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The primary results for the mixed carbon material used for high flux steady-state tokamak operation in China

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Abstract

Several types of carbon mixed materials have been developed in China to be used for high flux steady-state tokamak operation. Performance evaluation of these materials is necessary to determine their applicability as PFCs for high flux steady state. This paper describes the primary results of carbon mixed materials and the effects of dopants on properties are primarily discussed. Test results reveal that bulk boronized graphite has excellent physical and mechanical properties while their thermal conductivity is no more than 73 W/m K due to the formation of a uniform boron–carbon solid solution. In case of multi-element doped graphite, titanium dopant or a decreased boron content is favorable to enhance thermal conductivity. A kind of doped graphite has been developed with thermal conductivity as high as 278 W/m K by optimizing the compositions. Correlations among compositions, microstructure and properties of such doped graphite are discussed. © 2001 Published by Elsevier Science B.V.

Keywords: Material mixing; Carbon

1. Introduction

A tokamak device named HT-7U is being designed and is under construction in China. The device is designed to operate at experimental conditions of high flux steady state with long duration discharge. The operation conditions of high flux steady state impose severe requirements on wall materials [1–4]. These wall materials have to fulfill several criteria: high thermal conductivity [5–7] to remove the heat deposited on the surface of wall materials, large thermal shock resistance [8] to withstand thermal damage due to thermal stress, fine-grain structure with low porosity to reduce hydrogen inventory and the degradation of properties, and a favorable behavior concerning resistance to physical sputtering, chemical erosion and RES [9,10].

Mixed carbon materials have been selected as candidates for first wall plasma facing materials, which can

be produced by doping some elements like B, Si, Ti into carbon substrate. The doped carbon materials have not only improved physical, thermal and mechanical properties, but also a behavior of reduced chemical erosion and RES at high temperatures [11,12]. Before such materials are practically applied in the tokamak device as plasma facing components, substantial R&D [13–15] is needed to evaluate some critical properties and elucidate the correlation between performance and microstructure of carbon mixed materials.

Although mixed carbon materials are promising candidates for PFCs, the addition of dopants to carbon will affect the properties of the pure materials. At elevated temperatures, diffusion, segregation, sublimation and phase transitions would take place [16]. To R&D plasma facing wall materials for high flux steady-state operation, these effects should be carefully taken into account [17]. This paper describes the primary results of the carbon mixed materials for steady-state tokamak operation. Primarily, the aim of this paper is to discuss the effect of dopants on properties and microstructure, and the correlation between properties and microstructure as well. The results presented in this paper are

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considered to represent only partially the experimental investigation that is still in progress.

2. Experimental

2.1. Preparation of materials

Several kinds of carbon mixed carbon materials have been developed in the Institute of Coal Chemistry, Chinese Academy of Sciences (ICC, CAS). These materials include bulk boronized graphite using B_4C as additives, boronized graphite using boron substituted mesophase pitch as binders and multi-element doped graphite with the additions of boron carbide, silicon and titanium. They were produced by hot-pressing methods under a pressure of 30 MPa and heat-treatment temperatures varying from 2200°C to 2600°C depending on their compositions.

Atomically distributed boronized graphite was prepared with boron substituted mesophase pitch as binder and coke powders as fillers. Boron substituted mesophase pitch (BSMP) was synthesized by copyrolysis of a filtered coal tar pitch with a borane complex. BSMP together with coke powders were ground in a ball mill and the mixture was heat-pressed under 30 MPa and the heat-treatment temperature was no more than 2200°C. The content of boron in such doped graphite was 2 wt%.

2.2. Investigation of properties and microstructure

Investigation of properties and microstructure of the mixed carbon materials were performed using different methods. Thermal conductivity was measured by laser flash. X-ray diffractometer with $Cu K_\alpha$ radiation was used for primary structure characterization. SEM and optical microscopes were used to observe surface and fracture topography. Open porosity was measured by determining pore volume of water which filled the open pores of the samples. Pore structure is detected by Quantachrome Autoscan Mercury Porosimetry. The definite content and the chemical state of each element after high temperature heat treatment were specified by XPS experiments.

3. Result and discussion

3.1. The effects of dopants on properties and microstructure of carbon mixed materials

3.1.1. Bulk-boronized graphite using B_4C powders as additives

Table 1 lists the properties of the bulk-boronized graphite and also pure graphite in order to have a comparison. Compared with pure graphite, the boronized graphites possess characteristics of excellent physical and mechanical properties in all cases. These characteristics can be summarized as high density and mechanical strength, low open porosity and electrical resistivity. Nevertheless, a tendency towards decreasing thermal conductivity is also observed with the increase of B_4C content. In the case of BDG-10, its thermal conductivity is as low as 36 W/m K, which is only one half of that for pure graphite. As thermal conductivity is an important parameter influencing the thermal erosion behavior and thermal stresses which will dominate the lifetime and reliability of PFCs, the low thermal conductivity of the boronized graphite will limit their application as plasma facing materials for high flux steady-state tokamak operation, though chemical erosion behavior was greatly improved due to the doping of boron or boron carbide [18].

To understand the nature of low thermal conductivity of boronized graphite, one should have more insight into the effects of B_4C dopant on the evolution of property and microstructure during heat-treatment at high temperatures up to 2400°C. Boronized graphites formed by a strong diffusion of B_4C particles in the carbon substrate during heat-treatment. In the temperature range of 1600–2100°C, diffusion of boron atoms at the surface of the graphite crystal led to the formation of a perfect graphitic structure [19]. In this stage B_4C acts as a catalyst to accelerate the graphitization of carbon substrate and the feature in this stage is of decreased interlayer spacing (d_{002}) and a significant increase of crystal thickness L_c . In the temperature range of 2100–2400°C, boron atoms replace the carbon atoms in graphite crystal lattice and a uniform boron–carbon solid solution phase is formed [20]. Although the boron content in the boron–carbon eutectic solid solution is no more than 1% (wt), it

Table 1
Properties of bulk-boronized graphite

Material	B_4C content (wt%)	Density (g/cm^3)	Open porosity (%)	Electrical resistivity ($\mu\Omega m$)	Bending strength (MPa)	Thermal expansion coefficient ($10^{-6}/K$)	Thermal conductivity (W/m K)	Grain size (μm)
Graphite	0	1.83	10.0	12.4	34	4.5	76	33
BDG-5	5	1.97	6.9	7.5	53	4.2	73	31
BDG-7	7	1.99	6.4	6.7	74	3.9	44	37
BDG-10	10	2.04	5.3	6.4	81	3.7	36	40



Fig. 1. Topography of fractured cross-section of BDG-10.

has a great effect on reducing the thermal conductivity of boronized graphites due to the introduction of defects in graphite lattice leading to increased phonon scattering. With increasing B_4C content, those B_4C additives precipitate, segregate and locate mainly on the grain boundaries (Fig. 1), resulting in more and more imperfection in graphitic structure. This may be responsible for the further reduction of thermal conductivity. On the other hand, the large size of B_4C particles change the failure mode from viscoelastic to brittle fracture, and the distribution of dopant becomes inhomogeneous. It was proposed by Hirooka et al. [21] that boron atoms act as trapping centers for interstitial carbon atoms. Such a process could possibly lead to a reduction in the interstitial carbon diffusion rate. In order to influence most effectively the migration and recombination of the interstitials, the dopants should be distributed on atomic scale. Hence, a fine grain structure or atomic dispersion of dopants would be advantageous to minimize the amount of eroded material and to reduce the RES yield.

3.1.2. Atomically distributed boronized graphite

In order to prepare boronized graphite with the boron atoms distributed on an atomic scale, boron substituted mesophase pitch has been synthesized. Copolyrolysis of a filtered coal tar pitch with a borane complex resulted in the formation of the boron substituted mesophase pitch, in which boron atoms have re-

acted into the polyaromatic molecule. Boronized graphites were produced utilizing the boron substituted mesophase pitch as binder and because the relatively low heat-treatment temperature no more than 2100°C , the frame characteristics of polyaromatic molecule of the boron substituted mesophase pitch were kept and boron atoms in doped graphite distributed on atomic scale. The content of boron in the doped graphites was 2 wt%. The properties and microstructure of such materials were preliminarily investigated.

A more substantial change in microstructure of the doped graphite is achieved using boron substituted mesophase pitch as binders and as boron source. Optical observation shows that a dense, uniform and homogeneous texture of BPDG-02 was obtained.

The change of the microstructure goes along with a significant increase of physical properties, especially density and strength (shown in Table 2). Investigations of thermal properties of such doped graphite are in progress in order to have a comparison with other kinds of doped graphites and the results will be reported later.

3.1.3. Multi-element doped graphite with boron carbide, silicon and titanium

Multi-element doped graphite with boron carbide, silicon and titanium were prepared and their properties are given in Table 3. For these doped graphites, similar physical and mechanical properties were observed except for a large difference in their thermal conductivity. In the case of BSDG-105, the addition of silicon together with boron carbide has no evident effect on enhancing thermal conductivity comparing with BDG-10. For BTDG-105, however, the thermal conductivity is almost two times that for BDG-10. The effect of using titanium as additional filler to enhance thermal conductivity can be attributed to the formation of TiB_2 [22] by the reaction of Titanium with boron atoms which have replaced the carbon atoms in graphitic crystal lattice during heat-treatment at high temperatures, decreasing the imperfection of graphitic structure. For BSDG-33, thermal conductivity reached 100 W/m K . The high thermal conductivity of BSDG-33 might be attributed to the small amount of boron content in doped graphite and the introduction of Si dopant.

In general, the dopants, the distribution of dopants, graphitic structure and size of graphite crystal control

Table 2

Properties of the boronized graphite (BPDG-02) prepared with boron substituted mesophase pitch and carbon-mixed materials (STDG-315)

Material	Boron/dopant content (wt%)			Density (g/cm^3)	Electrical resistivity ($\mu\Omega \text{ m}$)	Bending strength (MPa)	Compressive strength (MPa)
	B	Si	Ti				
BPDG-02	2			1.99	6.61	57	122
STDG-315		2.5	15	2.11	1.96	49	95

Table 3

Properties of the doped graphite with the elements of boron carbide, silicon and titanium

Material	Dopant content (wt%)			Density (g/cm ³)	Open porosity (%)	Bending strength (MPa)	Thermal expansion coefficient (10 ⁻⁶ /K)	Thermal conductivity (W/m K)
	B ₄ C	Si	Ti					
BSDG-105	10	5	0	2.10	4.7	103	3.1	40
BSDG-33	3	3	0	2.00	6.5	–	–	100
BTDG-105	10	0	5	2.17	4.0	104	3.3	73

the comprehensive properties. For R&D of PFCs, one should take these factors into account. Analysis of the above data can lead to a conclusion that optimized compositions of a small amount of boron and introduction of silicon and titanium elements are advantageous to improve thermal conductivity.

3.2. Property and microstructure analysis of doped graphite STDG-315 with high thermal conductivity

A kind of doped graphite named STDG-315 has been developed in the ICC, CAS. Its physical and mechanical properties were listed in Table 2. Fig. 2 shows the dependence of thermal conductivity on temperatures for STDG-315. Its thermal conductivity is high up to 278 W/m K at room temperature, and has a value of 176 W/m K at 800°C.

Pore structure of the doped graphite in Fig. 3 demonstrates that pores existing in the doped graphites are very small and pore diameter distributed mainly in the range of 20–50 nm. The pore characteristic is favorable to reduce hydrogen retention and prevent the serious degradation of thermal properties due to radiation [23].

The high performance of STDG-315 is closely related with their composition and microstructure. STDG-315 is fully graphitized with d_{002} reaching the minimum

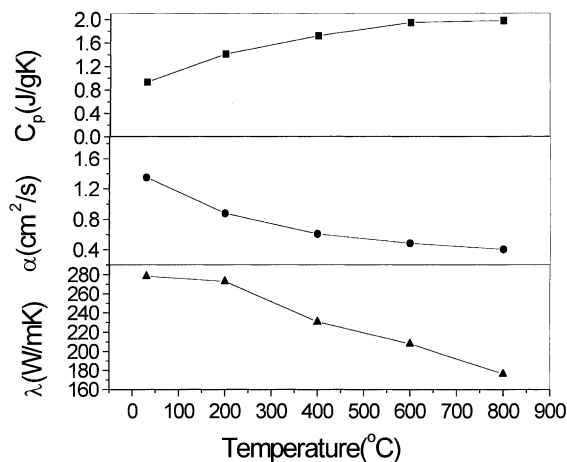


Fig. 2. Temperature dependence of thermal conductivity of STDG-315.

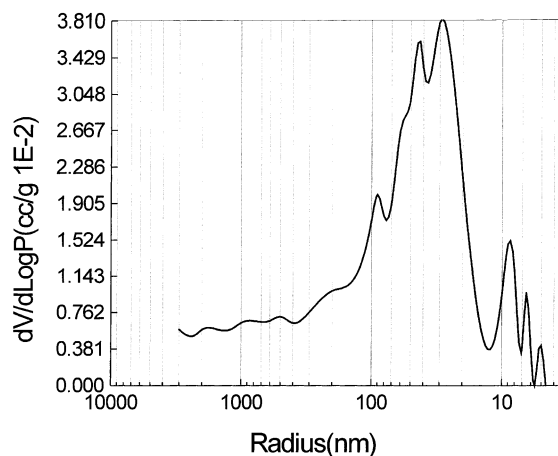


Fig. 3. Pore structure of STDG-315.

value of 3.3498 nm and large size of graphite crystal (L_c is about 96 nm). A dense texture has been observed (Fig. 4(a)) and a ratio of 92% to theoretical density (2.33 g/cm³) is obtained. Enrichment of dopants is also observed in Fig. 4(b) (specified by A) which can be attributed to the diffusion and depletion of dopants at high temperatures around 2600°C. Phase composition of the doped graphite was determined with X-ray diffraction pattern. XRD analysis demonstrates shows that there are only diffraction peaks for graphite and TiC. There is a complex interaction between the dopants of silicon and titanium and carbon substrate in STDG-315. The dopants mainly act as catalysts to accelerate the graphitization of carbon substrate during the heat-treatment at high temperature. When introduced into carbon substrate, the additives of silicon and titanium have reacted with carbon to form silicon carbide and titanium carbide. When the heat-treatment temperature is around 2600°C, almost all silicon carbide decomposes into silicon and carbon and the dopant of silicon will deplete out of the doped graphite. The content of silicon in STDG-315 decreases from original content of 2.5 wt% to about 0.2 wt%, which is determined by XPS experiment. Although this process has provided driven force for the graphitization of carbon substrate, the depletion of silicon will result in the formation of cavities (Fig. 5). To prevent the degradation of performance of doped

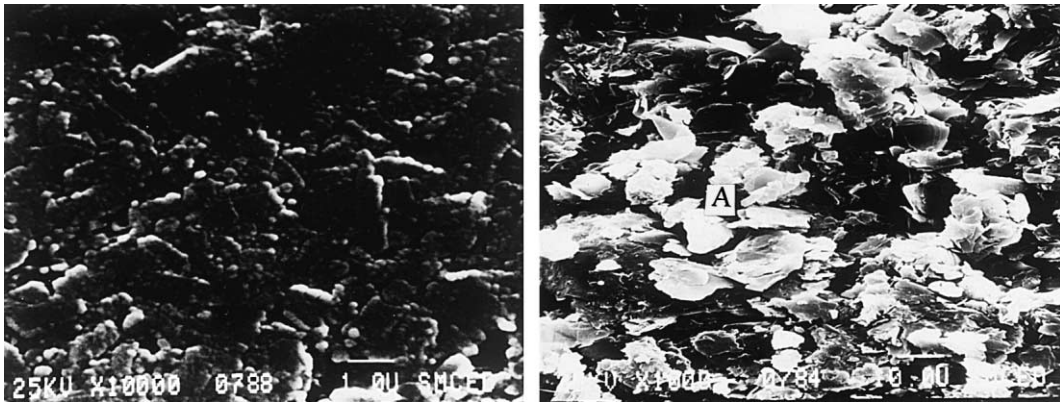


Fig. 4. Microstructure of STDG-315 (a) surface topography; (b) dopants distribution.

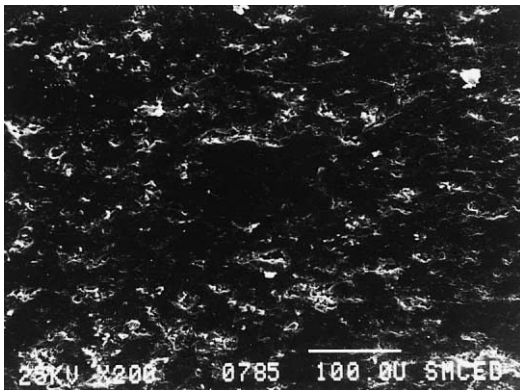


Fig. 5. Cavity formed due to depletion of dopants.

graphite, the content of silicon and the heat treating temperatures should be strictly controlled.

4. Conclusion

Carbon mixed materials for high flux steady-state toakmak operation have been developed in China. This paper described the primary results of carbon mixed materials and discussed the correlation among composition of dopant contents, distribution of dopants and microstructure and preparation parameters. It can be summarized as follows:

1. Bulk boronized graphite has excellent physical and mechanical properties while its thermal conductivity is no more than 73 W/m K due to the formation of a uniform boron-carbon solid solution that has formed.
2. Atomically distributed boronized graphite was developed using boron substituted mesophase pitch as binders as boron source.
3. In case of multi-element doped graphite, titanium additives or a decreasing boron content is favorable to enhance thermal conductivity.

4. A kind of doped graphite has been developed whose thermal conductivity amounts to 278 W/m K by optimizing the compositions.
5. To develop carbon mixed materials for high flux steady-state toakmak operation, compositions of dopant contents, distribution of dopants and microstructure should be further optimized.

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