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Preparation of SiC–C composite fibre by carbothermic reduction of silica

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The SiC-coated carbon fibre (SiC–C composite fibre) was prepared by the carbothermic reduction of silica. The composite fibre was examined by X-ray diffraction, scanning electromicroscopy and chemical analysis. Thermogravimetry was used to determine the reduction rate of silica, and the formation mechanism of the SiC film was revealed by a kinetic study. The oxidation resistance of the composite fibre was evaluated by heating in an oxygen gas stream.

1. Introduction

Carbon fibre exhibits a very poor oxidation resistance even at temperatures as low as 700 K, although it has many advantages, such as low specific weight, and excellent mechanical strength at elevated temperatures. Consequently, its applications as a high-temperature material have been mostly limited to a non-oxidizing atmosphere.

Effective oxidation protection for carbon fibre at higher temperatures must be developed. Two approaches have been presented to protect carbon from oxidizing: (1) the use of inhibitors to slow down the oxidation rate of carbon, and (2) the use of barriers to the diffusion of oxygen [1–12]. P_2O_5 and B_2O_3 have been found to be effective as inhibitors in reducing the rate of oxidation by blocking the active sites on the carbon surface. On the other hand, ceramic coatings are known to be a barrier to the oxidation of carbon. SiC has often been used as the coating material. These coatings are made by reaction of the surface carbon with silicon [1], chemical vapour deposition [11], and impregnation of silicone resin [12].

In the present work, the phenolic resin-based carbon fibres were coated with an SiC layer, prepared by the carbothermic reduction of silica. A kinetic study was carried out in order to clarify the reaction mechanism and to optimize the SiC layer as a barrier to oxygen. In particular, the effects of temperature and silica/carbon fibre ratio on the kinetics were investigated in detail. Furthermore, the fibre was heated under an oxygen atmosphere for the purpose of evaluating its oxidation resistance at elevated temperature.

2. Experimental procedure

The thermobalance unit used for thermogravimetry (TG) is composed from an analogue type automatic recording balance and a carbon resistance furnace or an SiC resistance furnace. In order to clarify the preparation mechanism of the carbon fibre coated with SiC (the SiC–C composite fibre) and to evaluate the oxidation resistance of the fibre, two types of experiment were carried out.

2.1. Experiment A (preparation of SiC–C composite fibre)

Carbon fibre was prepared from chop-like phenolic resin fibre (Kynol Fibre, mean diameter 20 μm, mean length 200 μm; Japan Kynol Co.). Kynol fibre was heated continuously at 10 K min^{-1} and held at 1273 K for 7.2 ks. The silica powder was silicic anhydride (mean particle size 143 μm, Wako Pure Chemical Industries Ltd). Carbon fibres were thoroughly mixed with silica powders in the desired molar ratio.

The experimental temperature was measured with a Pt–6% Rh/Pt–30% Rh thermocouple positioned close to the sample in the carbon resistance furnace. Argon was flowed from the bottom of the furnace at 2.5×10^{-5} m^3 s^{-1}. A 2 g sample was charged in a graphite crucible of 26 mm inner diameter and 50 mm depth. The graphite crucible was suspended in the hot zone of a furnace with a graphite rod and a stainless steel wire attached to the balance. The mass loss was recorded automatically during each experiment.

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2.2. Experiment B (oxidation of SiC–C composite fibre)

SiC–C composite fibre samples, prepared by the above method, were used. A sample of 0.5 g was charged in a magnesia crucible of 26 mm inner diameter and 35 mm depth. The magnesia crucible was suspended in the SiC resistance furnace (alumina reaction tube of 44 mm inner diameter) with an alumina rod and a platinum wire attached to the balance. The mass change was recorded automatically by heating continuously at 3 K min^{-1} up to 1573 K in an oxygen stream at 8.8×10^{-6} m^3 s^{-1}.

Upon completion of the TG measurement for experiments A and B, the sample was cooled rapidly by raising the crucible to the low-temperature zone of the furnace. The reaction products were examined by both X-ray diffraction and chemical analysis, and the morphology of the fibre was observed by scanning electron microscopy.

3. Results

3.1. Preparation of SiC–C composite fibre

Fig. 1 shows TG curves for carbon fibre–SiO_2 mixtures with carbon to SiO_2 molar ratios of 3:1 ($n_C/n_{SiO_2} = 3$) heated at various temperatures. Fig. 2 shows TG curves for carbon fibre–SiO_2 mixtures with different n_C/n_{SiO_2} at 1923 K. W_0 and ΔW are the initial mass of the carbon fibre–SiO_2 mixture and the mass loss measured by a thermobalance, respectively. A gradual decay of the reaction rate is observed. The mass loss is due to the evolution of both SiO and CO. As shown later, the SiO/CO ratio varies with the reaction temperature and the carbon to silica molar ratio, and even with the reaction time. Therefore, an estimate of the rate of the reaction between carbon and SiO_2 cannot be made from TG alone. In particular, the carbothermic reduction of silica at $n_C/n_{SiO_2} = 1$ indicates a vigorous decrease in a mass, because the reduction product is almost pure SiO.

Fig. 3 shows XRD patterns of carbon fibre–SiO_2 mixtures with $n_C/n_{SiO_2} = 3$ heated at temperatures from 1773–1973 K. Silica powders as starting material are crystalline quartz, whereas the Kynol-based carbon fibre is amorphous. On heating at high temperatures, quartz transforms to cristobalite. Large amounts of unreacted silica are retained below 1923 K. At 1973 K, peaks of unreacted silica weaken while peaks of β-SiC become sharper. The diffraction pattern of carbon is noticed only faintly, although free carbon is significantly retained in samples, as shown later in Fig. 9. This is because the carbon fibre is completely surrounded by β-SiC.

3.2. Oxidation of SiC–C composite fibre

Fig. 4 shows examples of the mass changes of Kynol-derived carbon fibre and SiC–C composite fibres heated continuously at 3 K min^{-1} in oxygen. Carbon fibre was prepared by firing Kynol at 1273 K for 7.2 ks. W_{FC}^i and ΔW are the initial mass of free carbon in SiC–C composite fibre and the mass change determined by a thermobalance, respectively. W_{FC}^i can be calculated by a method described later. The large mass loss observed below 1200 K is due to the oxidation of the unreacted core (free carbon) of SiC–C composite fibre. Therefore, the mass gain above 1300 K arises from the oxidation of the SiC film. Thus, below 1200 K, $100(\Delta W/W_{FC}^i)$ corresponds to the oxidised fraction of free carbon in SiC–C composite fibre. Kynol-based carbon fibres are oxidized rapidly at 680 K and are lost entirely at 750 K. The composite fibres, which were prepared by carbothermic reduction for 18 ks at 1923 K and 10.8 ks at 1973 K, retain 62% and 82% of free carbon, respectively. In particular, there is no further mass loss in the latter fibre at 1000 K. This suggests that only a part of the fibre, which was not coated with SiC film because of insufficient mixing of carbon fibre with silica powder, was oxidized. On the other hand, more than 80% free

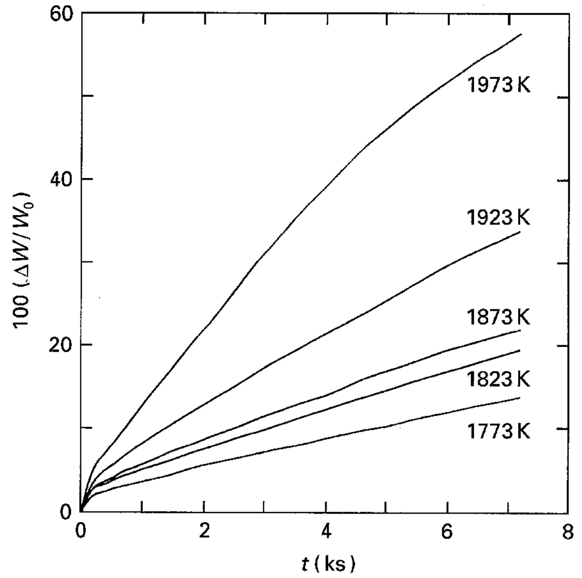

Figure 1 TG curves of SiO_2–carbon fibre mixture with $n_C/n_{SiO_2} = 3$ heated at various temperatures.

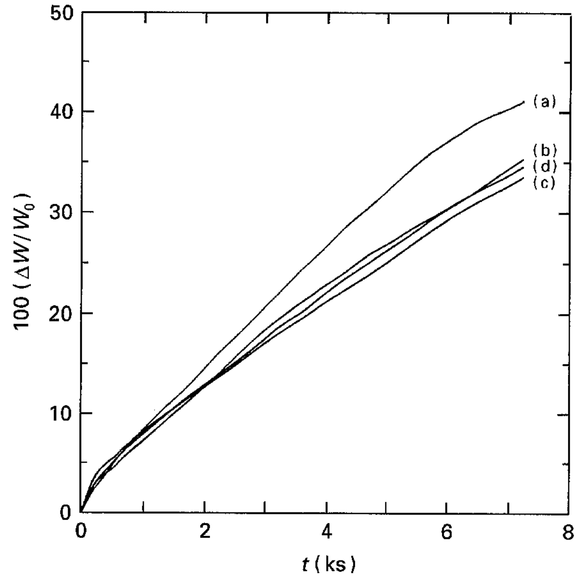

Figure 2 TG curves of SiO_2–carbon fibre mixtures with various n_C/n_{SiO_2} heated at 1923 K: SiO_2 to C: (a) 1 to 1, (b) 1 to 2, (c) 1 to 3, (d) 1 to 5.

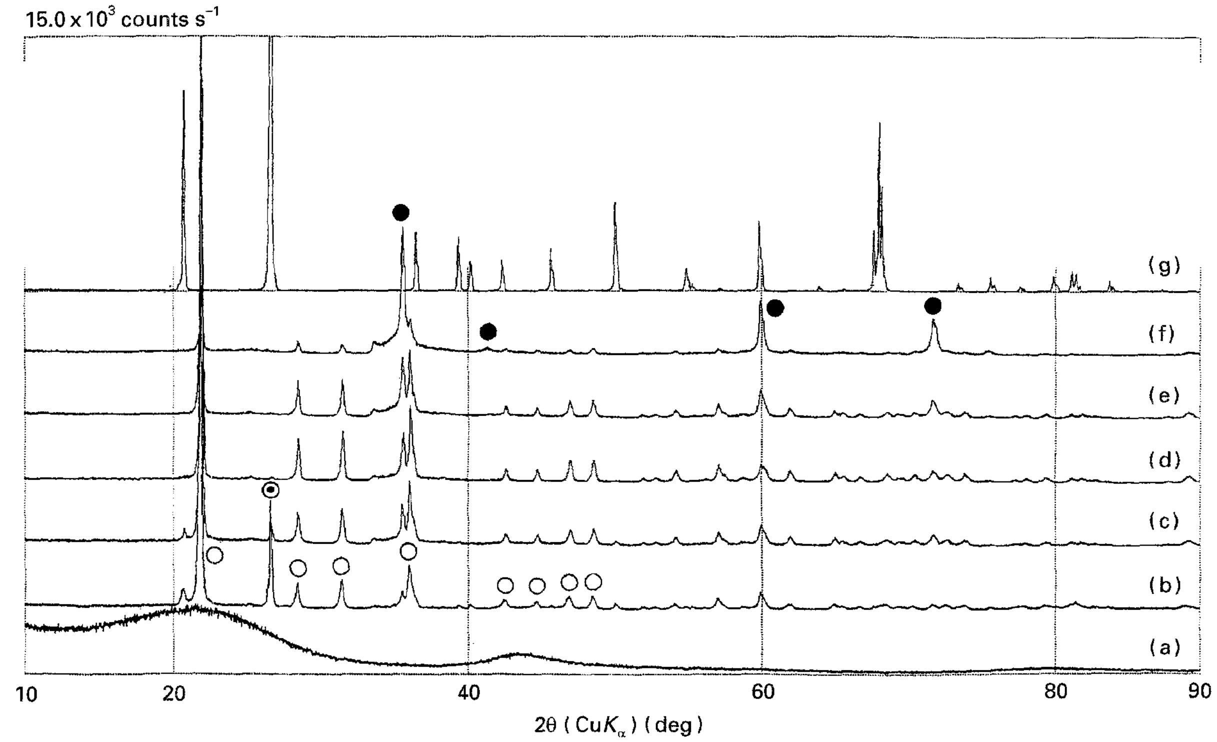

Figure 3 X-ray diffraction patterns of (a) carbon fibre and SiO_2–carbon fibre mixtures heated at (b) 1773 K, (c) 1823 K, (d) 1873 K, (e) 1923 K and (f) 1973 K, and (g) quartz powder. (○, ⊙, ●) Cristobalite, graphite and β-SiC, respectively.

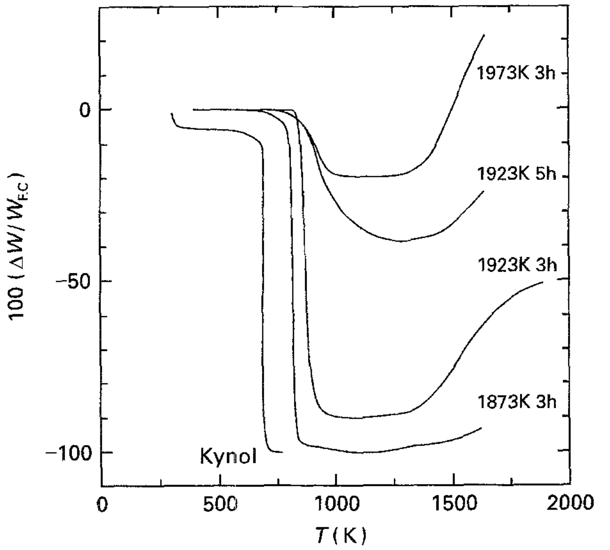

Figure 4 TG curves of SiC–C composite fibre heated continuously in an oxygen stream.

carbon is oxidized from all the other composite fibres. Fig. 5 indicates the morphologies of the surface and the cross-section of as-oxidized SiC–C composite fibre. The core of the composite fibres, which exhibited a great loss of mass during oxidation, was nearly all lost (a, b, e, f). Oxygen readily permeated the carbon core, because of the imperfect SiC coating (a, b) and the coarsened SiC crystals (e, f). Thus, all oxidizable carbon has been removed from within the composite fibre, leaving a hollow SiC shell. On the other hand, almost all of the carbon core remained in the composite fibres, which were perfectly coated with fine crystals (c, d).

4. Discussion

4.1. Reaction products

The formation of SiC by the carbothermic reduction of silica is given by the overall reaction

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g) \quad (1)$$

SiC is formed by the gas-phase reaction rather than the solid-phase reaction. At high temperatures, silicon monoxide is readily formed by the reduction of silica with carbon

$$SiO_2(s) + C(s) = SiO(g) + CO(g) \quad (2)$$

A part of the SiO gas reacts with carbon to produce SiC

$$SiO(g) + 2C(s) = SiC(s) + CO(g) \quad (3)$$

and the remainder of the SiO evaporates outwards as it is. Reaction 1 is interpreted as being due to a combination of Reactions 2 and 3.

The following relations are obtained from both the material balance of SiO_2 and the stoichiometry of reactions

$$W_{SiO_2{}^i} = W_{SiO_2(1)} + W_{SiO_2(2)} + W_{SiO_2(3)} \quad (4)$$

$$\Delta W = W_{SiO_2(1)}(2M_{CO}/M_{SiO_2}) + W_{SiO_2(2)}[(M_{SiO} + M_{CO})/M_{SiO_2}] \quad (5)$$

$$\%SiC = 100[W_{SiO_2(1)}(M_{SiC}/M_{SiO_2})]/W^f \quad (6)$$

where $W_{SiO_2{}^i}$ is the mass of SiO_2 in the initial sample, $W_{SiO_2(1)}$ the mass of SiO_2 converted into SiC, $W_{SiO_2(2)}$ the mass of SiO_2 converted into SiO, $W_{SiO_2(3)}$ the mass of SiO_2 unreacted, M_i the molecular weight of component i, %SiC the analytical value of SiC in the final sample, and W^f the mass of the final sample (solid residues). Substituting the numerical

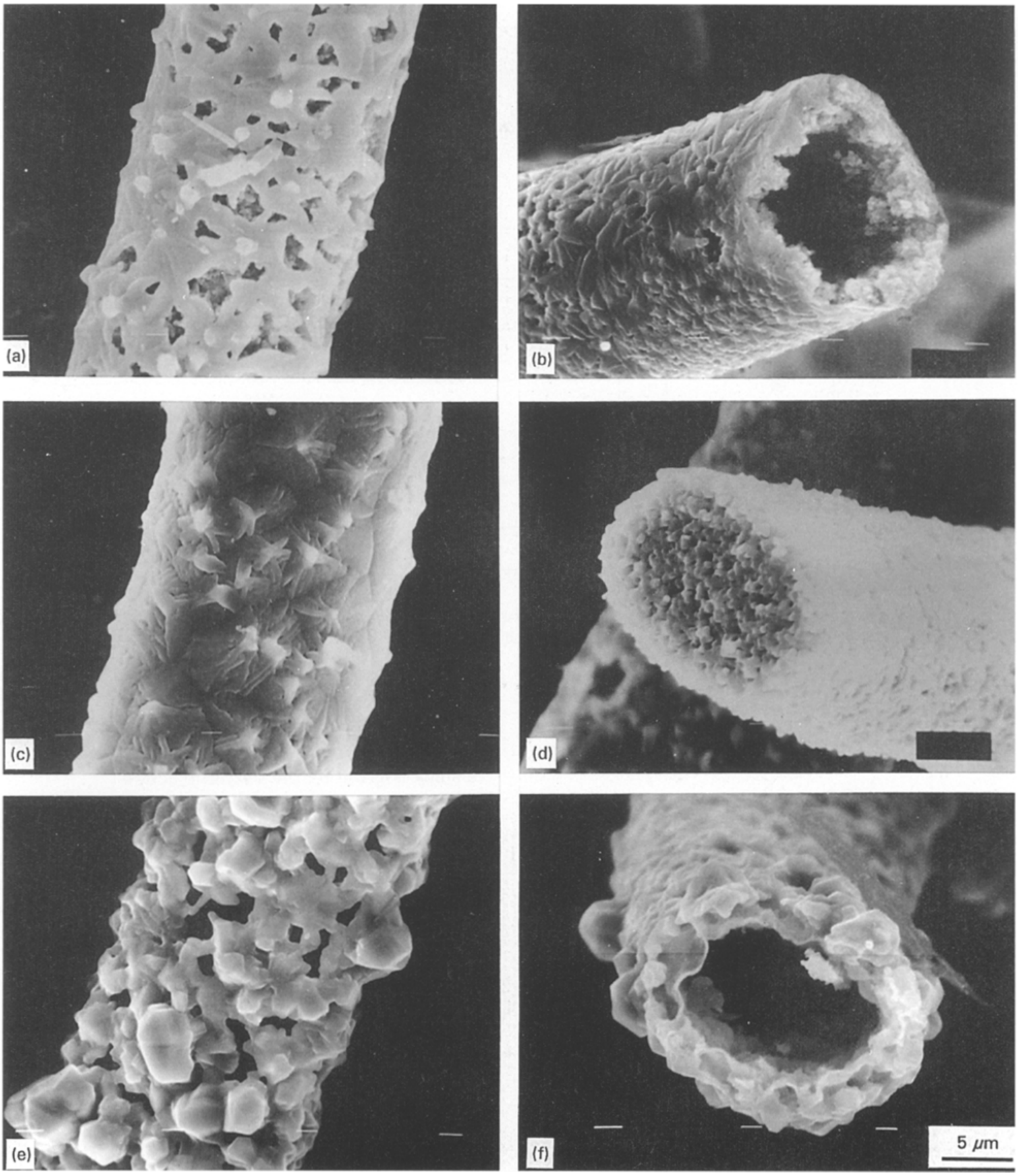

Figure 5 Scanning electron micrographs of SiC–C composite fibre heated continuously in an oxygen stream. (a, b) Fibre prepared at 1873 K for 3 h, (c, d) fibre prepared at 1973 K for 3 h, (e, f) fibre prepared at 1973 K for 4 h.

values of $W^{i}_{SiO_2}$, %SiC and W^{f} in Equations 4, 5, and 6, the values of $W_{SiO_2(1)}$, $W_{SiO_2(2)}$ and $W_{SiO_2(3)}$ are obtained.

Fig. 6 indicates the mole fractions of SiC, SiO and retained silica as a function of the carbothermic reduction temperature. The mole fraction of SiC increases monotonically with an increase in temperature. On the other hand, the mole fraction of SiO decreases with increasing temperature up to 1923 K, but increases at 1973 K.

Fig. 7 indicates the relationship between the mole fraction of SiC, SiO and retained SiO_2 and the molar ratio n_C/n_{SiO_2}. SiO evaporates significantly from the mixture with $n_C/n_{SiO_2} = 1$. The amount of SiO decreases remarkably with increasing n_C/n_{SiO_2}, and in the mixture with $n_C/n_{SiO_2} = 5$, nearly all SiO_2 converts into SiC.

At 1923 K and $n_C/n_{SiO_2} = 3$, the plots of the mole fraction of SiC, SiO and retained SiO_2 versus time are as shown in Fig. 8. On prolonged heating, SiC decreases slightly. This suggests that the following overall reaction proceeds between SiO_2 particles and the SiC layer and that the SiC layer cannot grow over a definite thickness

$$SiC(s) + 2SiO_2(s) = 3SiO(g) + CO(g) \qquad (7)$$

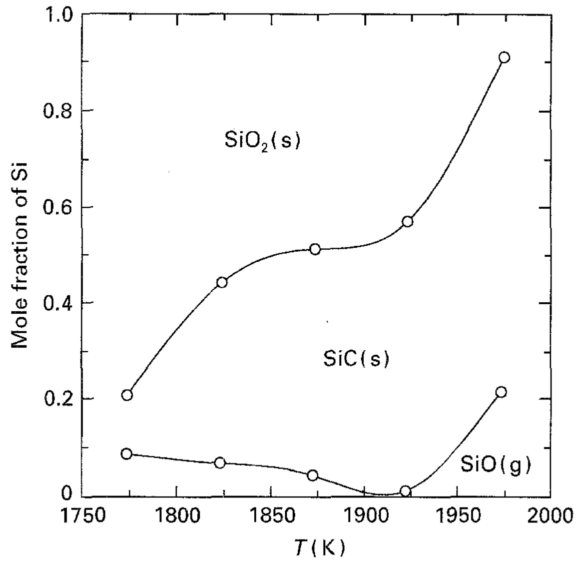

Figure 6 Relation between the mole fraction of reaction products and temperature ($n_C/n_{SiO_2} = 3$, 10.8 ks).

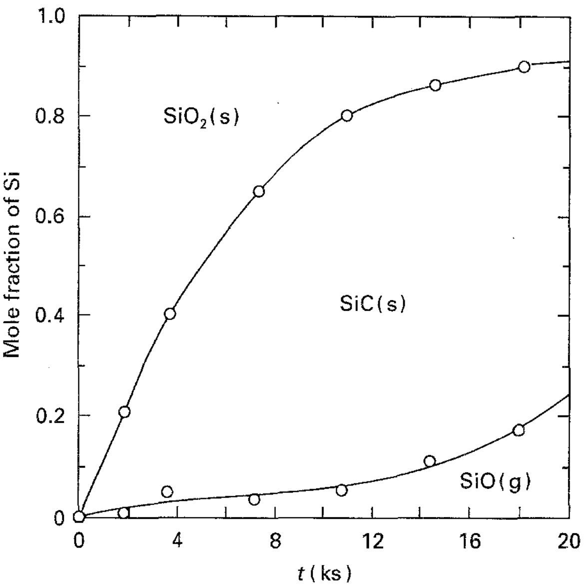

Figure 8 Relation between mole fraction of reaction products and time ($n_C/n_{SiO_2} = 3$, 1923 K).

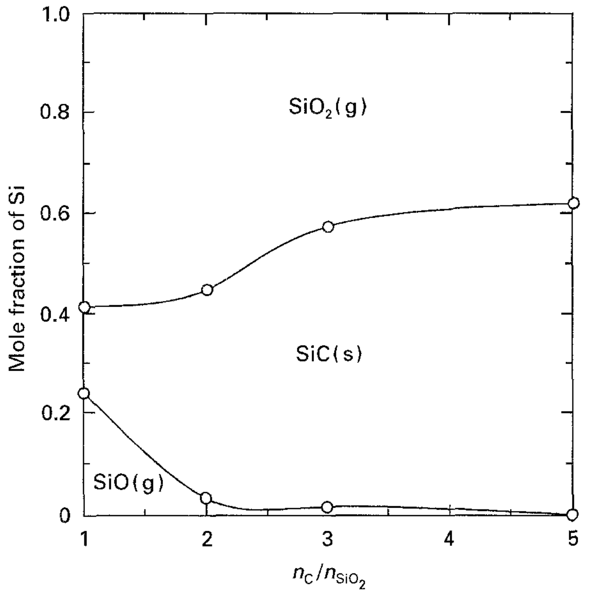

Figure 7 Relation between mole fraction of reaction products and n_C/n_{SiO_2} (1923 K, 10.8 ks).

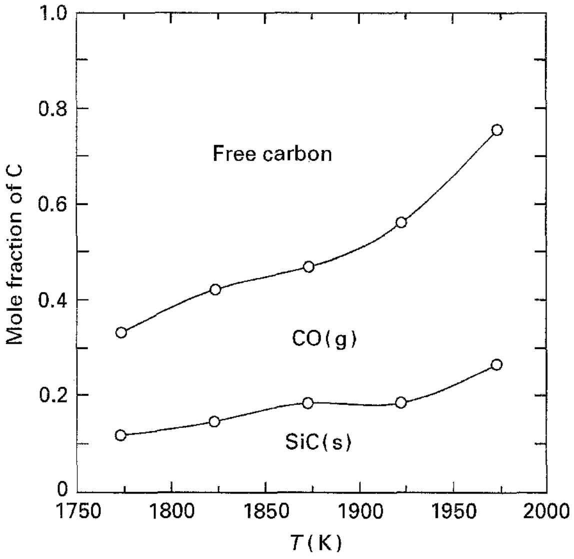

Figure 9 Mole fraction of carbon fibre converted to SiC and CO ($n_C/n_{SiO_2} = 3$, 10.8 ks).

The carbothermic reduction of SiO_2 converts carbon into SiC and CO. Then the unreacted carbon is retained as free carbon in the core of the composite fibres. Fig. 9 shows the variation of the mole fraction of carbon as SiC, CO and free carbon with reaction temperature. Naturally, both SiC and CO increase and free carbon decreases with increasing temperature. Significant amounts of unreacted carbon are still retained after reduction at 1973 K. However, carbon could not be detected by X-ray diffraction, because it was thickly coated with SiC.

4.2. Reaction mechanism and kinetic analysis

In previous reports [13–16], SiC powders were prepared by the carbothermic reduction of silica using SiO_2–C powder mixtures and the reaction mechanism was investigated in detail. The solid-state Reaction 1 initiates at the contact points between SiO_2 and carbon. Once both SiO and CO are formed, the reactions proceed at the surfaces of both SiO_2 and carbon particles via the gas phase

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) \quad (8)$$

$$2C(s) + SiO(g) = SiC(s) + CO(g) \quad (9)$$

$$C(s) + CO_2(g) = 2CO(g) \quad (10)$$

It was found that silica particles were consumed and carbon particles were coated with SiC. The formation of SiC was considered to be controlled by the chemical process at the surface of the carbon particles in the early stages and by solid-state diffusion through the SiC layer to the interface between SiC and unreacted carbon in the later stages [13–16].

As can be seen from Fig. 5, the SiC layer is formed around the cylindrical carbon fibre. Therefore, the preparation mechanism of SiC–C composite fibres will be similar to that of SiC particles. The reaction interface recedes towards the centre of the fibre as SiC is produced. Consequently, the kinetics is considered to follow the contracting-disc formula for chemical control in the early stages and for diffusion control in the later stages [17] respectively

$$(1 - X)^{1/2} = k_r t \qquad (11)$$

and

$$(1 - X)\ln(1 - X) + X = k_d t \qquad (12)$$

where k_r and k_d are the rate constants, and X is the reacted fraction of carbon fibre.

The carbothermic reduction was interrupted at given time intervals, and the retained free carbon was determined by chemical analysis. Thus, X was obtained from the mass ratio of retained carbon to carbon in the initial sample. Fig. 10 indicates that ΔW is approximately proportional to X within 10.8 ks. At 14.4 ks and longer, the deviation from a linear relation is due to the occurrence of Reaction 7. Because all the kinetic data shown in Fig. 1 are within 7.2 ks, X can be calculated from the following equation

$$X = (1 - W_C^f/W_C^i) \cdot (\Delta W/W^f) \qquad (13)$$

where W_C^f is the mass of free carbon in the final sample ($W_C^f = \%C^f \times 10^{-2} W^f$; $\%C^f$ is the analytical value of free carbon in the final sample), W_C^i is the mass of carbon in the initial sample, and ΔW^f is the final mass loss measured using a thermobalance.

Application of the rate equations to the kinetic data is shown in Figs 11 and 12. The plots satisfy Equation 11 in the initial stages and Equation 12 in later stages of the reaction. This result indicates that the rate-determining step shifts from the interfacial reaction to solid-state diffusion when the carbon fibre was completely coated with SiC.

Fig. 13 shows Arrhenius plots for the rate constants k_r and k_d. The apparent activation energies are

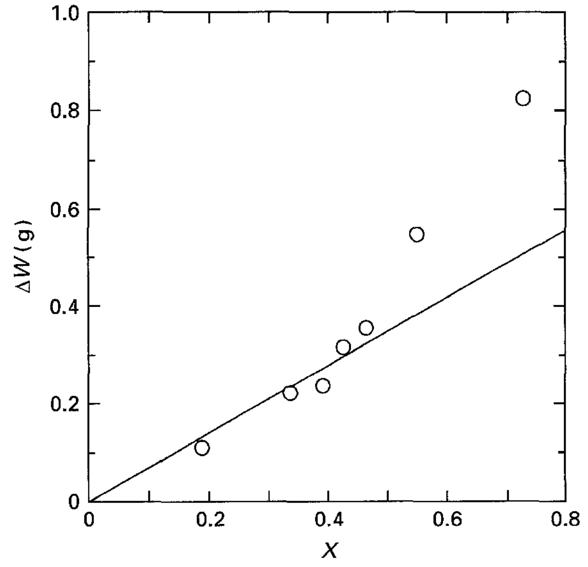

Figure 10 Relation between mass loss and reacted fraction of carbon fibre ($n_C/n_{SiO_2} = 3$, 1923 K).

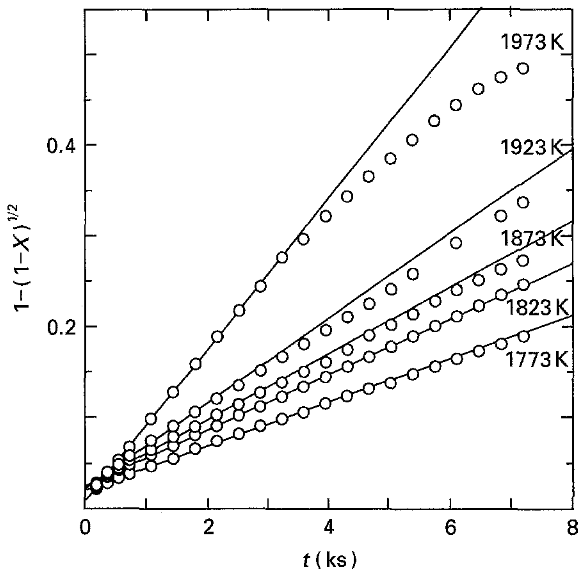

Figure 11 Plots of $1 - (1 - X)^{1/2}$ versus time ($n_C/n_{SiO_2} = 3$).

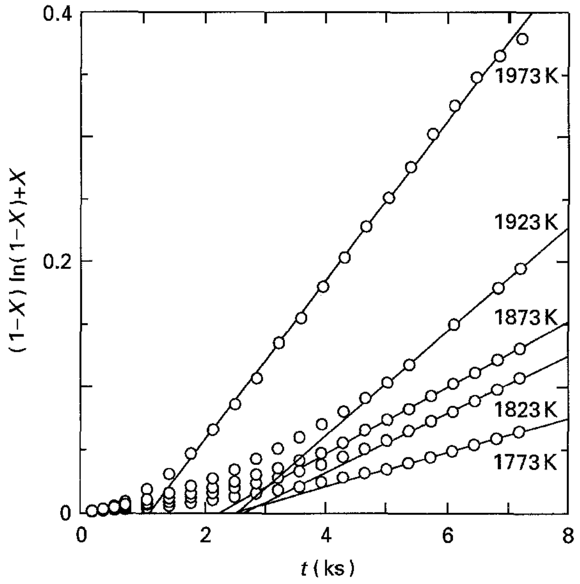

Figure 12 Plots of $(1 - X)\ln(1 - X) + X$ versus time ($n_C/n_{SiO_2} = 3$).

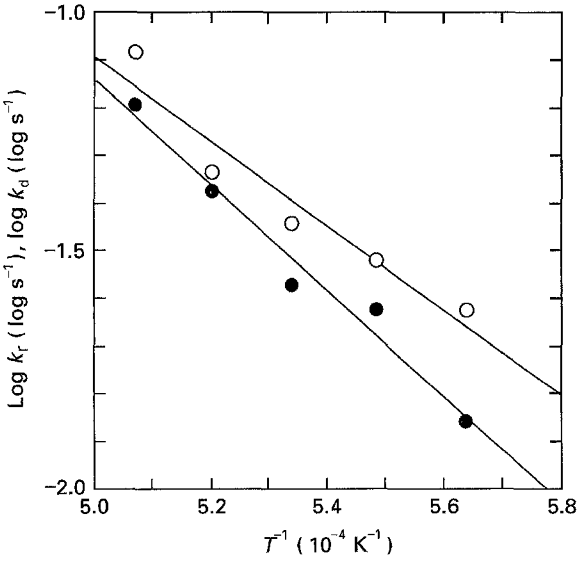

Figure 13 Arrhenius plots for rate constants (○) k_r and (●) k_d.

168 kJ mol^{-1} for reaction control and 210 kJ mol^{-1} for diffusion control. These values are much smaller than the activation energies for preparation of SiC from SiO_2-graphite powder mixture [13, 14, 16]. This may be attributed to the difference in reactivity and porosity of the carbonaceous materials employed. Obviously, the different reactivity can be reflected in the different activation energies for reaction control. On the other hand, the different porosity leads to different activation energies for diffusion control, as described below.

The carbon fibre has a very large porosity compared to graphite. Therefore, SiC film on the former was considered to be more porous than that on the latter. Consequently, the SiO_2–carbon fibre reaction is followed by gaseous diffusion through pores in SiC and the reaction at the interface between SiC and unreacted carbon, while the SiO_2–graphite reaction is followed by reaction at the surface of SiC and solid-state diffusion through the dense SiC film. The activation energy for the gaseous diffusion should be smaller than that for the solid-state diffusion.

4.3. Oxidation resistance of C–SiC composite fibre

When SiC particles were prepared by the carbothermic reduction of SiO_2, carbon remained in the core [16]. The gas permeability of the SiC film may be dependent on the density of carbon as a raw material. Previously, SiC particles were prepared from a graphite–SiO_2 [13] and carbon black–SiO_2 [15] mixtures. Carbon black is more dense than graphite, therefore, the unreacted carbon could hardly be removed from the carbon black-derived SiC by the oxidation treatment, although it could be significantly removed from the graphite-derived SiC. Because of the high porosity of the phenolic resin-based carbon fibre employed in the present work, the SiC film is also considered to be porous. As shown in Fig. 4, the oxidation of the C–SiC composite fibres resulted in the decrease in a mass at temperatures from 700–1300 K. Furthermore, compared to the oxidation of the uncoated carbon fibre, oxidation of all the composite fibres was initiated at higher temperatures, apparently because the oxygen diffuses inwardly through pores in the SiC film to oxidize the carbon fibre in the core. Therefore, thickening in the SiC film will be effective in retarding the oxidation of the core, because of extending the diffusion distance of oxygen. The mean depth, d, of the SiC layer can be approximately estimated from the following equation

$$d = r_0[1 - (1 - X)^{1/2}] \qquad (14)$$

where r_0 is the initial mean radius of the carbon fibre (~ 10 µm). Fig. 14 shows the relationship between the maximum oxidized fraction of free carbon, $100(\Delta W_{\max}/W_{\mathrm{F\cdot C'}})$ and d. The value of d increases with increasing duration and temperature of the preparation of the C–SiC composite fibre. Below 4 µm depth, an increase of d tends to improve the oxidation resistance of the composite fibre. The composite fibre (c) at 3.6 µm depth retained about 60% free carbon. Fibre (d) showed excellent oxidation resistance, despite the thin SiC layer of 3.3 µm. However, in the other composite fibres, 70% or more free carbon was oxidized. In particular, composite fibre (h) which was prepared from the mixture with n_C/n_{SiO_2} ratio of 2, was oxidized severely, although it had a thick SiC film of 5.7 µm. Furthermore, it was noted that fibre (g) had a poor oxidation resistance. This was because the prolonged heating at elevated temperature led to a high permeability of the SiC film to gas, as a result of the coarsening of β-SiC crystals (Fig. 5e, f). Thus, compared to increasing thickness of the SiC film, its densification is much more effective in inhibiting the oxidation of the carbon fibre.

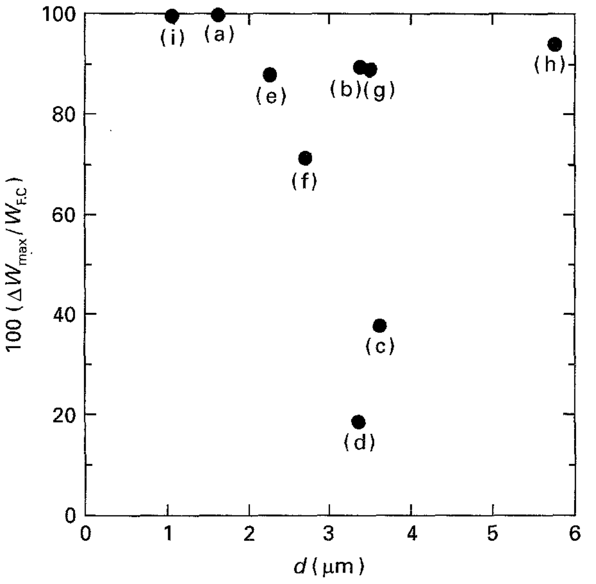

Figure 14 Relation between maximum oxidized fraction of free carbon in SiC–C composite fibre and depth of SiC layer. (a) $n_C/n_{SiO_2} = 3$, 1873 K, 3 h; (b) $n_C/n_{SiO_2} = 3$, 1923 K, 3 h; (c) $n_C/n_{SiO_2} = 3$, 1923 K, 5 h; (d) $n_C/n_{SiO_2} = 3$, 1973 K, 3 h; (e) $n_C/n_{SiO_2} = 3$, 1973 K, 1 h; (f) $n_C/n_{SiO_2} = 3$, 1973 K, 2 h; (g) $n_C/n_{SiO_2} = 3$, 1973 K, 4 h; (h) $n_C/n_{SiO_2} = 1$, 1923 K, 3 h; (i) $n_C/n_{SiO_2} = 5$, 1923 K, 3 h.

5. Conclusions

1. From mixtures of phenolic resin-based carbon fibre with silica particles, SiC–C composite fibres were prepared by the carbothermic reduction of silica, and then their oxidation resistance was evaluated.

2. Mole fractions of SiC and SiO produced by carbothermic reduction were correlated with reduction temperature and molar ratio, n_C/n_{SiO_2}. The yield of SiC increased with increasing temperature and n_C/n_{SiO_2}.

3. The SiC film grew towards the centre of the fibre. The formation of SiC is considered to be controlled by the chemical reaction on the carbon fibre in the initial stages and by the gaseous diffusion through the SiC film in later stages.

4. A perfect SiC coating is necessary for the inhibition of the oxidation of the composite fibre. However, prolonged heating at high temperatures was harmful to the oxidation resistance because of the coarsening of SiC crystals. The composite fibre prepared from the mixture with $n_C/n_{SiO_2} = 3$ at 1973 K for 10.8 ks exhibited excellent oxidation resistance.

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