The Korean Journal of Ceramics, **5** [2] 115 - 118 (1999)

Preparation of Carbon Composite with High Oxidation Resistance by $MoSi_2$ Dispersion

S. Goto, M. Kodera, S. Toda, H. Fujimori and K. Ioku

Fac. of Engr., Yamaguchi University, Ube, 755-8611, Japan

(Received September 23, 1998)

Carbon composites with $MoSi_2$ dispersion were prepared by hot-pressing at 1700°C under 30 MPa for 1 h using polysilazane as binding material. The composites consisted of C, $Mo_{4.8}Si_3C_{0.6}$ and SiC. Bulk density and porosity of the carbon composites with 10 vol% $MoSi_2$ was 1.8 g cm^{-3} and 34%, respectively. This composite was oxidized about 0.05 mm from the surface of the carbon composite after oxidation test at 1500°C for 10 h in air. Formation of the SiO_2 glass layer was observed by SEM. When this composite suffered damage in the coating layer, it had hardly farther oxidation because of its self-repairing property The composite prepared in this study indicated good oxidation resistance.

Key words : Carbon Composite, $MoSi_2$, Oxidation Resistance, Self-reparing

I. Introduction

Carbon composites are promising materials for use at ultra high temperatures, such as gas turbines, spaceplane airframes or engines, because carbon composites are useful materials at more over 2000°C in anti-oxidation atmosphere.[1] But in air, the carbon composites oxidize at relatively low temperature of about 500°C. So oxidation resistance of the carbon composites is a significant problem. At present the surfaces of carbon composites are sometimes coated with anti-oxidation reagents such as silicon carbide by CVD, PVD and so on.[2-4] But as for using only coating system on the surface of the carbon composites, when a crack or even a pinhole occurs in the coated thin layer, carbon composites react with oxygen and carbon will be burnt out immediately.

In this study, oxidation resistant carbon composites were prepared by dispersing with $MoSi_2$ particles which possess self repairing of anti oxidation layer.[5,6] These also contained polysilazane as the sintering additives and were prepared by hot-pressing at 1700°C with 30 MPa for 1 h.[7] Then the oxidation resistance, mechanical and thermal properties of composites were investigated.

II. Experimental Prodedure

Artificial graphite was mixed with $MoSi_2$ particles (0~10 vol% that is 0~21 mass%) and a polysilazane/xylene solution. Artificial graphite was supplied by Toyo Tanso Co., LTD. $MoSi_2$ particles were obtained from Japan New Metals Co., LTD, and the polysilazane/xylene solution was procured from Tonen corporation.

After xylene was volatilized in N_2 atmosphere from the mixtures, they were calcined at 800°C for 1 h in N_2 atmosphere. They were then hot-pressed at 1700°C under 30 MPa for 1 h in N_2. Full load was applied at 1000°C. The heating rate from 500°C to maximum temperature was 5°C/min.

The phases formed were identified by using a X-ray diffractometer (MXP^3, MAC Science Co., LTD.). The chemical composition of specimens was analyzed by X-ray fluoresence analysis (3080E, Rigaku Co., LTD.). The morphology of the composites was observed by SEM (JSM-25S, JEOL, LTD.). Bending strength was measured by three-point flexure method using a universal testing machine (AG-500A, Shimadzu Co., LTD.) at a room temperature. Specimens were rectangular bars with dimensions of 3×4×40 mm (JIS). Thermal expansivity was measured by using a SL-2000M, Shinagawa Refractories Co., LTD. in air.

Oxidation resistance was discussed with the results of weight change by heat treatment at temperatures of 1300°C, 1400°C and 1500°C for a certain time in air. The samples had a dimension of 3×4×20 mm. These weight changes were measured in two ways. One was treated at a temperature for one cyclic duration and the other was treated at temperatures between a high temparature and room temperature with several cycles. The weight changes during cyclic treatment are useful for discussion of the ability of self repairing of oxidation resistance layer produced. Weight changes data were converted to the oxidized depth (mm) from surface of the carbon composites. The morphology of the specimens after heat treatment was observed by SEM.

III. Results and Discussion

1. Phases in the composites

The carbon composites of 90×90×4.5 mm in size were

Table 1. Crystalline Phases of the Carbon Composites Prepared by Hot-pressing at 1700°C

Amount of $MoSi_2$ as additives (vol%)	Crystalline phases in composites
0	C, α-Si_3N_4
3~10	C, SiC, $Mo_{4.8}Si_3C_{0.6}$

prepared by hot-pressing. Table 1 presents results of the X-ray diffraction analysis. The phases existing in the composites without $MoSi_2$ addition were C[8] and Si_3N_4.[9] The phases existing in the $MoSi_2$-containing composites (3~10 vol%) were C, β-SiC[10] and $Mo_{4.8}Si_3C_{0.6}$.[11,12] The composites with $MoSi_2$ consisted of SiC, instead of Si_3N_4 in the composites without $MoSi_2$, and $Mo_{4.8}Si_3C_{0.6}$ instead of $MoSi_2$. $MoSi_2$ reacted with C to produce $Mo_{4.8}Si_3C_{0.6}$ and SiC during hot-pressing, as shown in equation (1). These SiC should act as the seeds for the conversion of Si_3N_4 to SiC.

$$4.8\ MoSi_2 + 7.2\ C \rightarrow Mo_{4.8}Si_3C_{0.6} + 6.6\ SiC \quad (1)$$

2. Strength and porosity

Fig. 1 shows the effect of the $MoSi_2$ addition on the bending strength and porosity of the composites. Three-point bending test were carried out for 3 specimens at each samples, but sample with $MoSi_2$ 10 vol% were only 1 specimens. Bending strength of the carbon composites increased with increasing of the amount of $MoSi_2$ (0~10 vol%) from 4 to 8 MPa. Porosity also increased with the increased amount of $MoSi_2$. Therefore it is presumed that degree of sintering did not increase but bonding strength was fortified by the addition of $MoSi_2$. Vickers hardness using a 5-gf load of the carbon composites with 0~10 vol% $MoSi_2$ dispersion was 350~450 MPa. The average value of Vickers hardness was 390 MPa.

3. Thermal expansion

The thermal expansion was measured up to 1450°C. The values of expansion of the carbon composites were almost same even though $MoSi_2$ particles having a high expansion were increased, the value was about 5.0×10^{-6} K.

4. Weight change by heat treatment

At first, the samples with size of $3\times4\times20$ mm were heated from room temperature to 1200°C with an increasing rate of 10°C/min in air. All carbon in the composites even when it contained 10 vol% $MoSi_2$ was burnt out completly. In this case, no resistance to oxidation occured. Next, the samples were put into the furnace held at a high temperatue of 1500°C. Carbon in a sample without $MoSi_2$ was burnt out completely, but samples with $MoSi_2$ dispersion had good resistance to oxidation. The oxidation residue of the composites with and without $MoSi_2$ heated at the temperatures of 1300~1500°C for 1 h were shown in Fig. 2. All samples with $MoSi_2$ up to 10 vol% did not have any oxidation resistance at 1300°C, but at 1400°C, samples with $MoSi_2$ more than 6 vol% showed a good resistance but one with $MoSi_2$ 3 vol% had poor resistance at 1400°C, while all samples with $MoSi_2$ showed a good resistance for oxidation at 1500°C in air.

The changes in oxidation residue (mass%) are influenced by the size of samples, while the oxidized depth from the surface of sample does not depend on the size. Then the data of weight change were converted to the oxidized depth (mm). The results were shown in Fig. 3. The oxidized depth of all specimens were about 1.5 mm at 1300°C for 1 h. Because of the sample size of 3 mm thickness, the depth of 1.5 mm means whole carbon in sample was burnt out. On the other hand the composites with $MoSi_2$ (6 vol%~) were oxidized only 0.3 mm at 1400°C for 1h as shown in Fig. 3. Further, the composites with $MoSi_2$ 10 vol% addition were oxidized only 0.05 mm at 1500°C for 1 h. This can be proved from the observation of the thickness of SiO_2 glass layer by SEM.

Fig. 4 shows oxidized depth of cyclic heat treatment test at 1500°C for 2 h. In the case of $MoSi_2$ 3 vol% addition, oxidized depth increased gradually from 0.3

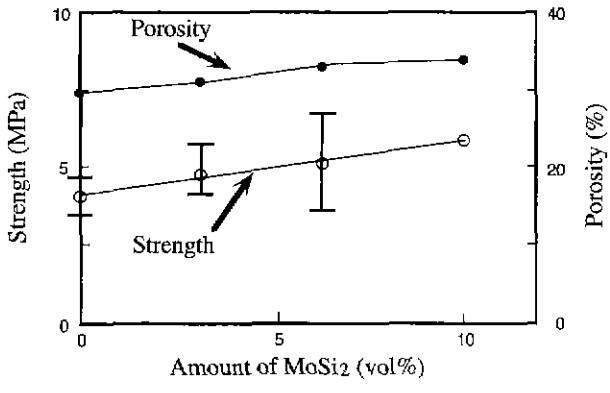

Fig. 1. Bending strength and porosity of the carbon composites with $MoSi_2$ dispersion.

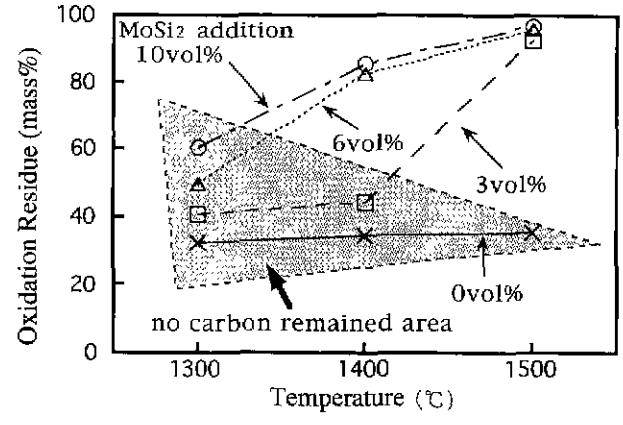

Fig. 2. Oxidation residue of the carbon composites with $MoSi_2$ after oxidation test at 1500°C for 1 h in air.

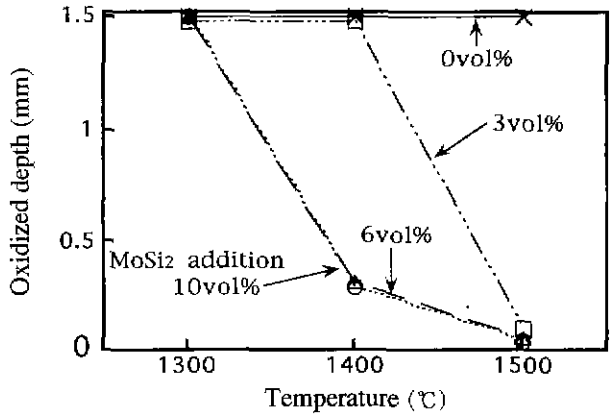

Fig. 3. Oxodized depth of the carbon composites with $MoSi_2$ after oxidation test at 1300, 1400 and 1500°C for 1 h in air.

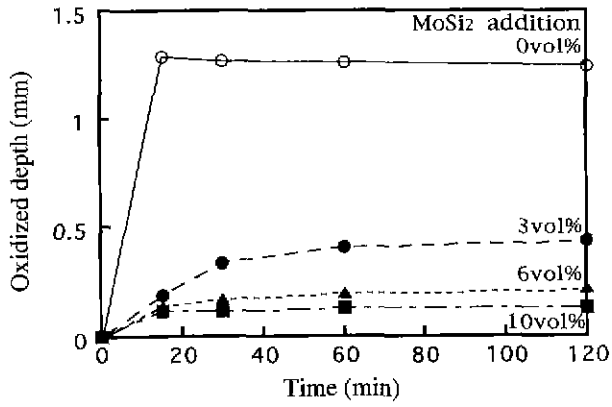

Fig. 4. Cyclic oxidation of the carbon composites with $MoSi_2$ dispersion at 1500°C in air.

mm for 15 min to 0.5 mm for 120 min. In contrast, the composite with $MoSi_2$ 10 vol% was oxidized 0.14 mm thickness for 15 min but it was almost constant by further more cyclic treatments. It was a proof of the ability of self-repairing of oxidation resistance layer due to $MoSi_2$. That of 6 vol% were located between those of 3 vol% and 10 vol%. The sample without $MoSi_2$ was burnt out completely by the heating treatment for 15 min.

5. Characterization of the oxidation resistance layer

The structure of the oxidized composites was observed by SEM. Fig. 5 shows the fracture surfaces of oxidized samples with $MoSi_2$ 3 and 6 vol% and without $MoSi_2$. Fig. 5(a) shows a structure of oxidized layer of the sample without $MoSi_2$ treated at 1500°C, which seems very porous and does not have any resistance against to the oxidation. Fig. 5(b) and (c) show the oxidized and unoxidized layer for the sample with $MoSi_2$ 3 vol% and 6 vol%, respectively. The oxidized layer of sample with $MoSi_2$ is clearly divided from unoxidized layer and seems significantly denser than that without $MoSi_2$. This dense structure should lead to have a good resistance to the oxidation.

The oxidation resistance layer is principally considered

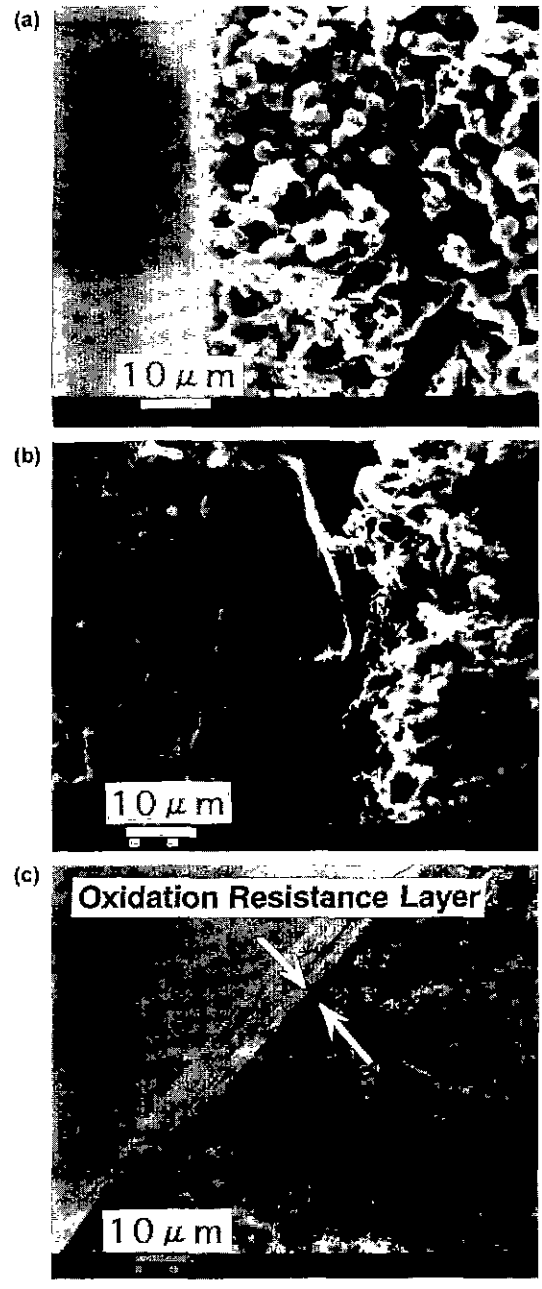

Fig. 5. *SEM observation of the sample after heat treatment* at 1500°C for 1 h in air; (a) without $MoSi_2$ addition, (b) 3 vol% $MoSi_2$ addition and (c) 6 vol% $MoSi_2$ addition.

to be SiO_2 glass. According to EPMA, the layer mainly composed of SiO_2. But a small portion of Mo was observed. In order to make clear the behavior of Mo, the intensity of X-ray diffraction of $MoSi_2$ (Peak: d=0.2026 nm) after the heating treatment at 1500°C in air was measured. And the ratio of Mo to Si were also determined by X-ray fluoresence. The results are shown in Fig. 6. This figure shows that the $(Mo/Si)/(Mo/Si)_0$ ratio had a linear relation to the amount of $MoSi_2$ after heat-treatment, where $(Mo/Si)_0$ is the initial ratio of Mo/Si. Therefore, it can be explained that most of all Mo component does not remain in

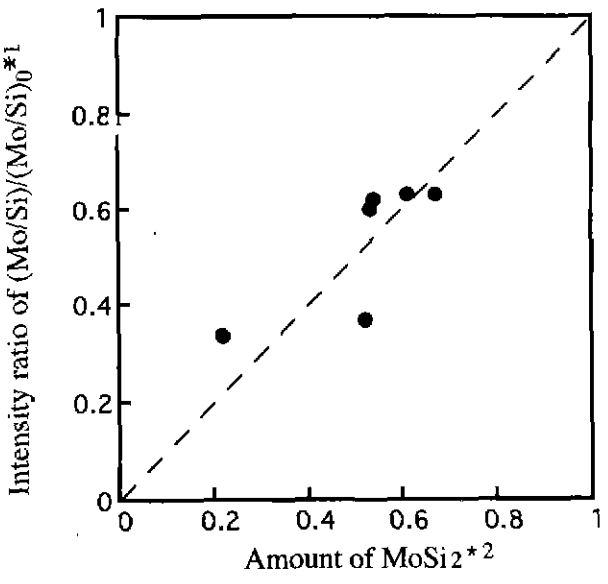

Fig. 6. Relation ship between contents of Mo and $MoSi_2$ in composites after oxidation test. *1: measured by XRF, *2: measured by XRD $(Mo/Si)_0$: the initial ratio of Mo/Si.

oxidized layer because Mo easily volatilizes as MoO_3 when $MoSi_2$ was oxidized.[13]

Thus, it was found that the oxidized layer hardly contains Mo. Whether composites contained $MoSi_2$ or not significantly affected to the development of the structure of oxidized layer, as shown in Fig. 5. This shown that most of all Mo volatilized as MoO_3. Therefore, it seemed that a very small amount of Mo significantly affected to the viscosity of the SiO_2 glass produced.

IV. Conclusion

Carbon composites with $MoSi_2$ dispersion were prepared by hot-pressing at 1700°C under 30 MPa for 1h using polysilazane as the binding material. The composites consisted of C, $Mo_{4.8}Si_3C_{0.6}$ and SiC. The oxidation resistance, mechanical and thermal properties of composites were investigated with the following results:

1. The composite prepared in this study indicated good oxidation resistance under some test conditions.

2. The composite with 10 vol% $MoSi_2$ addition was oxidized about 0.05 mm from the surface after oxidation test at 1500°C for 10 h in air.

3. It was found that the composite has the ability of self-repairing of oxidation resistance layer due to $MoSi_2$.

Acknowledgments

Anthors world like to thank JUTEMI for using Hot Press and other facilities and for their assistantc.

References

1. Y. Mishima and S. Iwata, "Strategy for Material Design and Development," *Soft Science, Inc.*, p. 340 (1985).
2. T. Suemitsu, A. Takashima and H. Nishikawa, "Improvement of Oxidation Resistance of Carbon/Carbon Composites by the Multi-Layer CVD Coating Technique," *J. Ceram. Soc. Japan.*, **103**(5), 479-493 (1995).
3. C. Kawai, J Teraki. T. Hirano and T. Nomura, "Fabrication of a Functionally Gradient Material of Tic-SiC System by Chemical Vapor Deposition," *J. Ceram. Soc. Japan.*, **100**(9), 1117-1121 (1992).
4. J. R. Strife and J. E. Sheehan, "Ceramc Coating for Carbon-Carbon Composites," *Ceramic Bulltein.*, **67**(2), 369-374 (1988).
5. A. K. Vasudevan and J. J. Petrovic, "A Comparative Overview of Molybdenum Disilicide composites," *Materials Science and Engineering*, **A155**, 1-17 (1992).
6. H. Klemm, K. Tangermann, C. Schubert and W. Hermel, "Influence of Molybdenum Silicide Additions on High-Temperature Oxidation Resistance of Silicon Nitride Materials," *J. Am. Ceram. Soc.*, **79**(9), 2429-2435 (1996).
7. S. Ohsawa. O. Wada, S. Kim, K. Yasuda, Y. Matsuo and S. Kimura, "Sintering of hBN Using Polysilazane," *J. Ceram. Soc. Japan*, **102**(7), 648-652 (1994).
8. JCPDS Files, # 41-1487.
9. JCPDS Files, # 41-0360.
10. JCPDS Files, # 29-1129.
11. JCPDS Files, # 43-1199.
12. Jorge L. Garin and Rodolfo L. Mannheim, "X-ray Powder Diffraction Pattern of $Mo_{4.8}Si_3C_{0.6}$," *Powder Diffr.*, **8**(1), 65-67 (1993).
13. Alan W. Searcy, "Predicting the Thermodynamic Stabilities and Oxidation Resistances of Silicide Cermets," *J. Am. Ceram. Soc.*, **40**(12), 431-435 (1957).