Oxidation kinetics of reaction-sintered silicon carbide

O P CHAKRABARTI and J MUKERJI

Central Glass and Ceramic Research Institute, Jadavpur, Calcutta 700032, India

Abstract. The oxidation kinetics of reaction-sintered silicon carbide has been studied over the temperature range 1200 to 1350°C. The material has a bulk density of $3.00\,g/cm^3$ and the unreacted Si content is 22.5% (v/v). The activation energy for oxidation is $28.75 \pm 2.61\,kcal/mol$. It is proposed that the diffusion of oxygen through the growing oxide film is the rate-controlling process.

Keywords. Oxidation; silicon carbide.

1. Introduction

Silicon carbide is an important non-oxide ceramic material which has found increased interest for high-temperature structural applications because of its excellent high-temperature strength and high resistance to oxidation. There are many publications on the oxidation behaviour of various types of silicon carbide. Most of the early studies (Ervin 1958; Jorgensen *et al* 1959; Adamsky 1959; Pultz 1967; Kurycheva and Bresker 1969) used powdered silicon carbide. Hinze *et al* (1975) and Singhal (1976) used commercially available hot-pressed material and studied oxidation in oxygen atmosphere. Costello and Tressler (1981) studied the oxidation kinetics of sintered and hot-pressed silicon carbide in air. Schiroky (1987) reported the oxidation behaviour of chemically vapour-deposited silicon carbide. However, oxidation of reaction-sintered silicon carbide has been the subject of very few investigations. Recently, Gogotsi *et al* (1989) reported the oxidation of reaction-sintered silicon carbide. In this paper, oxidation of reaction-sintered silicon carbide in the temperature range 1200–1350°C in air has been reported.

2. Experimental

2.1 *Material*

Reaction-sintered silicon carbide (RSSC) was prepared in our laboratory from commercial α-SiC powder of 400-mesh grit size. The powdered material contains $98.20\,wt\%$ SiC, $0.25\,wt\%$ free C, $0.4\,wt\%$ free Si, $0.5\,wt\%$ SiO_2 and $0.04\,wt\%$ Fe_2O_3. The material to be studied has a bulk density of $3.00\,g/cm^3$. Unreacted Si content, as measured by XRD as well as from density calculation, was found to be 22.5%. SEM (figure 1) reveals that the duplex material consists of original α-SiC, reaction-formed β-SiC, and an almost continuous matrix of unreacted Si.
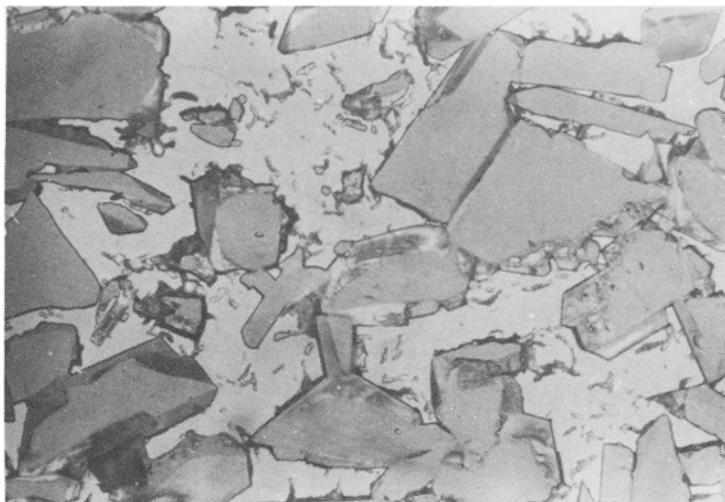
Figure 1. Optical micrograph of reaction sintered silicon carbide (× 450).

2.2 *Experimental procedure*

An electronic continuously recording microbalance capable of working under vacuum or under a controlled atmosphere and reading up to 0·01 mg and a platinum wound furnace wherein the temperature could be controlled within ± 1°C with the help of a saturable core reactor-type controller were used. Oxidation runs were made by binding sample chips with a platinum wire, avoiding direct contact between the sample and the platinum wire by passing the wire through several small Al_2O_3 sheath pieces. The entire binding assembly weighed 1·7552 g. The samples were taken in the form of chips of dimensions 20 mm × 15 mm × 1 mm cut from the RSSC billets. The samples were polished up to 1 μm diamond paste finish. The polished and cleaned specimen was suspended from one end of the electrobalance and held inside an Al_2O_3 reaction tube at the desired temperature (1200–1350°C). Changes in the weight of the specimen were continuously recorded on a strip chart recorder.

3. Results and discussion

The weight gain recorded was converted to weight gain per unit area and plotted against time (figure 2). All the curves show similar trends. After initial oxidation the weight-gain curves flatten out, showing protective action of the oxide layer formed. The maximum weight gain is 0·2530 mg/cm² at 1300°C after 15 h. The weight-gain data for the entire temperature range are found to fit best a parabolic reaction rate curve of the type $w^2 = kt$, where w is the weight gain per unit area, k the constant, and t time. A plot of w against corresponding $\sqrt{t}$ is shown in figure 3. The plot is a straight line for a given temperature and the slope of the straight line gives the value of k. The activation energy for oxidation is calculated from the Arrhenius equation $k = Ae^{-E/RT}$, where A is the pre-exponential factor independent of temperature, E the activation energy, and R and T the gas constant and absolute
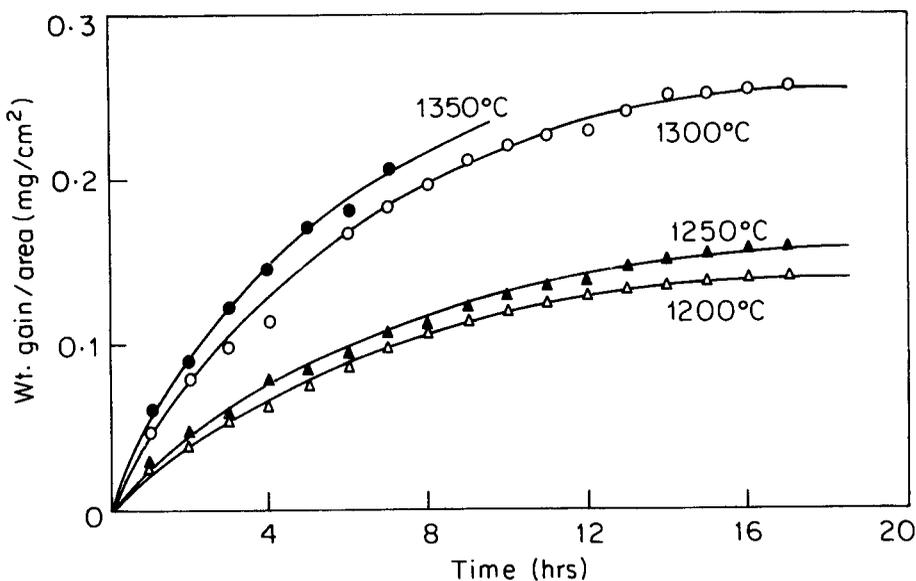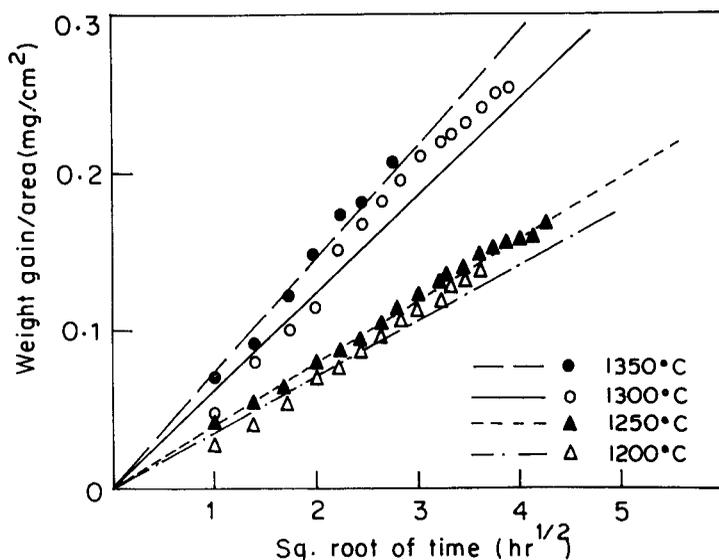
Figure 2. Oxidation weight gain vs time.

Figure 3. Oxidation weight gain vs time$^{1/2}$.

temperature. The Arrhenius plot of $\ln k$ against $1/T$ is shown in figure 4. All the points, corresponding to individual test temperatures, fit to a straight line where the gradient of the line gives the value of the activation energy. The value here is 28.75 ± 2.61 kcal/mol.

For silicon it is widely accepted that diatomic oxygen diffuses through the growing oxide film and controls the rate of oxidation (Deal and Grove 1965; Hopper *et al* 1975). Activation energy for oxidation of silicon agrees very well with the activation
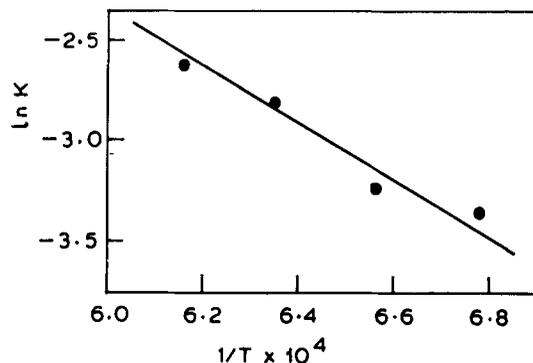
Figure 4. Plot of ln k vs $1/T$.

energy of 113 kJ/mol (26·9 kcal/mol) for molecular oxygen through fused silica (Norton 1961). At low temperatures, activation energies of sintered and hot-pressed silicon carbide are found to be 134 kJ/mol (31·9 kcal/mol) and 155 kJ/mol (36·9 kcal/mol) respectively (Costello and Tressler 1981), whereas at high temperatures high values are obtained (Singhal 1976; Costello and Tressler 1981). This suggests that inward diffusion of oxygen molecules may be responsible for oxidation of silicon carbide at low temperature, similar to the process occurring in the case of oxidation of silicon. But at high temperatures high activation energy indicates that oxygen transport mechanism is most unlikely and, alternatively, it has been concluded that outward desorption of CO(g) from SiC/SiO_2 interface is the rate-controlling process. As our material is duplex in nature, containing original α-SiC, reaction-formed β-SiC, and an almost continuous matrix of unreacted Si, the present result suggests that both Si and SiC oxidize and the oxidation process occurs by the inward oxygen transport mechanism. The CO desorption which is favoured in case of high-temperature oxidation of silicon carbide may not be rate-controlling.

4. Conclusion

(i) Parabolic oxidation kinetics are observed in case of oxidation of reaction-sintered silicon carbide.

(ii) The maximum weight gain is 0·2530 mg/cm^2 at 1300°C for 15 h. It indicates that the amount of scale formation is very negligible during the end-use condition of the reaction-sintered silicon carbide.

(iii) The activation energy for oxidation is found to be 28·75 ± 2·61 kcal/mol.

(iv) Inward oxygen diffusion through the oxide film is most favoured.

Acknowledgements

References

Adamsky R F 1959 *J. Phys. Chem.* **63** 305

Costello J A and Tressler R E 1981 *J. Am. Ceram. Soc.* **64** 327

Deal B E and Grove A S 1965 *J. Appl. Phys.* **36** 770

Ervin G 1958 *J. Am. Ceram. Soc.* **41** 347

Gogotsi G A, Gogotsi Yu G, Ostrovoi D Tu and Ivaschenko O V 1989 *Refractories* **30** 84

Hinze J W, Tripp W C and Graham H C 1975 *Mass transport phenomena in ceramics* (eds) A R Cooper and A E Heuer (New York: Plenum Press) p. 409

Hopper M A, Clarke R A and Young L 1975 *J. Electrochem. Soc.* **122** 1216

Jorgensen P J, Wadsworth M S and Cutler I B 1959 *J. Am. Ceram. Soc.* **42** 613

Kurycheva D D and Bresker R I 1969 *Ogneupory* **34** 57

Norton F J 1961 *Nature (London)* **191** 701

Pultz W W 1967 *J. Phys. Chem.* **71** 4456

Schiroky G H 1987 *Adv. Ceram. Mater.* **2** 137

Singhal S C 1976 *J. Mater. Sci.* **11** 1246