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The oxidation resistance improvement of matrix graphite of spherical fuel elements by slip-gelation process

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Abstract

A slip-gelation process was developed for improving the oxidation resistance of matrix graphite of spherical fuel elements. Functionally gradient SiC coating, which is a coating with a compositionally gradient SiC/C layer, was produced by this process by carefully controlling the experimental parameters. The influence of experimental conditions on coating properties was also studied. Oxidation tests showed that samples with dense gradient SiC coating have good oxidation resistance at high temperature in air and good thermal shock resistance. © 1998 Elsevier Science B.V.

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1. Introduction

Carbon and graphite materials are used as matrix materials for spherical fuel elements of the 10 MW High Temperature Reactor Test Module (HTR-10), which is under construction at the authors' institute, the Institute of Nuclear Energy Technology (INET), Tsinghua University. Graphite is stable to temperatures as high as 3000°C in inert or vacuum environment, but oxidizes in an oxidizing atmosphere at temperatures as low as 500°C. So under accidental air or water ingress conditions, it is possible that the matrix graphite of fuel elements will be destroyed by oxidation in such a manner that eventually the release of fission products is possible [1]. Therefore, the improvement of oxidation resistance of core carbon and graphite would be advantageous [2] for further improving the integrity of reactor cores of advanced high temperature gas-cooled reactors. Up to now, two kinds of methods have been proposed for protecting carbon and graphite materials [3]: dispersing fine particles of carbides and borides in carbon materials, and coating the carbon materials with a thin film of carbides or oxides. Dispersing fine particles of carbide and borides in carbon materials can act as inhibitive additives to prevent carbon materials from oxidizing, but these inhibitive additives decrease the oxidation rate by only a few orders of magnitude, so it is useful only for short period time and at temperature below 1000°C [4]. Oxidation resistant coatings are widely used method to protect carbon materials from oxidation.

The development of oxidation resistant coatings on carbon materials began in the early 1930s, when a patent was granted to National Carbon Company in the USA in 1934 [5]. Since then different kinds of coatings were proposed. In general, three types of coatings were developed: monolayer coatings, multilayer coatings and functionally gradient coatings. Monolayer and multilayer coatings usually have a clear interface between the coating layer and the substrate, thus the coating tends to crack or peel off due to the thermal stress induced at the interface caused by different thermal expansion coefficient between coating and substrate especially under thermal shock conditions. Therefore, in order to enhance the bonding between the coating layer and the substrate, and to minimize the thermal stress at the interface, the development of functionally gradient coating is essential. The material changes in composition from coating material to the material of substrate in gradient coating, thus thermal stress can be minimized.

Fujii et al. [6] reported that SiC/C gradient coatings were obtained by chemical vapor deposition (CVD) and chemical vapor impregnation (CVI) on graphite of type IG-110, which is a nuclear grade isotropic graphite used in

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the high temperature engineering test reactor (HTTR), HTTR is under construction at the Japan Atomic Energy Research Institute. Kim et al. [7] also reported that SiC/C gradient were synthesized by CVD process through adjusting the ratio of propane, methane and silicon tetrachloride in input gas. Yamamoto et al. [8] prepared SiC/C gradient coating for carbon–carbon composites by melt silicon infiltration and sol–gel process. This paper describes the preparation method of the functionally gradient SiC/C coating on graphite material and some results of oxidation tests.

2. Experimental

2.1. l. Materials

The matrix graphite of spherical fuel elements of HTR-10 was used in the experiments. The matrix graphite is made from 64 wt% natural flake graphite, 16 wt% petroleum coke graphite and 20 wt% resin binder. The manufacture process is shown in Fig. 1. The properties of the matrix graphite are summarized in Table 1.

The matrix graphite is cut into small specimens with size of 20 × 15 × 8 mm. The surface of the specimens is polished with 5.0 μm diamond paste, washed and dried. Si powder (mean diameter 1 μm), α-SiC powder (mean diameter 0.1 μm) and nuclear grade graphite powder (mean diameter 1 μm) are used in the coating process.

2.2. Slip-gelation process

A new process for preparing oxidation resistant coatings for carbon materials was developed from conventional melt infiltration process [9]. The preparation procedure is shown in Fig. 2. To produce a SiC primary layer, a slip which consists of α-SiC powder and graphite powder, is mixed and then milled with specified amount of binder and crosslinking agent. The slip is sprayed on the substrate, and dried. A packing slip which consists of α-SiC and Si powder, is mixed and milled with specified amount of binder and crosslinking agent. Then the substrate with primary SiC layer is dipped into packing slip, and in the meantime, the initiator is added to packing slip to make the slip gel. The gelation body is dried in an oven at a temperature between 50°C and 200°C. The oxidation resistant SiC/C coating is obtained by heating the packing body to a temperature between 1500°C and 1900°C for 1 to 3 h in a graphite resistant furnace.

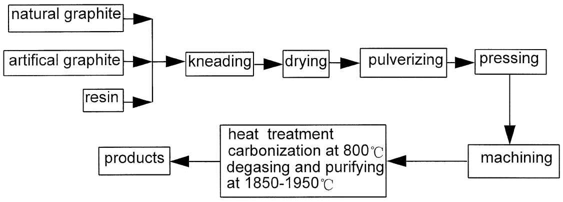


Fig. 1. Manufacture process of matrix graphite of fuel element.

Table 1
Characteristic data of the matrix graphite of HTR-10 fuel elements

Property	Unit	Value
Density	kg/m^3	1730
Ash content	$\times 10^6$	130–190
Li content	$\times 10^6$	0.007–0.023
Boron equivalent	$\times 10^6$	< 0.15
Thermal conductivity (at 1000°C)	W/m K	30
Anisotropy of thermal expansion $\alpha_\perp/\alpha_\parallel$		1.09

2.3. Coating characterization

Coating quality was assessed through examining the surface for cracks and pin holes by SEM. Elemental analysis of Si in the cross section of coating was obtained by electron probe microanalysis (EPMA). The crystalline phases of coatings were evaluated by X-ray diffractometer (XRD). The diffractograms were analyzed for interplanar distance ‘*d*’ values, which were compared with standard data to ascertain the nature of coated materials.

2.4. Thermal analysis

Thermogravimetric analysis was carried out in natural convection condition between 1000°C and 1200°C. The sample was supported in a silica basket hung on a Pt wire from a Mettler balance with a sensitivity of 0.1 mg, and mass changes were sampled as a function of time by a personnel computer. Thermal cyclic tests were carried out

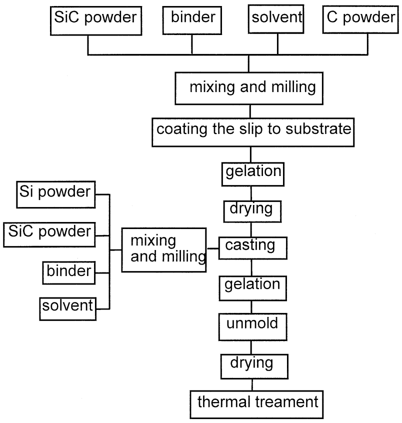


Fig. 2. Slip-gelation process.

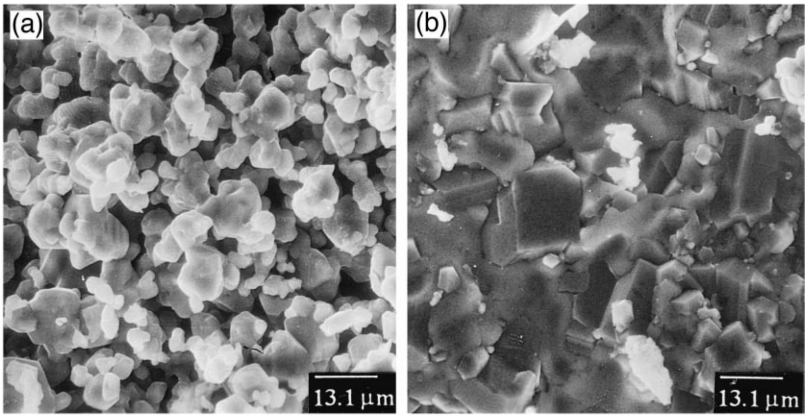


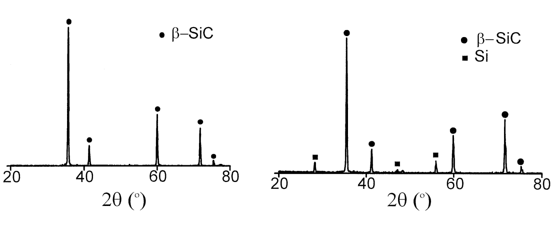
Fig. 3. Surface morphology of two typical samples.

in a molybdenum heater furnace from 1400°C or 1600°C to room temperature.

3. Results and discussion

3.1. Coating characterization

The surface morphology of samples obtained under different experimental conditions was observed by SEM to determine the quality of coatings. Fig. 3 shows the surface morphologies of two typical samples. Fig. 3(a) shows that spherical silicon carbide particles are formed and lots of pin holes exist in the coating. These pin holes may become the paths of oxygen which causes the oxidation of graphite. Fig. 3(b) indicates that prismatic silicon carbide particles are formed and the coating is dense. Experimental results also indicate that when thermal treatment temperature is below 1600°C, the color of the coating is green and only β-SiC was detected by XRD, but when thermal treatment temperature is above 1700°C, the coating is dark green. The change of the color seems to be caused by free silicon in the coating. Fig. 4 shows the XRD results of two typical samples. In Fig. 4(a) only β-SiC peak was observed, while Fig. 4(b) shows that Si peaks exist in the coating.



(a) (2 hours thermal treatment at 1500 ℃) (b) (2 hours thermal treatment at 1800 ℃)

Fig. 4. XRD results of two typical samples.

3.2. Concentration gradient of SiC in graphite

Typical characteristics of X-ray images of Si obtained by EPMA for the cross-section of a coating is shown in Fig. 5. This figure exhibits that the coating has a gradient in concentration of Si and no clear interface between dense SiC layer and graphite matrix is observed.

3.3. Oxidation behavior

Oxidation tests were performed on graphite, SiC coated graphite with pin holes (similar to sample a) and graphite with dense SiC coating (similar to sample b) at 1200°C. Fig. 6 shows the weight loss curve of these samples. The weight loss of graphite is near 60% after 1 h oxidation, while the weight loss of sample (a) is only 8% after 10 h oxidation, and no weight loss is observed for sample (b). This indicates that SiC coating greatly improves the oxidation resistance of graphite. The oxidation rate calculated from the weight loss data is shown in Fig. 7. It shows that the oxidation rate of graphite increases with the increasing

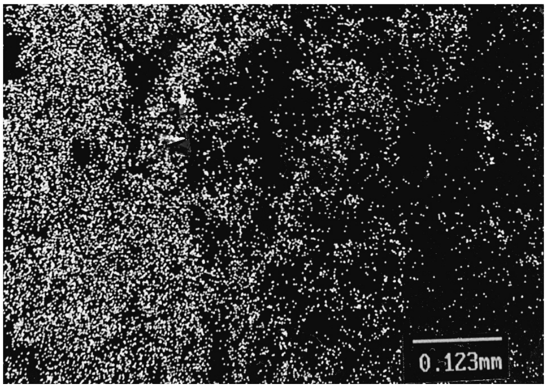


Fig. 5. Characteristic X-ray images of Si in the cross section of a typical sample.

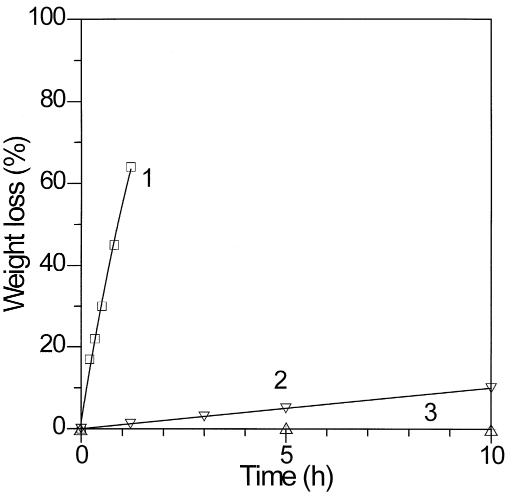


Fig. 6. Oxidation results of three samples.

of time, this increase is due to the surface area increasing caused by the oxidation of graphite. The oxidation rate of sample (a) does not change much. In this case oxygen first have to pass through the pin holes, then can oxygen react with graphite. The diffusion rate of oxygen passing through the pin holes is much less than that of chemical reaction rate at high temperature, therefore the overall reaction is limited by oxygen diffusion. As the size of the pin holes does not change much in oxidation, the overall reaction rate does not change much either.

The good oxidation resistance of sample (b) is attributed to dense SiC coating. Dense SiC coating totally separates oxygen from the graphite substrate, therefore dense SiC coating protect the graphite substrate from oxidization. It is known [10] that the oxidation of SiC at high oxygen partial pressure takes place according to the following reaction:

$$\mathrm{SiC(s)} + \tfrac{3}{2}\mathrm{O_2(g)} \rightarrow \mathrm{SiO_2(s)} + \mathrm{CO(g)}. \tag{1}$$

It is called passive oxidation. Silica, which is the product of passive oxidation, makes silicon carbide to be a very good antioxidation material, as silica exhibits the lowest oxygen diffusivity among the refractory oxides at high temperature. Therefore silicon carbide is the best candidate as an oxygen barrier [11]. In passive oxidation, different kinds of silica may generate, such as amorphous silica, α-crystobalite and β-crystobalite. It shows [12] that oxygen diffusion rate in α-crystobalite is much higher than that of amorphous silica, the oxygen diffusion rate of amorphous silica is higher than that of β-crystobalite. Amorphous silica may crystallize to β-crystobalite at high temperature.

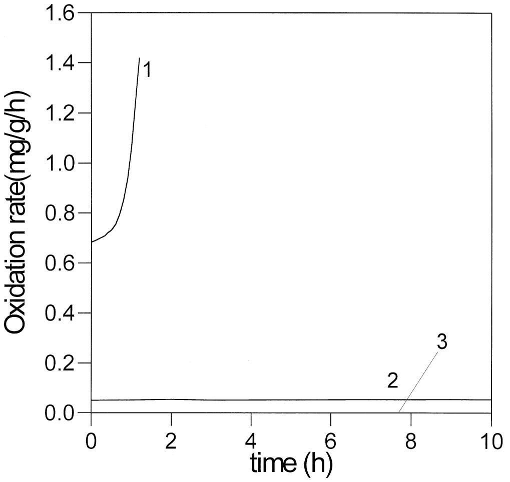


Fig. 7. Oxidation rate of three samples.

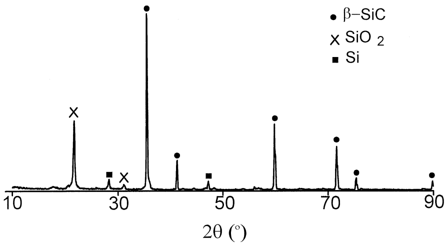


Fig. 8. X-ray diffractogram of one sample after oxidizing 200 h at 1400°C.

The XRD pattern of one sample which oxidizes for 200h at 1400°C is shown in Fig. 8. The figure shows that silica formed during oxidizing is α-crystobalite. This figure also indicates that strong β-SiC peaks still exist. This result suggests that silica film formed on the surface of the sample during oxidation is strongly limited in its thickness. This is very important for long term oxidation protection.

3.4. Thermal cyclic tests

The thermal cyclic tests were conducted in a molybdenum heater furnace. The procedure of thermal cyclic test is shown in Fig. 9. First the furnace was heated to a specified temperature (1400°C or 1600°C), then a sample was placed into the furnace, held for a specified time (1400°C for 10 h

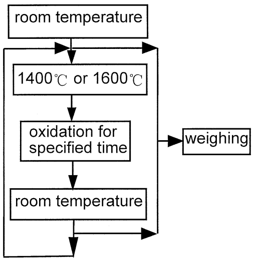


Fig. 9. Procedure of thermal cyclic tests.

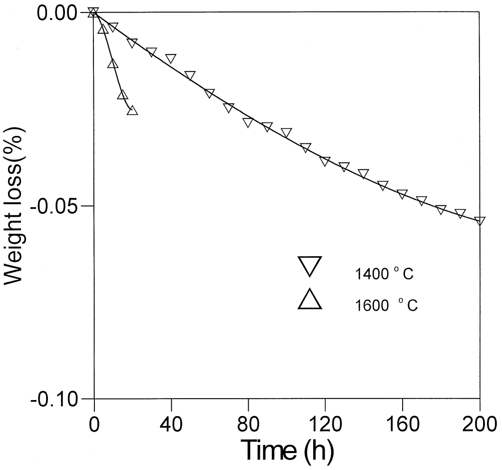


Fig. 10. Thermal cyclic results.

or 1600°C for 5 h), then taken out and cooled at room temperature. The surface temperature of the sample can fall down to 200°C within 5 min. After cooling, the sample was weighed and placed in the furnace again. It was found that the sample was totally intact after oxidizing for 200 h at 1400°C (20 thermal cycles) and 20 h at 1600°C (4 thermal cycles). As shown in Fig. 10 no mass loss could be measured after oxidation. The mass gain is due to the change of SiC to SiO_2 during oxidation [13]. After thermal cyclic oxidation, no cracks or chipping off was found at the surface of the sample. The high thermal shock resistance seems to be due to the concentration gradient of SiC layer which mitigates the thermal stress.

4. Conclusions

(1) Slip-gelation process has been developed to improve the oxidation resistance of matrix graphite of HTR-10's fuel elements. Dense gradient SiC coating can be obtained through controlling the experimental parameters.

(2) The oxidation behavior of matrix graphite with or without coating has been studied. It shows that coating can greatly improve oxidation resistance of graphite, and the dense coating can protect graphite from oxidizing at high temperature. XRD results shows that silica film formed during oxidation is very limited in its thickness.

(3) Thermal cyclic tests show that samples have good thermal shock resistance. The high thermal shock resistance seems to be due to the compositionally gradient SiC/C layer, which alleviates the thermal stress.

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