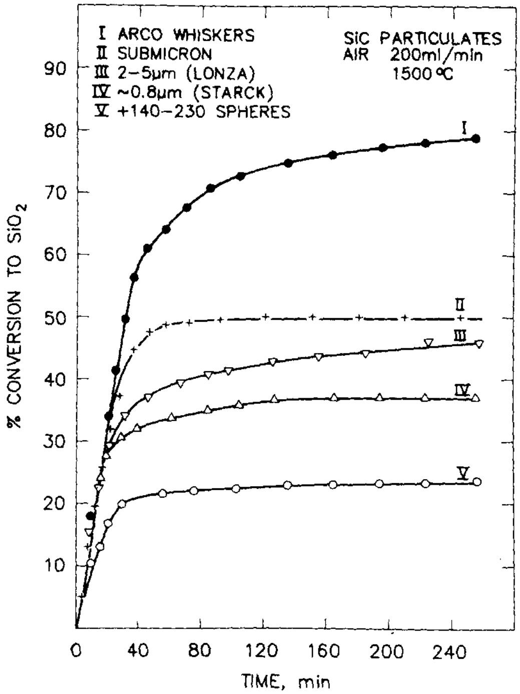


Fig. 7. Oxidation of SiC particulates and whiskers in flowing dry air at 1500°C. Total conversion to SiO_2 versus time.

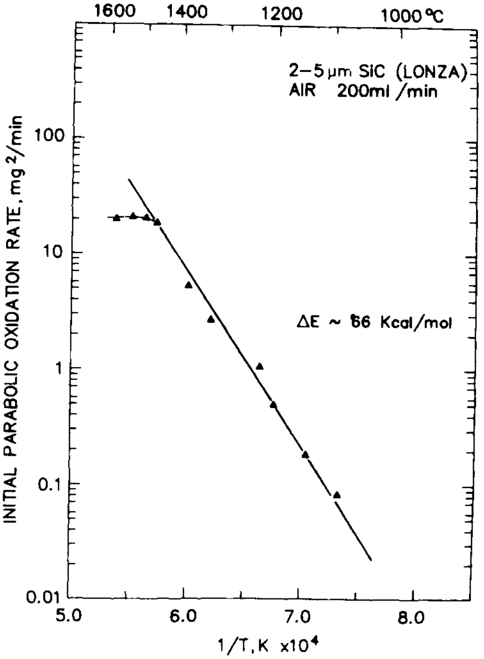


Fig. 8. Arrhenius plot for oxidation of SiC powder (Lonza 2–5 μm) in dry flowing air. Log (initial oxidation rate) versus 1/T K.

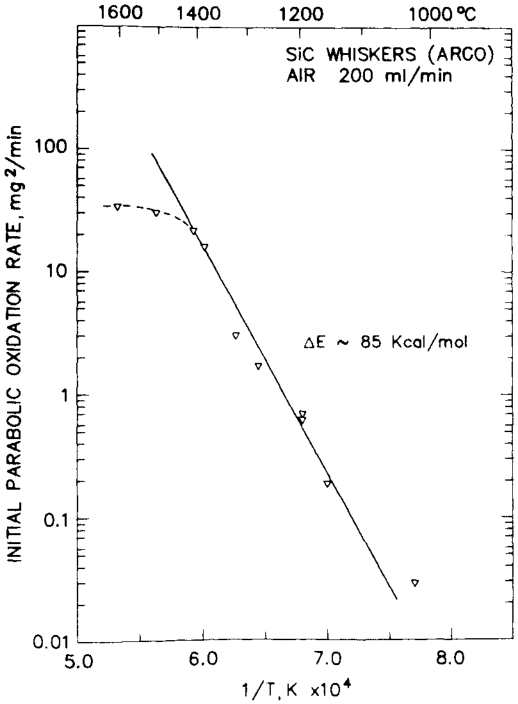


Fig. 9. Arrhenius plot for oxidation of SiC powder (Starck 0·8 μm) in dry flowing air. Log (initial oxidation rate) versus 1/T K.

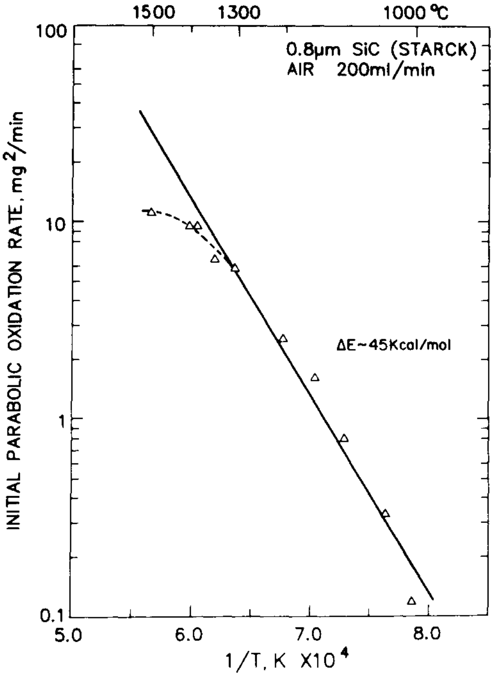


Fig. 10. Arrhenius plot for oxidation of SiC whiskers (Arco) in dry flowing air. Log (initial oxidation rate) versus 1/T K.

temperature for two powdered samples and for SiC whiskers. In each case, at temperatures below 1400°C, linear Arrhenius plots were obtained the slopes of which gave apparent activation energies in the range of 45–85 Kcal/mol (190–360 kJ/mol). Such values are similar to those reported in the literature for other particulate silicon carbide materials.[8] However at temperatures in excess of 1400°C, the overall rate of oxidation rapidly diminished, leading to a dramatic decrease in the slopes of the Arrhenius plots. For the particulate and fibrous silicon carbide materials investigated, the apparent activation energies, based on weight gain measurements as a function of time, effectively fell to zero at temperatures above 1500°C, as shown in Figs 9 and 10.

In order to provide a basis for an interpretation of the observations described above, the silicon carbide materials were examined in the scanning electron microscope in the as-received condition and after exposure to flowing air for 2 h at temperatures exceeding 1350°C. Micrographs of the five silicon carbide materials before the oxidation experiments are shown in Fig. 11. As shown, the morphology of the particles varied from finely crystalline to spherical or fibrous with a high aspect ratio.

The appearance of the 2–5 μm (Lonza) SiC material after 2 h exposure to flowing air at 1500°C is illustrated by the micrograph in Fig. 12. It is evident that considerable coarsening of the particles has taken place, many of the

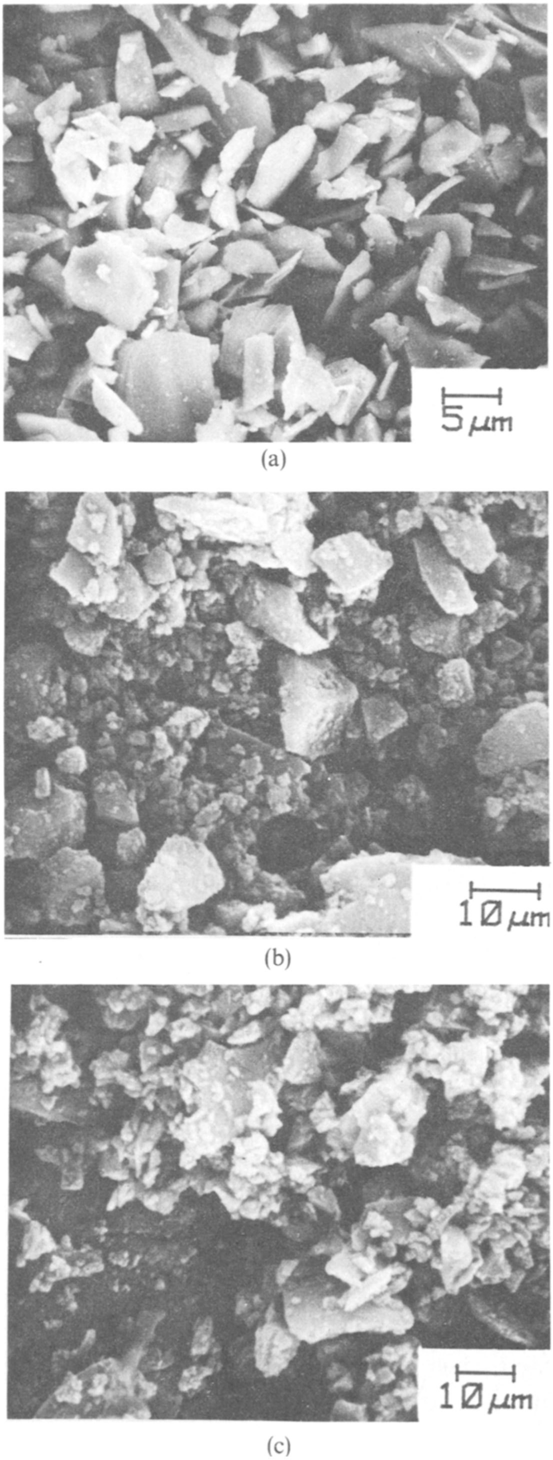
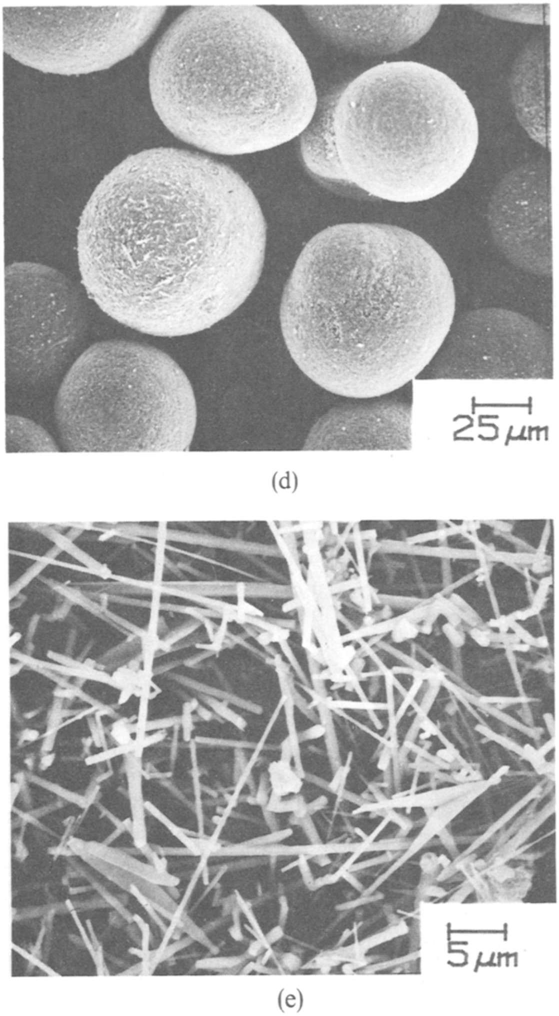


Fig. 11. Appearance of SiC particulates before oxidation. (a) Lonza 2–5 μm; (b) Starck 0·8 μm; (c) General Electric sub-micrometer).



(d)

(e)

Fig. 11.—*contd.* (d) General Electric spheres (– 140 + 230 mesh); (e) Whiskers (Arco).

crystals being fused together with a mobile glassy phase of silica. A micrograph of the 0·8 μm (Starck) material after oxidation for 2 h at only 1350°C is shown in Fig. 13. Again the discrete particles have been cemented together by the viscous silica glass formed by the oxidation reaction. The glassy silica phase is clearly evident in Fig. 14, which shows the appearance of particles of the sub-micrometer (GE) material following oxidation in air for 2 h at 1500°C. In this case flow of the silica film has resulted in fusion of the individual particles to form a porous sponge-like structure. The large (25–75 μm) spheres shown in Fig. 15 exhibited less coalescence than the other materials, but some fusion of the smaller particles was observed and silica

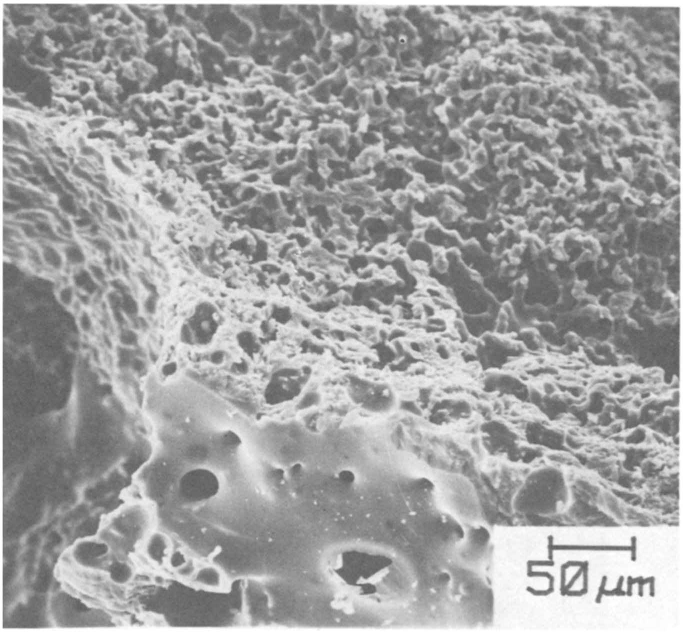


Fig. 12. Appearance of SiC particulates (Lonza 2–5 µm) after exposure to flowing air for 2 h at 1500°C.

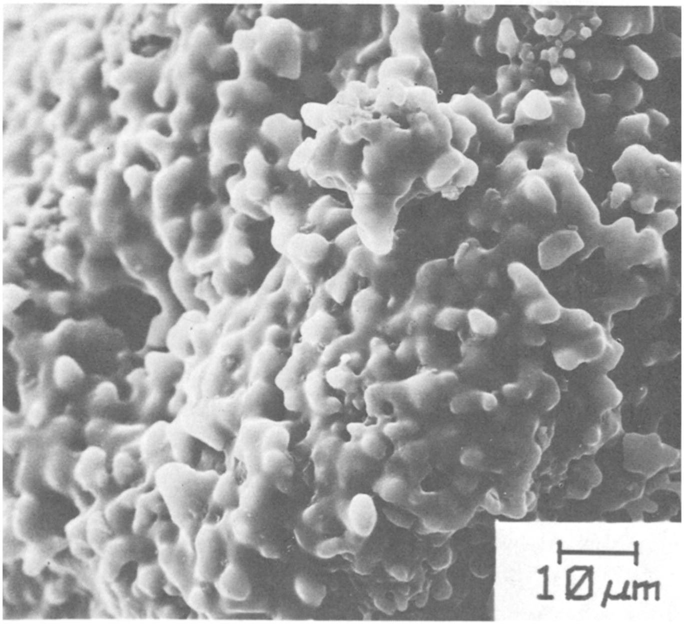


Fig. 13. Appearance of SiC particulates (Starck 0·8 µm) after exposure to flowing air for 2 h at 1350°C.

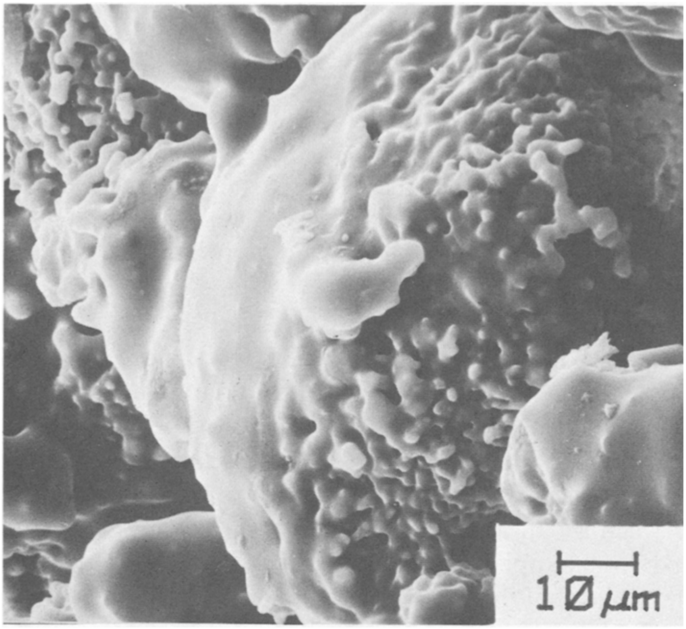


Fig. 14. Appearance of SiC particulates (GE sub-micrometer) after exposure to flowing air for 2 h at 1500°C.

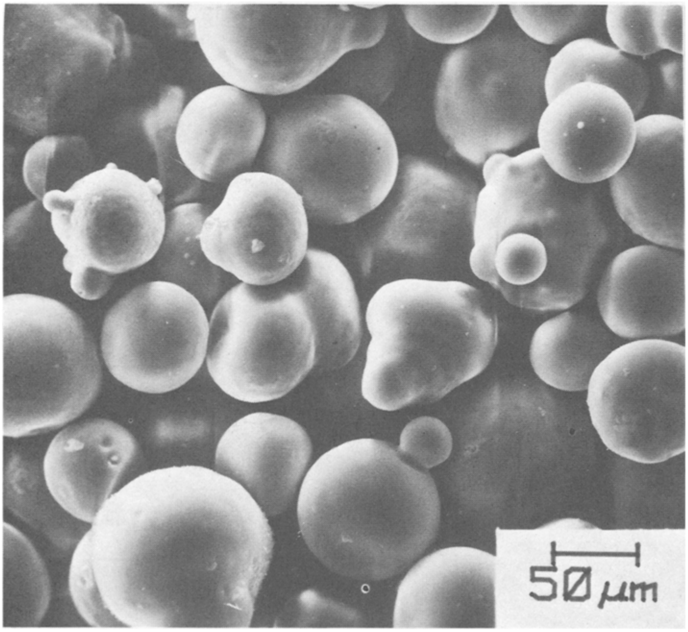


Fig. 15. Appearance of SiC spheres (GE) after exposure to flowing air for 2 h at 1500°C.

droplets could be identified on many of the spherical surfaces after 1500°C oxidation. On the other hand the silicon carbide whiskers showed extensive coarsening following this oxidation exposure and, as shown in Fig. 16, clear evidence of bonding of the whiskers by the glassy silica phase.

Sintering of the particles following oxidation at 1400°C and above was also clearly visible to the naked eye. After oxidation at 1200°C and below, even for periods of several hours, the particles remained friable and unbonded to each other. After 4 h heating in air at 1200°C, the powdered residue was white due to conversion to silica. On the other hand, after oxidation at 1400°C and above, even for periods of 1 h, the particles were found to have fused into a bonded network as a result of the flow of the silica glass from particle to particle. The residue also remained grey as the bulk of the material had not been converted to silica. Although it has been shown that the presence of alumina increases the oxidation rate of hot pressed silicon carbide[10] and lowers the viscosity of the silica scale, no evidence of reaction between the alumina crucibles and the silicon carbide was found, even at oxidation temperatures as high as 1600°C. Electron microprobe analysis confirmed that the viscous surface phase contained only silica, with minute amounts of calcium (in the case of the Arco whiskers and the Lonza material) and potassium (in the case of the General Electric sub-micrometer material).

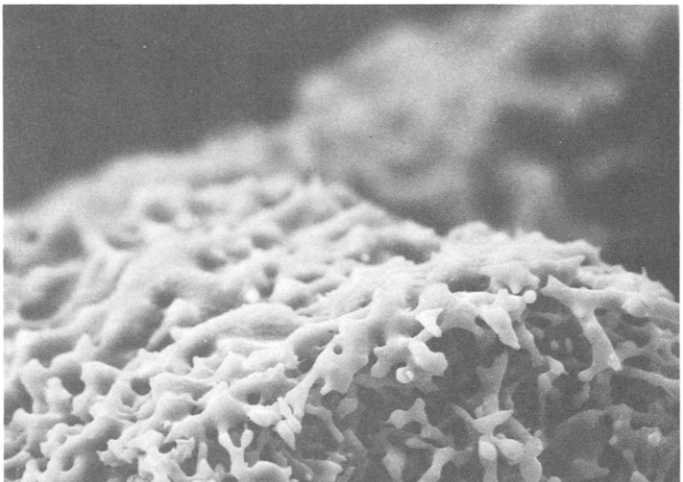


Fig. 16. Appearance of SiC whiskers (Arco) after exposure to flowing air for 2 h at 1500°C.

Although the growth of a SiO_2 scale is expected on silicon carbide during oxidation at elevated temperatures, as the melting point of silica (β-cristobalite) is 1713°C the formation of a mobile film of silica at temperatures as low as 1350°C is somewhat surprising. However, according to Hummel,[13] the presence of metastable forms of silica, such as high quartz or high tridymite could lead to melting at considerably lower temperatures. According to published data,[14] the viscosity of fused silica falls by three orders of magnitude between 1200 and 1400°C and it is evident from the present study that interparticle flow of the siliceous film results in loss of surface area and an effective smothering of the oxidation reaction.

4.2 Silicon carbide fibers

The weight changes which were observed on heating various lengths of the 30 μm silicon carbide fiber in flowing air at a linearly increasing temperature rate are shown in Fig. 17. Between 600 and 900°C weight losses were predominantly due to gasification of the carbonaceous layer on the outer surfaces of the fibers. However, starting at about 800°C, gasification of the core carbon took place and this process continued at higher temperatures until the core had completely burned away and the fibers were hollow.

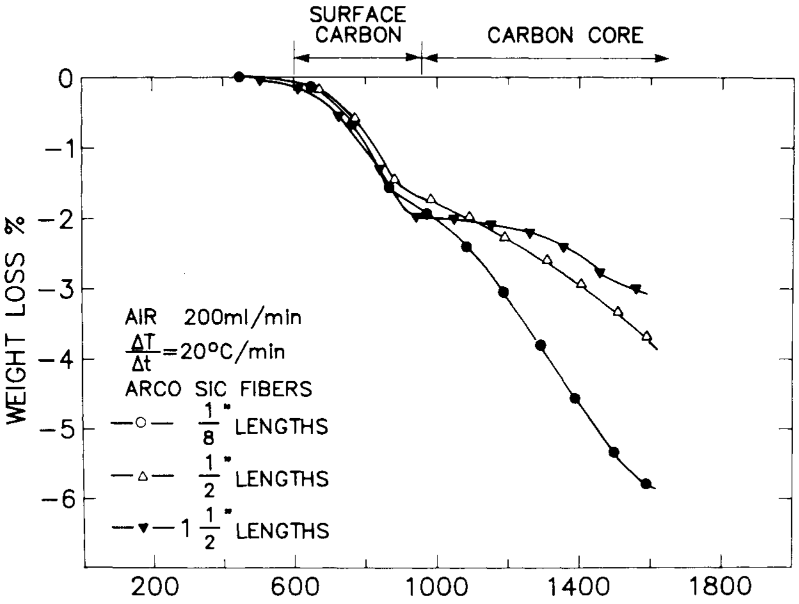
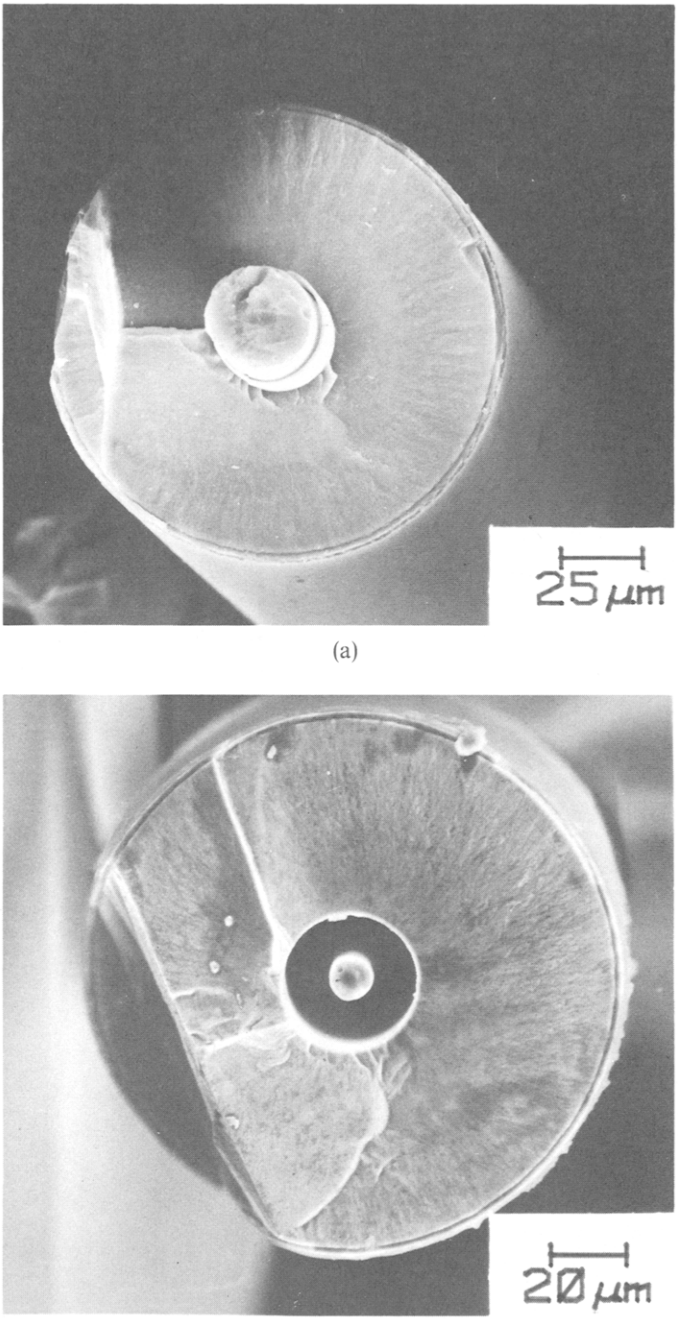


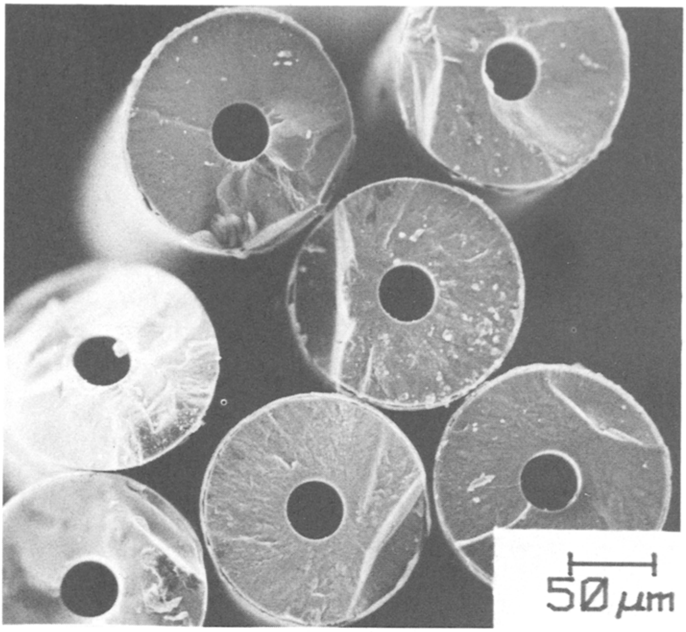
Fig. 17. Oxidation behavior of SiC fibers (Avco, 140 μm). Weight losses on heating various lengths of chopped fibers in flowing dry air at linearly increasing temperature.



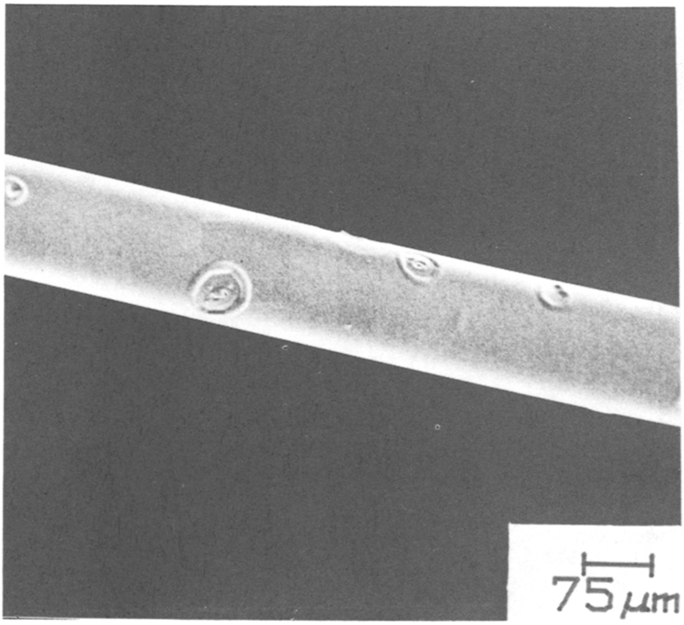
(a)

(b)

Fig. 18. Appearance of SiC fibers (Avco, 140 μm). (a) as received; (b) after 2 h exposure to flowing air at 800°C.



(c)



(d)

Fig. 18.—*contd.* (c) after 10 min heating to 1600°C in flowing air; (d) surface appearance of the fibers after heating to 1600°C for 10 min.

Chopping the fibers into shorter lengths accelerated the gasification process by facilitating access of oxygen to the carbon core, as shown in Fig. 17. Weight losses due to gasification of carbon on heating in air completely masked any weight gains from the oxidation of the silicon carbide, however as the surface area of the large diameter fibers was very small, the weight gain involved would have been difficult to measure in any case. Figure 18 shows the appearance of the silicon carbide fibers; (a) in the as-received condition with the carbon core intact, (b) after partial burnoff of the core and (c) after complete removal of the carbon core. Following a short exposure to air at 1600°C (Fig. 18(d)), the surfaces of the fibers exhibited cratered regions probably resulting from the flow of a semiliquid film of silica at this temperature. The ends of the oxidized fibers also exhibited a rounded appearance after this heat treatment. The formation of a viscous silica film was expected from the observations of the high temperature oxidation behavior of the particulate and whisker forms of silicon carbide described above.

5 CONCLUSIONS

Particulate and whisker forms of commercial silicon carbide oxidize in air according to a parabolic rate law below about 1200°C, but at temperatures above 1350°C a mobile glassy film of silica reduces the extent of oxidation by cementing the particles together and reducing the effective surface area. This process would be expected to occur near the surface of, for example, a SiC/ceramic composite if the SiC reinforcement particles are in physical contact.

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