ELSEVIER

Journal of Nuclear Materials 305 (2002) 77–82

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Letter to the Editors

The preparation of fine-grain doped graphite and its properties

Zhuangjun Fan [a,*], Lang Liu [a], Jiangang Li [b], Jinren Song [a], Junling Chen [b], Jingli Shi [a], Gergtai Zhai [a]

[a] *Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, People's Republic of China*
[b] *Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, Anhui 230031, People's Republic of China*

Received 5 February 2002; accepted 1 July 2002

Abstract

Fine-grain doped graphite was prepared by the ball-milling dispersion method for the first time. Such composite has not only high thermal conductivity and excellent bending strength (116 MPa), but also better oxidation resistance at elevated temperature and outgassing properties than those of composite doped with normal size carbides. Correlations between microstructure and properties of such composites are also discussed in detail.

1. Introduction

Carbon-based materials (CBM) are widely used for plasma-facing components of present-day fusion facilities and are intended for future reactor applications. It is well known that doping elements such as B, Si, Ti into the carbon substrate can reduce chemical erosion and radiation enhanced sublimation at elevated temperature [1–6]. Whereas recent investigations suggest that [7], besides the dopant elements, microstructure such as dopant distribution, dopant particle size and porosity, also has an important effect on the properties of CBM. Carbon doped fine-grain carbides show very favorable properties. For example, fine-grain carbides with a homogeneous distribution lead to more effective reduction of chemical erosion [8], and improve the resistance to radiation-induced degradation of thermal and mechanical properties than is found in conventional materials [9]. However, the oxidation behavior of fine-grain doped graphite due to the reaction with water/oxygen at elevated temperature ($T > 1273$ K) as well as the outgassing under high heat load has not yet been investigated in detail.

In present paper, fine-grain doped graphite material was prepared by a new method, ball-milling dispersion. The properties of fine-grain doped graphite, especially outgassing under high heat load and oxidation resistance behavior, as well as the correlations between properties and microstructure of such composite were investigated and compared with those of doped graphite with the same content of normal size carbides.

2. Experiment

2.1. Preparation of materials

Multi-elemental (B, Si, Ti) doped graphite was made from petroleum coke, 3 wt% B_4C powder (average particle size ~3 μm), 3 wt% Si powder (average particle size ~74 μm), 7.5 wt% Ti powder (average particle size ~35 μm) and coal tar pitch. Other materials used were organic solvent (tetrahydrofuran) and a dispersant (S27000, made in Japan).

Two mixing processes were used in this research. One was the conventional method (CM), in which the powders were mixed by a high speed mixing machine, the other was a ball-milling dispersion method (BM). The mixed powders then were compacted in a hot-pressing machine under a pressure of 15 MPa with heat-treatment temperature 2500 °C. The resulting samples were named CM and BM respectively.

* Corresponding author. Tel.: +86-351 408 3952; fax: +86-351 408 5506.
E-mail address: fanzhj666@163.com (Z. Fan).

0022-3115/02/$ - see front matter
PII: S0022-3115(02)00919-4

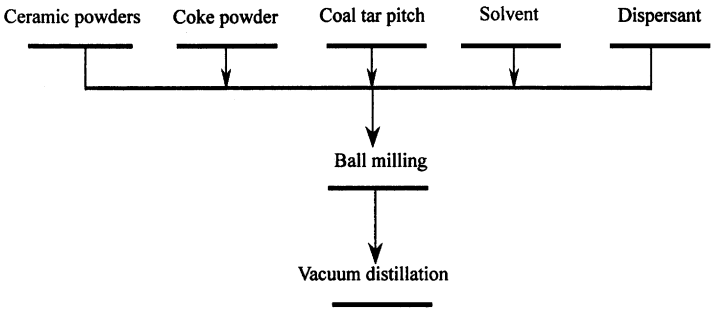


Fig. 1. Ball-milling dispersion process.

2.2. Ball-milling dispersion process

Ball-milling dispersion, a new process for not only reducing the size of B_4C, Si and Ti but also dispersing these particles homogeneously in the mixed powders is shown in Fig. 1. The process consists of three steps. First, the mixed powders, solvent and dispersant were put together into the ball-mill, and milled for 50 h. Then the mixture was treated with vacuum distillation in order to remove solvent.

2.3. Experimental device and conditions

The properties and microstructure of samples were investigated using different methods. The mixed powders size was measured by transmission electron microscopy (TEM). The crystallite phases of materials were determined by X-ray diffraction (XRD) with CuK_α radiation. Surface and fracture topography was observed by the use of scanning electron microscopy (SEM). The distribution of ceramic particles was analyzed by backscattering electron spectroscopy (BE).

The oxidation behavior of the composites was investigated by two methods. One was TG: the tests of samples with the size of 3 mm × 3 mm × 3 mm were carried out in a thermal analyzer of TG/DTA 92 (Setaram, France). The detectable variation in mass of the thermobalance was 1 μg. The temperature of the thermobalance furnace was raised at a rate of 20 °C min^{-1}. The oxidative atmosphere was air with the gas flow rate of 90 mL min^{-1}. The other was investigation of isothermal oxidation behavior: the samples with the size of 10 mm × 10 mm × 10 mm were oxidized by dry air with the air flow rate of 200 mL min^{-1} at 1200 °C and were weighed at different time intervals; the mass of the samples was determined on an electrobalance with accuracy of ±1 μg.

Tests of outgassing properties were carried out with an electron beam irradiation test simulator of Institute of Plasma Physics (Chinese Academy of Sciences). The specimens were mechanically fixed on a copper block that was actively cooled with water. The surface temperature of the center region of the sample of diameter 5 mm was measured with infrared pyrometer. The gases emitted from the heated sample surface were detected with a quadrupole mass spectrometer (QMS). The electron beam energy was 10 keV, the power was 6 MW/m^2 and duration was 30 s.

3. Results and discussion

3.1. The milled powders of EM

The sizes of raw material particles and the dispersion of doped elements in carbon will significantly affect the properties of prepared graphite. Thus how to decrease the diameter of doped particles and disperse them in carbon homogeneously becomes the key to the preparation of this specific graphite material. Fig. 2 shows the

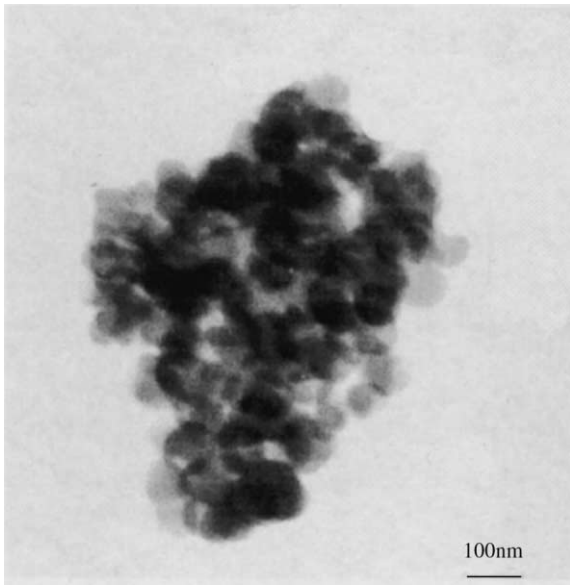


Fig. 2. TEM micrograph of the mixture powders after decompress distillation.

TEM of ball-milled mixture – Si, B_4C, Ti, and coke powder of BM after ball-milling dispersion for 50 h. It can be seen that compared with raw materials, the sizes of both Si, B_4C, Ti and coke powder are reduced greatly ranging from 30 to 100 nm. In the present work, tetrahydrofuran was used as ball-milling dispersion intermediate for its unique physical property. Since tetrahydrofuran is a polar aprotic solvent, it cannot only dissolve coal tar pitch, but also disperse both nonpolar particles, such as coke powders, and polar powders, such as B_4C, Si, Ti. During the ball-milling process, the large particles of coke and Si, B_4C, Ti are broken into small particles by mechanical force, and then dispersed homogeneously in coal tar pitch dissolved in tetrahydrofuran. Therefore, after removing tetrahydrofuran by vacuum distillation, homogeneously mixed small particles of coke and Si, B_4C, Ti wrapped by coal tar pitch were prepared.

3.2. Properties and microstructure of BM composite

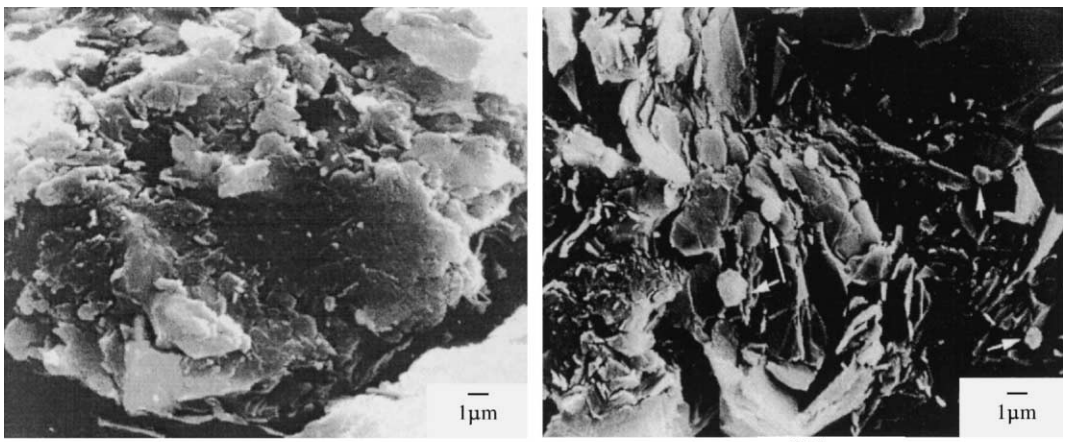
The properties of CM and BM are listed in Table 1. It can be seen that compared with CM, the density of BM increases slightly, the open porosity and thermal conductivity decreases slightly. What is interesting is that the bending strength of BM (116 MPa) increases greatly.

The bending strength of materials is closely related with its microstructure. It is well known that the smaller the graphite grain, the higher the strength of materials is. Being calculated from XRD results, the size of graphite crystallite of BM ($L_c = 30$ nm) is much smaller than that of CM ($L_c = 50$ nm) due to the smaller coke powders prepared by ball-milling dispersion process. On the other hand, defects also decrease the strength. Figs. 3 and 4 show topographies of fractured cross-sections of BM and CM. It can be seen that BM has a fine-grained structure, with ceramic particles ranging from 100 to 300 nm, dispersed uniformly on the surface of graphite. Whereas, ceramic particles in CM are obviously large and congregate on the surface of graphite with their sizes up to 3 μm (specified by arrows), which results in more defects compared with that of BM. Therefore the smaller graphite crystallite and the fewer defects in BM than in CM give rise to its high bending strength.

As far as the conductivity of graphite materials is concerned, smaller graphite crystallites lead to lower thermal conductivity. However, in the present work, the decrease of graphite crystallite of BM compared with CM does not result in great loss of thermal conductivity. We suggest there may be two reasons as follows. On the one hand, as mentioned above, the defects in BM are fewer than those in CM, which makes phonon scattering at carbon grain boundaries decrease, and subsequent

Table 1
Properties of doped graphite materials

Material	Density (g/cm^3)	Open porosity (%)	Bending strength (MPa)	Electrical resistivity ($\mu\Omega m$)	Thermal conductivity (W/m K)
CM	2.11	6.5	82	2.43	210
BM	2.13	5.1	116	3.03	200



BM CM

Fig. 3. SEM photographs of fractured cross-section of BM and CM.

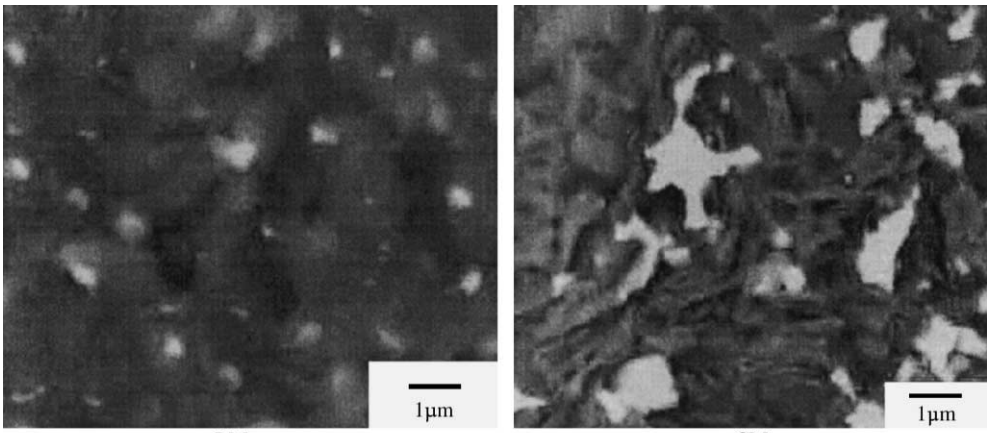


Fig. 4. Backscattering electron images of BM and CM.

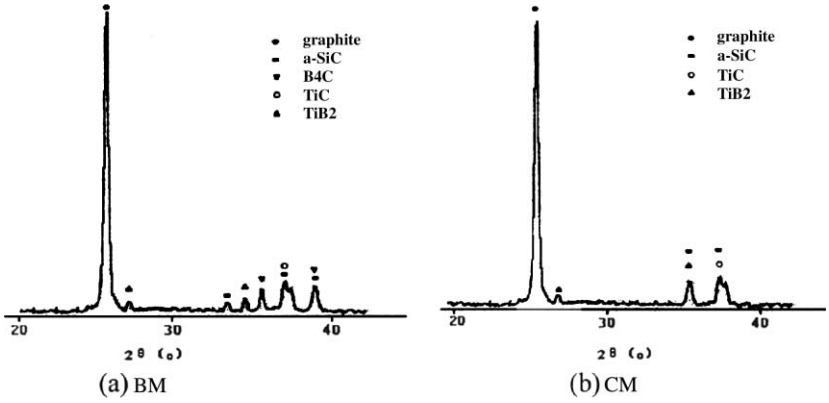


Fig. 5. XRD results of two samples.

less loss of thermal conductivity [10]. On the other hand, doped B, which is used to effectively improve the resistance to chemical erosion [11,12], can diffuse easily during heat-treatment to replace the carbon atoms in the crystal lattice. Unfortunately, this solubility of B in the graphite lattice would result in the great loss of thermal conductivity of graphite [13]. From XRD results of BM and CM as shown in Fig. 5, it can be seen that with the same concentration of B_4C in raw materials, BM showed a B_4C peak while CM showed none. This means less B is dissolved in the graphite lattice in BM than in CM. Hence the decrease of defects and the lower solubility of B in the graphite lattice of BM effectively inhibit the loss of thermal conductivity.

In addition, it is considered that the starting mixture powders with high surface energy and lattice distortion energy induced by ball-milling can improve sintering ability, which would lead to high density and low porosity.

3.3. Oxidation resistance behavior

Fig. 6 shows TG analysis of composites CM and BM at temperatures up to 1500 °C respectively. In the range of 600–1000 °C, the weight loss rate of BM is a little higher than that of CM because of the smaller graphite crystallites of BM, which leads to higher surface area and existence of more active sites easily reacting with oxygen. However, the oxidation rate of BM is significantly lower than that of CM in the range of 1000–1500 °C. In order to further understand the oxidation resistance behavior of BM at elevated temperature, isothermal oxidation behavior of the composites at 1200 °C in air was investigated as shown in Fig. 7. It can be seen that the burn off of BM at 1200 °C, like that of TG results at 1500 °C, is much less than that of CM (almost half of CM at 85 min).

As discussed above, for BM the carbides are much smaller than in CM and are dispersed homogeneously in

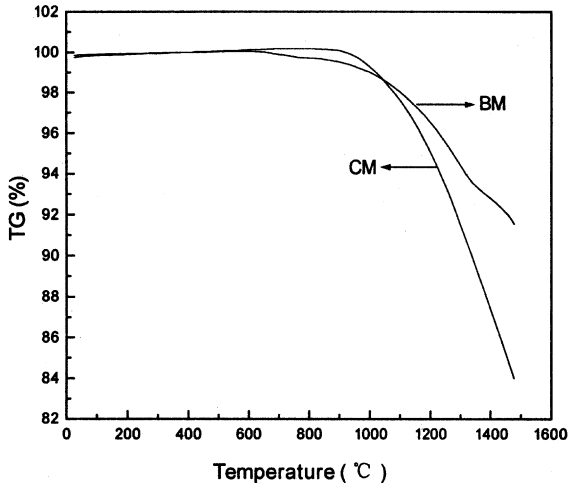


Fig. 6. TG analysis of composite CM and BM up to 1500 °C.

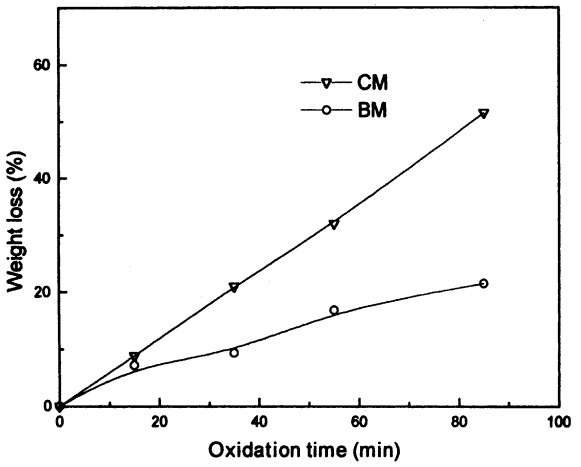
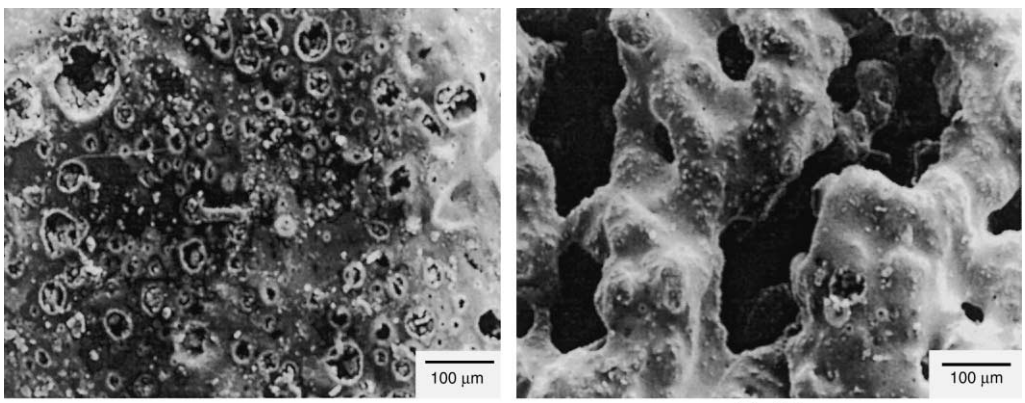


Fig. 7. Isothermal oxidation behavior of the composites at 1200 °C.

the carbon substrate. Therefore when being oxidized at elevated temperature, these small particles show higher oxidation rate than that of CM [14]. Consequently a continuous and uniform borosilicate glass, which would effectively prevent oxygen from diffusing into the interior of composite [15], is formed on the surface of BM as shown in Fig. 8. Besides, small pores about 30 μm are also found on the surface of BM; this may be attributed to evaporation of boron oxide at elevated temperature. In contrast, ceramics oxides in CM are not dispersed as homogeneously as those in BM, which results in more carbon substrate exposed to oxygen. It is this exposed carbon that easily reacts with oxygen and forms large pores (about 300 μm shown in Fig. 8) on the surface of CM.

3.4. Outgassing behavior

In order to simulate the outgassing property, samples were irradiated with electron beam with a flux of 6 MW/m^2 for 30 s. After irradiation, the surface temperature of BM and CM is 1320, 1210 °C respectively and both of them show no crack. The residual gas analysis (RGA) is carried out before and after irradiation as shown in Fig. 9. It is observed that the outgassing properties of two samples have no difference before irradiation. After irradiation, however, the emissions of H_2 (mass numbers 2), H_2O (mass numbers 18), CO (mass numbers 28), especially CO_2 (mass numbers 44) of BM is much less than that of CM. The lowering of emissions may be due to two reasons: Compared with CM, BM has compact fine-grained structure with uniform dispersion of carbides and low porosity, which leads to higher surface energy resulting in adsorbtion of much more emitting gases after irradiation. On the other hand, BM has low reactivity of carbon with H_2O or O_2 (see Figs. 6 and 7). It is observed that almost no CO_2/S emitted from BM after irradiation.



(a) BM (b) CM

Fig. 8. SEM surface graphs of composites after oxidation at 1200 °C for 85 min.

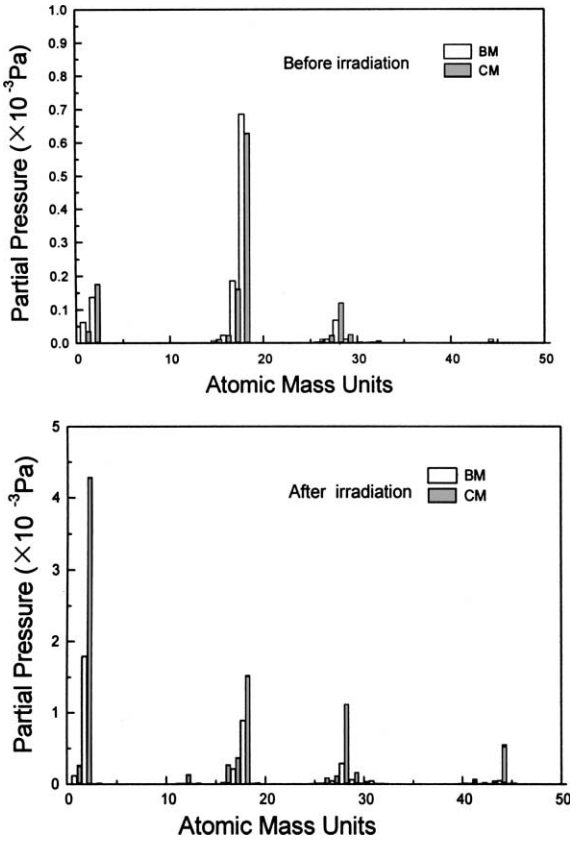


Fig. 9. QMA results before and after irradiation.

4. Conclusions

In the present work, fine-grain doped graphite, which possesses excellent physical and mechanical properties, oxidation resistance and outgassing property, was prepared by ball-milling dispersion method (BM) for the first time. The following are the main results:

(1) For fine-grain doped graphite prepared by the ball-milling method, small carbide particles (about 100–300 nm) are dispersed homogeneously in the graphite substrate, which consequently decreases the defects of materials.
(2) Because of this special structure, BM has not only high thermal conductivity, but also excellent physical and mechanical properties, especially high bending strength (116 MPa).
(3) The homogeneously dispersed small carbides in BM can quickly react with oxygen at elevated temperature and form a continuous and uniform borosilicate glass, which would effectively prevent oxygen from diffusing into the interior of the composite.
(4) The outgassing property of BM is superior to that of CM due to the compact fine-grained structure of BM, which can suppress the reaction of carbon with H_2O or O_2 much more effectively.

Acknowledgements

This research was partially supported by the Foundation of Nation Great Science Engineering.

References

[1] J. Roth et al., Nucl. Fusion Suppl. 1 (1991) 63.
[2] J. Roth et al., J. Nucl. Mater. 191–194 (1992) 45.
[3] A.Y.K. Chen et al., J. Nucl. Mater. 227 (1995) 66.
[4] P. Franzen et al., J. Nucl. Mater. 226 (1995) 15.
[5] J.P. Qian et al., J. Nucl. Mater. 191–194 (1998) 706.
[6] J. Roth et al., Phys. Scr. T 64 (1996) 67.
[7] M. Balden, Phys. Scr. T 81 (1999) 64.
[8] C. García-Rosales et al., J. Nucl. Mater. 290–293 (2001) 173.
[9] Dienst et al., J. Nucl. Mater. 174 (1990) 102.
[10] T. Kinoshita et al., Acta Mater. 45 (1997) 2001.
[11] J. Roth et al., J. Nucl. Mater. 191–194 (1992) 45.
[12] Y. Gotoh et al., J. Nucl. Mater. 196–198 (1992) 708.
[13] Q.G. Guo et al., J. Nucl. Mater. 290–293 (2001) 191.
[14] W.G. Zhang et al., Carbon 36 (1998) 1591.
[15] C.H. Wu et al., J. Nucl. Mater. 220–222 (1995) 864.