

# THE SELF-PROTECTION BEHAVIOR OF C/SiC<sub>n</sub>/B<sub>4</sub>C COMPOSITES

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## Introduction

Self-protection is an attractive method for oxidation protection of carbon material, which can be achieved through selecting favor kinds and contents of ceramics. Among the various combinations of carbon and different kinds of ceramics, the carbon-B<sub>4</sub>C-SiC system has been found to possess an excellent inhibitory effect against air oxidation at temperature above 1273 K[1]. It was also found that an unintergating layer with scattered holes and voids formed at temperature of 1173 K, due to the combination of the excessive evaporation of B<sub>2</sub>O<sub>3</sub> and the fact that SiO<sub>2</sub> was not able to be formed amountly at this temperature consistently[2][3].

An ideal self-protection against oxidation should be identified as: i. The formation of protective layer must be as quickly as possible in case of rapid recession and degradation of carbon material; ii. The formation of protective layer must occur in a wide range of temperature; iii. The layer must be stable and uniform without any cracks and voids and with very low oxygen permeability at the same time; iv. The formation of protective layer can occur whenever and wherever newly exposed surface of the material appears. The aims of this paper are to investigate the self-protection process of C/SiC/B<sub>4</sub>C composite materials with SiC nano-powder (SiC<sub>n</sub>) additive during oxidation in oxygen.

## Experimental

The raw materials used for preparation of C/SiC<sub>n</sub>/B<sub>4</sub>C composites were pitch based needle green coke, SiC and B<sub>4</sub>C powder. The average particle sizes of B<sub>4</sub>C and SiC<sub>n</sub> were 1.2μm and 18nm. The mixture of coke powder, B<sub>4</sub>C and SiC<sub>n</sub> powder was ground using a vibratory ball-mill for 15hrs. The ratios of C:SiC<sub>n</sub>:B<sub>4</sub>C were 13:4:3. Then the mixed ground powder was compressed into cylindrical samples of Ø8x7mm under a pressure of 200MPa, and sintered for 1.5 hrs at 1573 K and then heat-treated at 2473 K for 6 hrs. The composites obtained were cut and polished carefully, and anisothermal and isothermal oxidation tests were carried out on these small cylinders in an oxygen flow by the method of

thermogravimetry analysis. Additionally, comparison tests on the composite with SiC micro-powder of 1.3μm in diameter were also carried out on the same experimental conditions.

## Results and Discussion

Fig.1 shows variations of the mass change per unit area of the composites with increasing temperature during anisothermal oxidation in pure oxygen. Drastic mass losses were observed at the beginning of the oxidation, as the temperature was about 800 K to 973 K. This initial recession of composites is considered to be due to the ablation of carbon powders on the surface layer, and the overall reaction is controlled by the rate of carbon-oxygen reaction indicated by the linear increment of the curve with the duration of time and elevating of temperature, although carbon consumption with a weight loss is predominant, the oxidation reaction of B<sub>4</sub>C was accelerated rapidly, which lead to a little weight gain theoretically due to the formation of B<sub>2</sub>O<sub>3</sub>. Thus, the net weight loss rate decreased from the temperature of 900 K or above. On the other hand, from temperature of 1100 K, the mass loss rate tended to slow down sharply. The overall weight kept nearly unchanged till to temperature of 1573 K. Therefore one can believe that a process of self-protection against oxidation is carrying on from this temperature. Further investigation of self-protection process is carried out employing an isothermal oxidation test at temperature of 1073 K and 1473 K (Fig. 2). Apparently, self-protection can be reached quickly for about 10 mins on the condition of being oxidized at 1473 K; but it took much longer time to reach a self-protection regime for that oxidized at 1073 K. The final weight loss of the composite oxidized at 1473 K was only a little larger than that at 1073 K, though the initial weight loss rate owing to ablation of surface carbon was faster. It is the decrease of time spending on achieving self-protective stage that makes for the loss. The morphologies of the surfaces of the composites after oxidation were investigated with SEM. The protective layers showed some differences on the density and uniformity, and that formed at temperature of 1473K was much more smooth with fewer voids (Fig.3 a and b). The behavior and effect of SiC nano-powder in the composite, which acted as an important role on the self-protection, were further

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investigated by comparison tests. The self-protective stage was also found for the composite with SiC micro-powder from 1100K to 1350K during anisothermal oxidation, however great mass loss was observed again after 1350 K (Fig.1). It can also be seen that the composite with SiC nano-powder obtained self-protection process at less mass loss and lower temperature than that with SiC micro-powder. Moreover, voids on the surface layer of the composite with SiC micro-powder were observed, and most of the SiC particles were not oxidized (Fig.3 d). Obviously, it was the excessive evaporating of B<sub>2</sub>O<sub>3</sub> destroyed the uniformity of the protective film.

From the above results, the effect of SiC nano-powder in the composite can be described as: 1.The reaction of nano-particle with oxygen began as low as about 973K, and the reactant SiO<sub>2</sub> can form a stable glass phase with B<sub>2</sub>O<sub>3</sub> at lower temperature which possesses smaller permeability for oxygen and less evaporativity at high temperature comparing to B<sub>2</sub>O<sub>3</sub> phase, which leads to the formation of protective layer; 2.For solid-gas reactions, the reaction rate is known as  $R \propto r^2$ . Thus high reactivity of nano-scaled SiC with O<sub>2</sub> can be predicted. Additionally, the SiO<sub>2</sub> layer formed during oxidation which covers the SiC particle and inhibits the diffusion of oxygen is much thinner comparing with that of particles with normal size. These two factors facilitate the

formation of SiO<sub>2</sub> in a relative rapid rate, which accelerates the process from the carbon recession to self-protection stage.

### Conclusions

1. A self-protection can be achieved for C/SiCn/B<sub>4</sub>C composite during anisothermal oxidation at 1173K at a heating rate of 10K/min.
2. The final mass loss during isothermal oxidation varies little at different temperatures, while the self-protective stage is reached at earlier time during oxidation at higher temperature.
3. The protective layer formed at 1473K is much more uniform with fewer voids than that at lower temperature.

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### References

1. McKee,D., in *Chemistry and physics of Carbon*, Vol. 23, ed. P.A.Thrower. Marcel Dekker, New York, 1991, p.173.
2. I.Ogawa, K. Kobayashi, *J. Mater.Sci.*, Vol. 27, P. 1161.
3. Kobayashi, *Carbon*, Vol.33, 1995, 4, p.397.

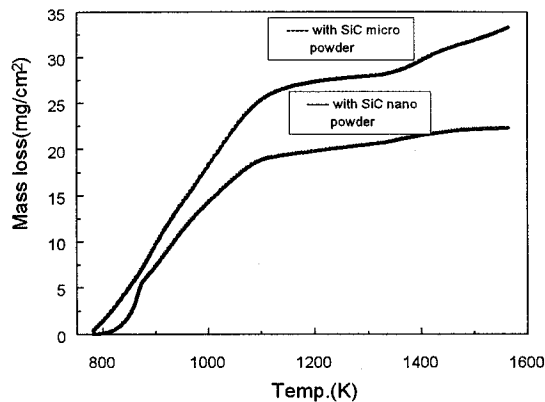


Fig. 1 Variation of the mass loss of C/SiC/B<sub>4</sub>C composite with temperature during anisothermal oxidation.

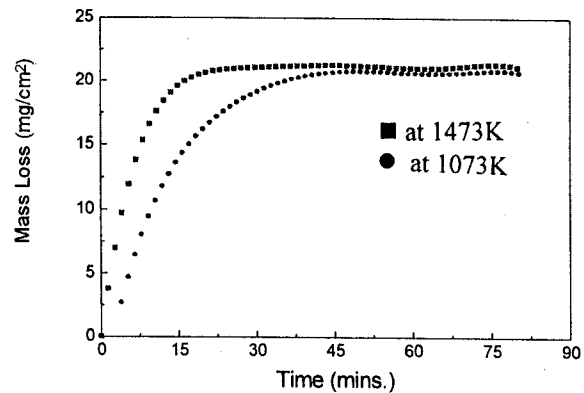


Fig. 2 Variation of the mass loss of C/SiCn/B<sub>4</sub>C composite with time during isothermal oxidation.

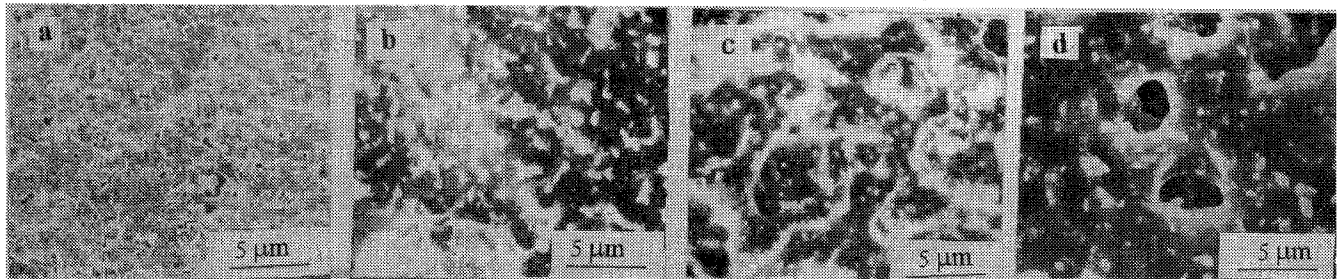


Fig. 3 SEM micrography of the surface layer of the composites after oxidation ( a: oxidized at 1073K; b:oxidized at 1473 K; c: oxidized from 773K to 1573 K; d: oxidized from 773K to 1573 K for the composite with SiC micro-powder)