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Oxidation resistance of carbon–ceramics composite materials sintered from ground powder mixtures of raw coke and ceramics

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Carbon–SiC–B_4C composite materials were prepared from ground powder mixtures of petroleum raw coke, SiC and B_4C by powder sintering, without the use of any special binder and hot-pressing process. Dense composites with a fine microtexture were obtained. Oxidation tests were carried out on the composites at temperatures from 1000 to 1300° C under an air flow. The oxidation resistance depended strongly on the SiC/(SiC + B_4C) ratio and total contents of SiC and B_4C in the composites, which determined the compositions of B_2O_3 and SiO_2 in the protective film formed at the surface of the composite block during oxidation. In optimum ratios, from 63 to 87%, the composites showed such a high oxidation resistance that they were comparable with Si_3N_4 at 1200° C.

1. Introduction

Carbon materials are widely used for engineering materials: electrodes in the metallurgical industries, moderator and structural materials in the nuclear industry, etc., and recently in more specialized parts such as rocket nozzles and high-temperature heat exchangers. The carbon materials, however, have essential disadvantages in properties such as high porosity, low mechanical strength and a low degree of oxidation resistance at high temperatures. Carbon–ceramic composites have been expected to be able to improve on these disadvantages of carbons. For instance, C–B_4C composites made by hot-pressing show a high bending strength reaching to 200 MPa [1, 2]. C–ZrB_2 composites made by the use of a binder pitch show a certain degree of resistance to corrosion in air flow even at temperatures around 2500° C [3]. With composites of carbon and carbide, that is, C–ZrC [4, 5], C–NbC [6] and C–MoC [7], an improvement either in mechanical strength, elastic behaviour or thermal conductivity has been observed.

However, the carbon–ceramic composites have not yet received practical applications. One of the reasons for this is probably that there is no established preparation technique suitable for mass-production of the dense composites. This is mainly caused by the weak sinterability of carbons and most refractory ceramic powders. In this essential problem, we have reported the fact that raw coke can be used as a carbon precursor for the composites if it is subjected to prolonged grinding, and dense carbon bodies were obtained from the ground raw coke by powder sintering without the use of a special binder and hot-pressing process [8]. This mechanochemical effect on sinterability occurred in powder mixtures of raw coke and ceramics such as SiC and B_4C [9–11].

On the other hand, C–B_4C composites have been reported to show a good oxidation resistance, which is one of the most important problems with a view to improving the disadvantages of carbons [1, 2]. In these composites, the improvement of oxidation resistance was supposed to be caused by the formation of a B_2O_3 protective film. If the film properties are improved by a new addition of ceramic to the composite, it results in still further improving the oxidation resistance. In this study, the oxidation resistance was examined for C–SiC–B_4C composites made by using ground raw coke as a carbon precursor.

2. Experimental procedure

The raw materials used for preparation of the composites were petroleum raw coke, α-SiC and B_4C powders. The average particle sizes of α-SiC and B_4C were 1 and 2 μm, respectively. The raw coke, which was industrially manufactured by the delayed coker process, contained volatile matter of 12%. It was ground by the use of a vibratory ball-mill and then washed in warm hydrochloric acid to remove the metal impurities. The powders thus obtained showed good sinterability, as reported previously [12].

The ground raw coke was mixed with SiC and B_4C powders with different ratios as shown in Table I. In the sample code used in Table I, the first number refers to the volume percentage of total SiC and B_4C in the mixture, which is calculated from the mixing weight ratio and the densities of each component, and the second number to the ratio of SiC to (SiC + B_4C) by weight in round numbers. The powder mixtures thus prepared were again ground in either a tungsten carbide

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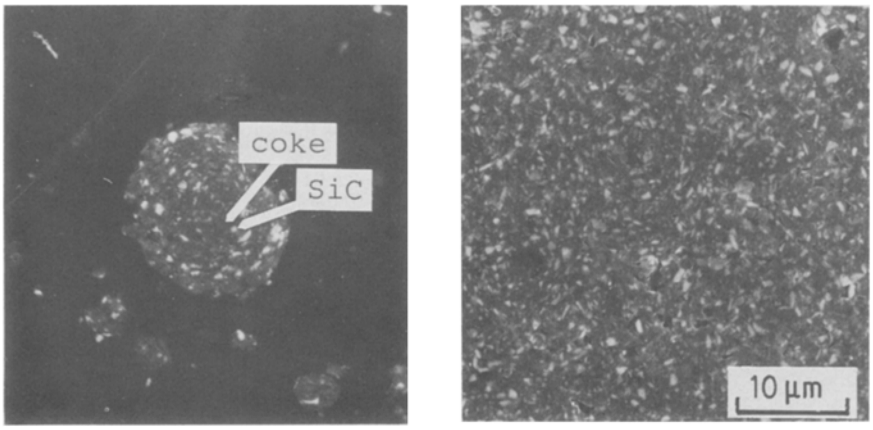

Figure 1 Scanning electron micrographs of (a) a polished section of a grain formed by grinding a powder mixture, and (b) the composite body made from the ground powder by heating.

mortar or an SiC-lined mill, and then compressed into rectangular pellets of 30 × 30 × 8 mm size under a pressure of 200 MPa. The pellets were heat-treated at 2000° C in an argon atmosphere under a atmospheric pressure after calcination at 1000° C.

The composites obtained were cut into pellets of 8 × 8 × 6 mm size, of which the surfaces were polished with fine-grained emery papers. On these small pellets, the following oxidation tests were carried out: the specimens were inserted quickly into a furnace heated at the desired temperature under an air flow of 2000 $cm^3 min^{-1}$, taken out after 1 h, and weighed. After repetition of this process five times, the specimens were held in the furnace for 17 h. A long-time oxidation test was also carried out at 1200° C under an air flow of 20 $cm^3 min^{-1}$. The weight change per unit surface area of a virgin specimen was determined from the weight before and after oxidation. The infrared (IR) absorption spectrum was measured by the reflection method on the surface of the oxidized composite.

3. Results

Fig. 1 shows scanning electron micrographs of the polished section of a grain formed by grinding a powder mixture (Fig. 1a), and a composite body made from the ground powder by heating (Fig. 1b). Particles of SiC and B_4C are dispersed in a matrix of raw coke in grains after grinding. The ground powder mixtures showed a high compressibility; they reached about 90% of the theoretical density calculated from the densities of raw coke and ceramic grains, and they gave dense composite bodies with a homogeneous dispersion of ceramic particles after heating. All the bodies showed a high density, a low water absorption ratio (less than about 0.5 wt %) and a high bending strength of 140 to 160 MPa.

Fig. 2 summarizes the weight loss by oxidation at different temperatures as a function of total oxidation time on samples with different ratios SiC/(SiC + B_4C). In the composites with a small content of SiC (Figs 2a and b), remarkable weight losses are observed at high oxidation temperatures. With an increase of SiC content, the weight loss at high temperatures becomes small and its dependence on oxidation time becomes small. On samples with a higher SiC content than 72% in SiC/(SiC + B_4C), however, the temperature dependence of weight loss becomes reversed: larger at low temperatures rather than at high temperatures (Figs 2c and d). At low temperatures, drastic weight losses are observed at the beginning of oxidation within 5 h. This initial consumption becomes remarkable with an increase of SiC content.

The initial consumption by oxidation is considered to be attributed to the incomplete formation of a protective film, which is mainly composed of B_2O_3. The film seems to be established gradually within 5 h. The weight loss due to oxidation at different temperatures during the period from 5 to 22 h is shown in Fig. 3 as a function of SiC/(SiC + B_4C) ratio. The optimum ratio for oxidation resistance is found to be from 63 to 87%. In this range the weight loss is roughly independent of the oxidation temperature, in contrast to strong dependences on the oxidation

TABLE I Compositions of raw powder mixtures of C–SiC–B_4C composites

Code	Coke (wt %)	SiC (wt %)	B_4C (wt %)	SiC/(SiC + B_4C)
20-0	68.3	0.0	31.6	0.0 (%)
20-16	67.8	5.2	27.0	16.1
20-30	66.9	9.8	23.2	29.6
20-42	66.3	14.2	19.5	42.1
20-53	65.7	16.2	18.1	52.8
20-63	65.2	21.8	13.0	62.6
20-72	64.7	25.3	10.0	71.7
20-80	64.2	28.5	7.3	79.6
20-87	63.8	31.5	4.7	87.0
20-91	63.5	33.2	3.2	91.2
25-84	57.1	35.8	7.1	83.5
48-68	34.6	44.4	21.0	67.8
48-86	32.4	58.4	9.2	86.4

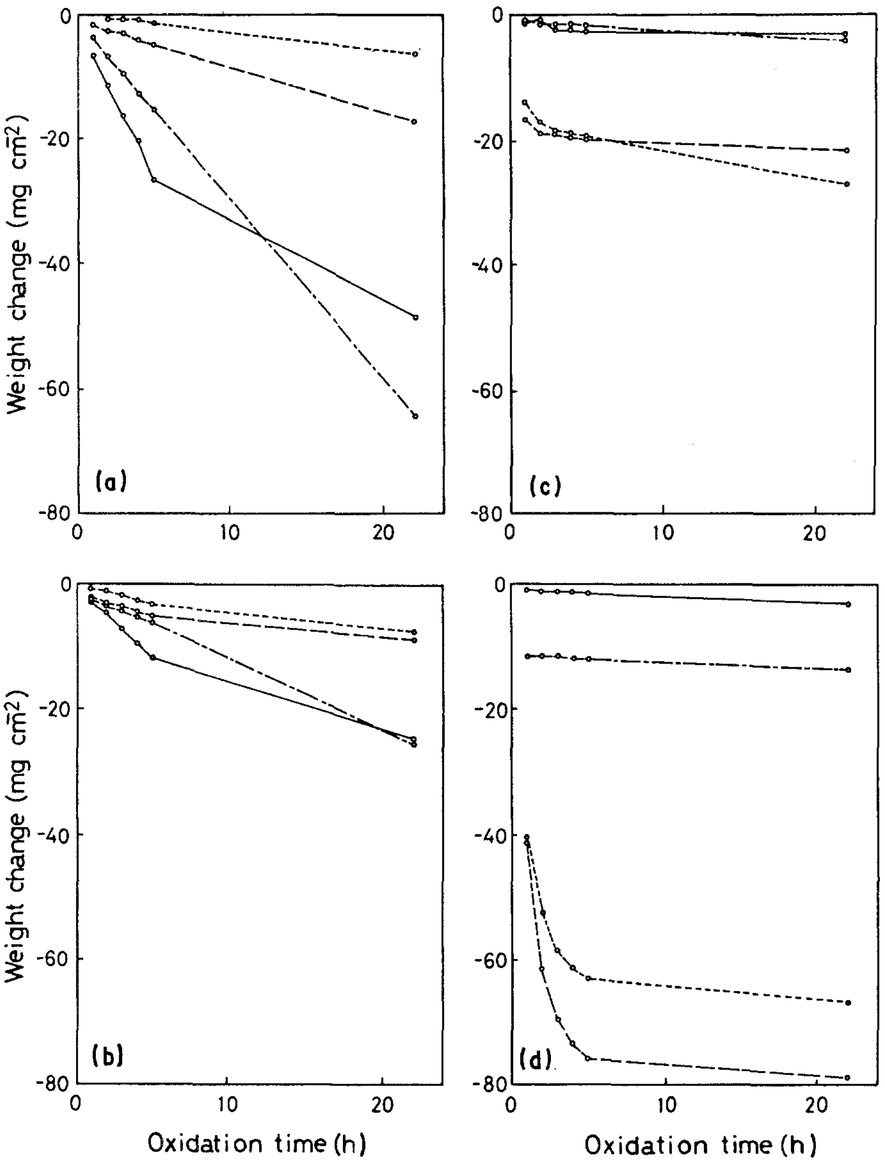

Figure 2 Changes of weight loss with oxidation time at various temperatures for composites with different ratios of SiC/(SiC + B_4C): (a) 20-40 (42.1%), (b) 20-53 (52.8%), (c) 20-72 (71.6%), (d) 20-80 (79.6%). (– – –) 1000° C, (——–——) 1100° C, (–·–) 1200° C, (——) 1300° C.

temperature and SiC content below 63%. Above 87% there seems to be not enough B_2O_3 liquid to cover all the surface of the composite. The composites, therefore, drastically lose the in oxidation resistance.

From the results mentioned above, the oxidation resistance of a composite seems to depend strongly on the nature of the protective film which is formed on

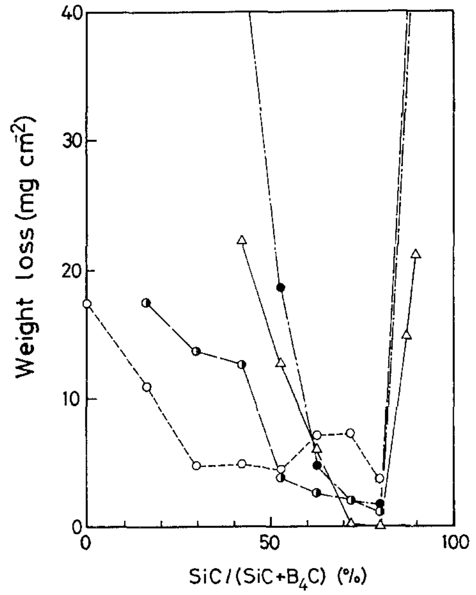

Figure 3 Relations between the weight loss by oxidation at different temperatures during the period from 5 h to 22 h and the ratio SiC/(SiC + B_4C) in the composites. (○) 1000° C, (◑) 1100° C, (△) 1300° C, (●) 1200° C.

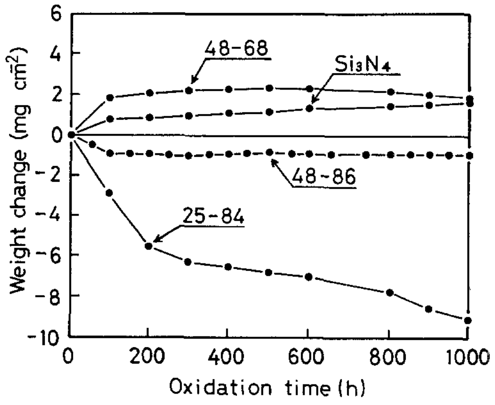

Figure 4 Comparison of weight changes between C–SiC–B_4C composites and Si_3N_4 solid at 1200° C under an air flow of 20 cm^3 min^{-1}.

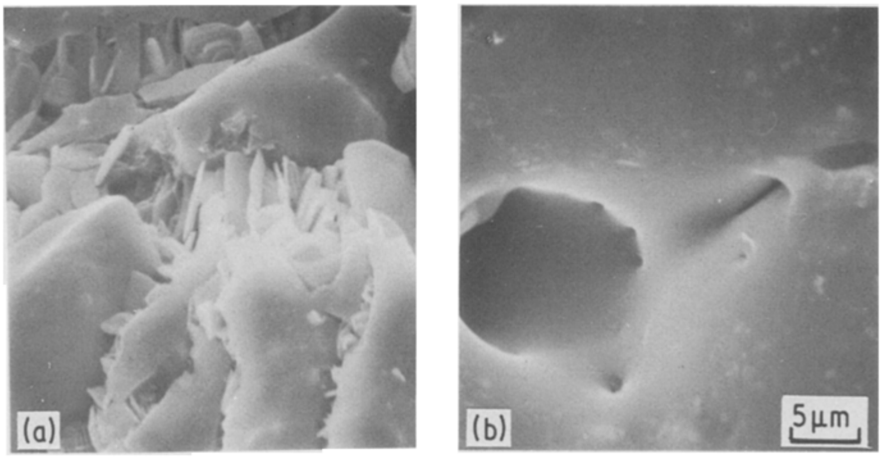

Figure 5 Scanning electron micrographs of the surfaces of the composites (a) 20-40 and (b) 20-80 after oxidation for 20 h at 1000° C.

the surface of the composite during oxidation, and the film formed is possibly determined by the ratio of SiC to B_4C and also by their total content in the composite. For composites with a high content of total of SiC and B_4C, long-time oxidation tests were carried out at 1200° C under an air flow of 20 $cm^3 min^{-1}$ (Fig. 4). Small changes in weight for Samples 46-68 and 48-86 are observed even after 100 h, which are comparable with that of an Si_3N_4 sample.

Fig. 5 shows scanning electron micrographs of the surfaces of composites oxidized for 20 h at 1000° C. The surface of the composite with a low content of SiC is covered with products including a lot of small particles (Fig. 5a). From X-ray diffraction measurements, these small particles were considered to be B_2O_3 crystals rather than SiO_2 crystals. With a high content of SiC, on the other hand, the composite shows a smooth surface suggesting the formation of a glass which seems to be a film with high viscosity formed during oxidation. The increasing amount of SiO_2 formed seems to increase the viscosity of the film.

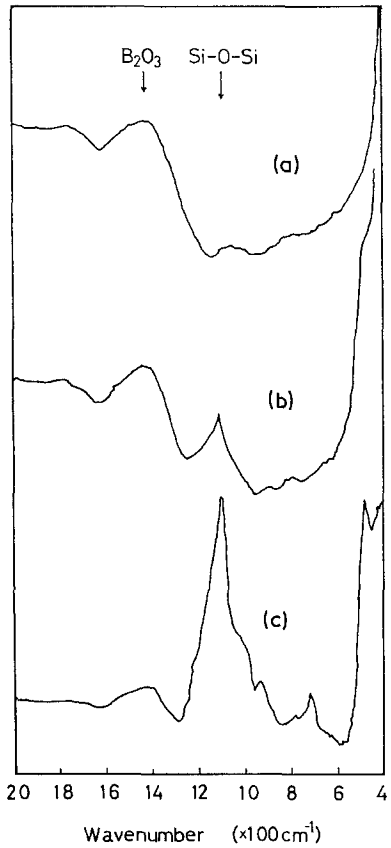

Figure 6 IR spectrum of the surface of the 20-63 composites oxidized for 22 h at various temperatures: (a) 1000° C, (b) 1200° C, (c) 1300° C.

IR absorption measurements on the oxidized surface of a 20-63 sample indicate that the SiO_2 content in the film also increases with an increase of oxidation temperature as shown in Fig. 6. The absorption intensity ratio of 1100 cm^{-1} to 1400 cm^{-1} peaks, which are assigned to Si–O–Si stretching vibration [13] and probably B_2O_3 glass [14], respectively, increases with increasing temperature.

4. Discussion

The oxidation of C–SiC–B_4C composites has been reported to result in the rapid formation of B_2O_3 at 500° C, and a gradual formation of SiO_2 from 800° C [11]. The conceivable states of these oxides at the testing temperatures are SiO_2 solid, B_2O_3 liquid and SiO_2–B_2O_3 eutectic solutions. The films to protect the composites from oxidation were supposed to be formed by the last two. B_2O_3, however, has a considerably higher vapour pressure at high temperatures [15] compared with SiO_2 [16]. The improvement of the oxidation resistance of the composites is caused by the formation of SiO_2–B_2O_3 eutectic solution, of which the vaporization at high temperatures is controlled by SiO_2. In the present work the weight change by oxidation varied with the SiC/B_4C ratio in the composite and with oxidation temperature. This oxidation behaviour seems to be closely related with the quantity of eutectic solution formed and its composition.

With a small content of SiC, eutectic films containing a little SiO_2 are rapidly formed, because the SiO_2 liquid has a high solubility in B_2O_3. In this case, however, the films are not very effective in protecting the composites because of their low viscosity and high vapour pressure. With a high content of SiC, on the other hand, the SiO_2 content in the films formed increases gradually with time and then it saturates. This is caused by the difference in the formation rates of SiO_2 and B_2O_3 from the respective carbides [11]. The higher the SiC content in the composite, the longer is the time required and the larger the weight loss occurring to form a stable protective film.

The time taken for a stable film to form depends also upon the oxidation temperature. At high temperatures it is shortened by the vaporization of B_2O_3, and the concentration of SiO_2 in the film occurs speedily.

Once a stable film has been formed, in the case of high SiC content, the weight change does not depend on the oxidation temperature (Fig. 3). According to the constitutional diagram [17] and the results of IR absorption measurement, the SiO_2 content in the films increases with an increase of temperature. The increase of SiO_2 at high temperatures results in a relatively high ability to resist the oxidation of the composites.

The $C-SiC-B_2C$ composites are regarded as unique carbon-based materials for use above 1000° C in an air atmosphere. The simple preparation process employed in the present work gives a high possibility that the composites may be widely used in industrial fields.

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References

1. K. MIYAZAKI, S. HAGIO and K. KOBAYASHI, *Yogyo-kyokaishi* **86** (1978) 56.
2. *Idem. J. Mater. Sci.* **16** (1981) 752.
3. E. M. GOLDSTEIN, E. W. CARTER and S. KLUZ, *Carbon* **4** (1966) 273.
4. V. S. DERGUNOVA, A. N. SHURSHAKOV, G. D. POSOS'EVA and L. N. LUTSENKO, *Sov. Powder Met. Metal Ceram.* **11** (1972) 642.
5. R. D. CARNAHAN, K. R. JANOWSKI and R. C. ROSSI, *J. Amer. Ceram. Soc.* **52** (1969) 475.
6. B. R. MICCIOLI, *Ceram. Bull.* **45** (1966) 671.
7. J. L. WHITE and K. KOYAMA, *J. Amer. Ceram. Soc.* **51** (1968) 394.
8. I. OGAWA, K. KOBAYASHI and H. HONDA, *TANSO* No. 93 (1978) 57.
9. I. OGAWA, T. HAGIO, H. YOSHIDA and K. KOBAYASHI, *Yogyo-kyokai-shi* **92** (1984) 392.
10. H. HAGIO, I. OGAWA, H. YOSHIDA and K. KOBAYASHI, Report of The Government Industrial Research Institute of Kyushu, Vol. 33 (1984) pp. 2154–59.
11. I. OGAWA, T. YAMAMOTO, T. HAGIO, H. YOSHIDA and K. KOBAYASHI, *Yogyo-kyokai-shi* **94** (1986) 409–14.
12. I. OGAWA and K. KOBAYASHI, *TANSO* No. 109 (1982) 41.
13. E. A. ROBINSON, *Can. J. Chem.* **41** (1963) 3021.
14. J. L. PERSONS and M. E. MILBERG, *J. Amer. Ceram. Soc.* **43** (1960) 362.
15. J. R. SOULEN, P. STHAPITANONDA and J. L. MARGRAVE, *J. Chem.* **59** (1955) 132.
16. H. J. T. ELLINGHAM, *J. Soc. Chem. Ind.* **63** (1944) 125.
17. T. J. ROCKET and W. R. FOSTER, *J. Amer. Ceram. Soc.* **48** (1965) 75.

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