Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 348 (2006) 108–113

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Study on the structural evolution of modified phenol–formaldehyde resin adhesive for the high-temperature bonding of graphite

Jigang Wang [a,*], Nan Jiang [b], Quangui Guo [c], Lang Liu [c], Jinren Song [c]

[a] *Department of Materials Science and Engineering, Southeast University, Nanjing, Jiangsu 210096, PR China*
[b] *Institute of Theoretical and Computational Chemistry, Nanjing University, Nanjing 210093, PR China*
[c] *Institute of Coal Chemistry, Chinese Academic of Sciences, Taiyuan 030001, PR China*

Received 7 May 2005; accepted 10 September 2005

Abstract

A novel adhesive for carbon materials composed of phenol–formaldehyde resin, boron carbide and fumed silica, was prepared. The adhesive property of graphite joints bonded by the above adhesive treated at high-temperatures was tested. Results showed that the adhesive was found to have outstanding high-temperature bonding properties for graphite. The adhesive structure was dense and uniform even after the graphite joints were heat-treated at 1500 °C. Bonding strength was 17.1 MPa. The evolution of adhesive structure was investigated. The results indicated that the addition of the secondary additive, fumed silica, improved the bonding performance greatly. Borosilicate phase with better stability was formed during the heat-treatment process, and the volume shrinkage was restrained effectively, which was responsible for the satisfactory high-temperature bonding performance of graphite.

PACS: 82.35Gh

1. Introduction

With the advancement of the research in fusion, aerospace, metallurgy and other fields, high-temperature materials are being more and more widely used. Carbon material is one of the most important high-temperature materials due to its outstanding thermal and physical properties. Their brittleness, however, cause many difficulties during the production or machining of carbon material components with large size or complex shape. One of the effective and reliable methods is the joining technique. Many conventional methods such as riveting/bolting, threading, welding, brazing and so on [1–6], are used in the past for the joining of carbon materials. As to the riveting or bolting, drilling some holes in the materials and the excessive rivet force often causes the degradation of the joint. Although their machining precision is high, there often appear breakages of threaded joints. Welding, brazing and other methods need costly metals to activate the inert surface of the

---

[*] Corresponding author. Tel.: +86 25 83795745.
E-mail address: jigangwang@seu.edu.cn (J. Wang).

doi:10.1016/j.jnucmat.2005.09.008

carbon materials [7–9]. The joining of carbon materials is still a research focus [10,11].

The high-temperature adhesives (HTAs) are one of the most promising methods because the loading is borne by the whole bonding plane besides its convenient process [12]. Conventional HTAs are inorganic adhesives, especially the ceramic adhesives for their satisfactory heat-resistance. Because of the poor joining strength of the inorganic adhesives, they are always combined with other joining methods. In addition, the inorganic adhesives often restrain the exertion of the thermal and physical properties of the carbon materials. As a result, the application of the HTAs is limited to some extent.

The organic resin will convert into amorphous carbon with high heat-resistance and physicochemical compatibility to carbon materials to be joined. Recently, some new types of HTAs using organic resin as matrix are developed [12–14]. In our previous works, an HTA using phenol–formaldehyde resin as matrix and boron carbide as additives is prepared [15]. In this paper, a novel HTA is prepared by means of the addition of fumed silica, super-fine silicon dioxide, based on the above HTA. Compared with the primary adhesive, this novel adhesive exhibits improved adhesive properties. And the bonding structure experiencing high temperatures still keeps dense and uniform compared with that of joints bonded by the primary adhesive.

2. Experimental procedures

2.1. Raw materials

The phenol–formaldehyde (PF) resin with thermosetting property was selected as adhesive's matrix. The viscosity of the resin was 1.53 Pa s, and the solid content was 80 ± 3%. The carbon residue of the PF resin after being treated at 900 °C was 46.5%. As the starting materials, boron carbide (B_4C) powder had the size of 2.5–3.5 μm and the purity of 85%. The fumed silica (SiO_2) with the size of 20–40 nm and the purity higher than 99.5% was used as the secondary additive. Some properties of the graphite substrates to be bonded are listed in Table 1 [15].

Table 1
Properties of graphite materials for bonding

Character	Density (g/cm^3)	Flexural strength (MPa)	Compressive strength (MPa)
Isotropic	1.8	25	46

2.2. Preparation of HTA and graphite specimens

The novel HTA was prepared using PF resin as matrix and ceramic powders, a mixture composed of B_4C and fumed silica, as additives. For comparison, the pure PF resin and the primary HTA composed of PF resin and B_4C were also used to bond graphite substrates. For convenience, the HTAs were abbreviated as $PF + B_4C$ and $PF + B_4C + SiO_2$, respectively.

Graphite substrates were cut into cuboids and bonded by the above HTAs. The detailed procedures are consistent with Ref. [15]. The bonded graphite joints were heat-treated at different temperatures ranging from 400 °C to 1500 °C, and all bonded specimens were heat-treated at a given temperature for 2 h.

2.3. Testing and analysis

The bonding strength of graphite joints treated at different temperatures was tested by using universal testing machine at room temperature. The pressure load was borne on the one part of the joints. And the moving velocity of the indenting hammer was 1.5 mm/min with direction parallels to the adhesive interface, namely the shear plane [15].

The Infra-red (IR) microscope with the type of FTS-25PC was employed for the investigation of the structure evolution of $PF + B_4C + SiO_2$ adhesive. A JEOL SJM-35C Scanning Electron Microscope (SEM) system was also applied to investigate the structural morphology of the debonded section of the graphite joints.

3. Results and discussion

3.1. The bonding properties of HTA

The bonding strengths of the HTAs and the pure PF resin are tabulated in Table 2. It can be seen that all graphite joints treated at 200 °C have satisfactory bonding strength. The failure-sites of these joints are located in the graphite matrix, while the joint zone still keeps scatheless due to the outstanding adhesive properties of the PF resin. The data in Table 2 also indicate an obvious difference of the bonding strength with further increase of heat-treatment temperatures. After being treated at 1500 °C,

Table 2
The bonding strength of the graphite joints bonded by pure PF resin and HTAs treated at different temperatures (MPa)

Adhesives	The bonding strength of graphite joints treated at different temperatures (MPa)						
	200 °C	400 °C	600 °C	800 °C	1000 °C	1200 °C	1500 °C
PF resin	Failure of graphite	7.7	2.8	1.6	–	–	1.2
PF + B_4C	Failure of graphite	8.6	6.3	13.2	15.8	13.2	9.3
PF + B_4C + SiO_2	Failure of graphite	9.8	8.3	18.4	19.3	17.1	17.1

the PF resin's bonding strength drops to 1.2 MPa with the failure mode of cohesive breakage in the bonding cement, while the modified HTAs still show good bonding performance.

The data in Table 2 also show an obvious difference between the bonding strength of the specimens bonded by PF + B_4C and PF + B_4C + SiO_2 at higher temperatures, especially above 800 °C. The adhesive strength of PF + B_4C + SiO_2 is distinctly higher than that of PF + B_4C. Even when the treatment temperature is high up to 1500 °C, the bonding strength of graphite joints bonded by PF + B_4C + SiO_2 still keeps a rather high level of 17.1 MPa, and demonstrates the satisfactory effect of the addition of fumed silica.

3.2. The structural evolution of the HTAs

By means of the IR analysis, the structure evolution of PF + B_4C + SiO_2 is investigated, and the spectrum of the above HTA heat-treated at different temperatures is listed in Fig. 1. Because no standard pattern of B_4C is provided, the B_4C reagent is analyzed separately (Fig. 1(a)). According to Fig. 1(a), 1076 cm^{-1}, 843 cm^{-1}, 702 cm^{-1} and 605 cm^{-1} can be attributed to the characteristic peaks of B_4C additive. Although the added amount of the fumed silica is much less than that of B_4C, the peaks at 752 cm^{-1} and 428 cm^{-1}, which originate from the characteristic absorption of Si–O–Si bond, are still shown on the IR patterns (Fig. 1(b)). Besides, it is worth noting that the peak at 1076 cm^{-1}, the characteristic absorption of B_4C, shifts to 1068 cm^{-1}. Because the stretching vibration of Si–O usually appears at 1060 cm^{-1} with a strong absorption, one can confirm that the absorption shift from 1076 cm^{-1} to 1068 cm^{-1} is the result of superposition of the above two characteristic absorptions. It can be seen from Fig. 1(b) that the organic groups of PF resin (1593 cm^{-1}, 1510 cm^{-1}, 1475 cm^{-1}, 1454 cm^{-1}, 1211 cm^{-1}, etc., which represent aromatic rings, C–H bond, and phenolic hydroxyl, respectively) are clearly shown after being cured at 200 °C. At 200 °C, all adhesives possessed outstanding bonding strength due to the excellent adhesive performance of the PF resin.

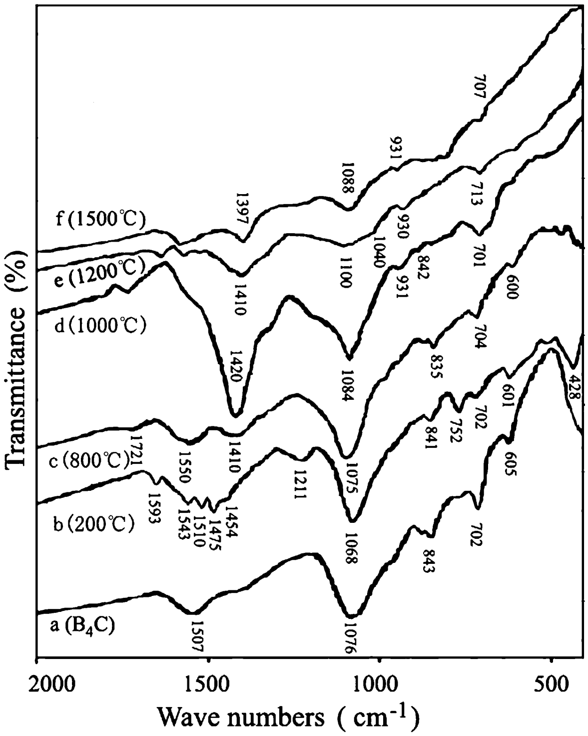

Fig. 1. IR transmission spectrum of PF + B_4C + SiO_2 adhesive heat-treated at different temperatures (a) B_4C reagent, (b) 200 °C, (c) 800 °C, (d) 1000 °C, (e) 1200 °C and (f) 1500 °C.

With further increasing of heat-treatment temperature, distinct differences of the bonding strength are shown according to different adhesives. When the heat-treatment temperatures increase from 200 °C to 800 °C, the peaks of organic groups almost disappear. Such results indicate that some organic groups are decomposed and released out from the bonding cement in the form of CH_4, CO, CO_2, H_2O and so on, and the PF resin nearly converts into amorphous carbon [16]. So, the bonding strength of pure PF resin is only 1.6 MPa at 800 °C mainly due to the drastic volume shrinkage.

Table 3
The viscosity values of B_2O_3 at different temperatures [19,20]

Temperature (°C)	600	700	750	800	900	1000	1100	1115
Viscosity (Pa s)	480	85	43.6	26	12	7.4	4.3	3.5

As to the modified HTAs, data in Table 2 show that the graphite joints still posses satisfactory bonding strength at higher temperatures. Because of the addition of fillers, the relative amount of resin is reduced, which benefits in decreasing the volatilization loss of small molecules. Besides, it is worth pointing out that the characteristic peak of B_2O_3, the wide absorption at $1410\ cm^{-1}$, appears at 800 °C (Fig. 1(c)). The appearance of B_2O_3 demonstrates the occurrence of the modification reactions between B_4C and the resin's volatiles, and the gradual exertion of modification effects occurs at elevated temperatures. The modification reactions can be expressed as follows [17]:

$$B_4C(s) + 6CO(g) = 2B_2O_3(l) + 7C(s)$$

$$B_4C(s) + 6H_2O(g) = 2B_2O_3(l) + C(s) + 6H_2(g)$$

Due to the modification reactions, some volatiles convert into amorphous carbon and remain in the bonding cement [15]. So the integrity of the skeleton of adhesive cement, namely the resin carbon, is improved effectively. Besides, the reference indicated that the chemical bonding force might be introduced at bonding interface because of the satisfactory wetting ability of B_2O_3 to graphite [18]. So, compared to pure PF resin, the bonding strength of HTAs is progressed obviously. When the heat-treatment temperature reaches 1000 °C, Fig. 1(d) shows that the absorption peak of $[BO_3]$ at $1410\ cm^{-1}$ increases markedly. This illustrates that the oxidation reaction of B_4C, namely the modification reaction, continues to occur to some extent. This result is consistent with our previous result [15]. The increasing of B_2O_3 benefits in the enhancement of the chemical bonding force between the bonding cement and graphite substrate [18]. So the bonding strength of modified HTAs keeps on increasing and reaches 15.8 MPa and 19.3 MPa, respectively.

But when the treatment temperatures are above 1000 °C, data in Table 2 show that the bonding strength of $PF + B_4C$ decreases again. From Fig. 1, it can be seen that, when the temperatures are above 800 °C [16], there is little change of amorphous carbon, which is the carbonization production of resin. So the re-appearance of volume shrinkage is mainly due to the volatilization and thermal reduction of B_2O_3 by carbon. Table 3 lists the viscosity values of B_2O_3 at different temperatures [19,20]. With the decrease of viscosity at the elevated temperatures, the volatilization loss velocity of B_2O_3 increases. Besides, the thermal reduction reactions occurring at higher temperatures will also destroy the integrity of bonding structure. The main mode of thermal reduction can be expressed as follows: $2B_2O_3 + 7C = B_4C + 6CO$ [15]. So there exists a demand to further improvement of the HTAs properties if the adhesive structures at high temperatures can be controlled properly.

The fumed silica is a special modified material with nano-size and exhibits a series of outstanding properties due to its size effect. Because of the particle strengthening effect of the fumed silica, the mechanical property is increased effectively. Besides, H-bonding force between PF resin matrix and the fumed silica can be formed due to the active Si–O function group on the surface of fumed silica. In other words, the cohesive force of the adhesive cement is strengthened at the initial bonding process. As a result, the bonding strength of $PF + B_4C + SiO_2$ is higher than that of $PF + B_4C$ adhesive from the beginning.

The main aim of adding fumed silica is to modify the microstructure of bonding cement at higher temperatures. As to the satisfactory bonding strength of $PF + B_4C + SiO_2$, one can confirm that some new structures are formed in the novel adhesive cement, being responsible for further improvement of the high-temperature bonding properties. An evidence is the disappearance of the absorption peak at $428\ cm^{-1}$, which stands for the deformation bending vibration of Si–O–Si bond, on the IR spectrum of 800 °C (Fig. 1(c)). The disappearance of peak at $428\ cm^{-1}$ is probably caused by substituting boron atom for silicon atom. Correspondingly, a new adsorption peak at $931\ cm^{-1}$, the characteristic peak of $\equiv$B–O–Si$\equiv$, appears on the IR pattern (Fig. 1(d)). This indicates that the fumed silica, the super-fine SiO_2, enters into the glassy structure of $[BO_3]$. In other words, a borosilicate composite phase is formed in the adhesive structure.

When the heat-treatment temperature reaches 1200 °C, in addition to the existence of the characteristic absorption of ≡B–O–Si≡ at 930 cm^{-1}, it is worth noting that the absorption peak of Si–O bond divides into two peaks, 1040 cm^{-1} and 1100 cm^{-1}, on the IR spectra (Fig. 1(e)), namely the red-shift and the blue-shift. The boron atom is a kind of special atom with deficient-electron property and it's electron-negativity value is higher than that of the silicon (2.0 and 1.8, respectively), so there exists the electron attraction between [BO_3] and [SiO_4] (Fig. 2). As a result, during the formation of the borosilicate glass, the electron density of the Si–O bond, which is close to the boron atom, decreases to some extent, while that of the neighboring Si–O bond is increased. So the original absorption peak of Si–O bond divides into two peaks at 1100 cm^{-1} and 1040 cm^{-1}, respectively. Such phenomenon indicates the degree of formation of borosilicate glass progressing at 1200 °C. The viscosity, stability and heat-resistance of glassy borosilicate are higher than that of glassy borate [21], so the bonding strength of graphite joints bonded by $PF + B_4C + SiO_2$ is higher than that of $PF + B_4C$ at higher temperatures (Table 2).

When the treatment temperature reaches 1500 °C, the B–O's characteristic peak at 1397 cm^{-1} and the superposition absorptions peaks of B_4C and fumed silica at 1088 cm^{-1} are still existing with some strength. Besides, the existence of Si–O–B at 931 cm^{-1} indicates that the partial borosilicate glass still exists in the bonding cement to some extent. Such phenomena illustrate the structure of graphite joints bonded by $PF + B_4C + SiO_2$ adhesive keeps a good relative stability in a wide temperature range. Correspondingly, compared to the adhesive structure of $PF + B_4C$ treated at 1500 °C (Fig. 3) [15], the de-bonded section's morphology of graphite joints bonded by $PF + B_4C + SiO_2$ still keeps dense and uniform structure (Fig. 4).

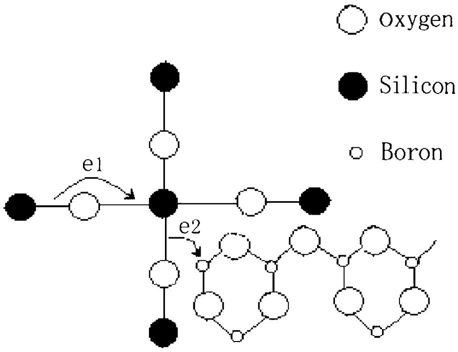

Fig. 2. Electron attractive interaction between [BO_3] and [SiO_4].

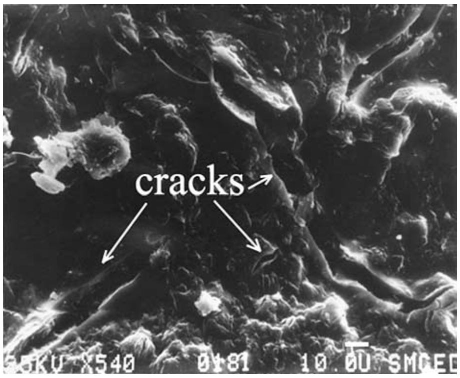

Fig. 3. The morphology of de-bonded section of graphite joints bonded by $PF + B_4C$ at 1500 °C.

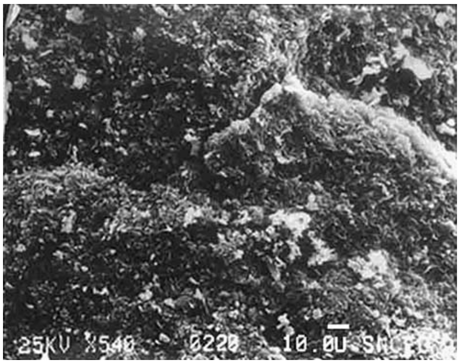

Fig. 4. The morphology of de-bonded section of graphite joints bonded by $PF + B_4C + SiO_2$ at 1500 °C.

4. Conclusion

The new HTA possesses satisfactory high-temperature bonding properties for graphite. At the heat-treatment temperature of 1500 °C, the bonding strength of graphite joints is still 17.1 MPa with the dense and uniform adhesive structure. The microstructural analysis indicates that the addition of mixture additives, boron carbide and fumed silica, improves the high-temperature bonding of graphite effectively.

(1) Through some reactions of boron carbide with volatiles released from resin, some parts may be converted into amorphous carbon and remain in the adhesive cement, so that the volume shrinkage below 800 °C can be controlled effectively. The formation of boron oxides also benefits in the improvement of bonding properties through the introduction of chemical bonding between adhesive cement and graphite substrate.

(2) The addition of the fumed silica improves the graphite joints' bonding properties: the bonding strength is improved due to the particle strengthening effect and the enhancement of cohesive force. Moreover, borosilicate phase with better viscosity, stability and heat-resistance is formed above 800 °C, and the adhesive structure still remains dense and uniform even after the joints are treated at 1500 °C.

Acknowledgements

This work is supported by 'National Natural Science Foundation of China' (Project No. 50303004), 'Jiangsu Province Natural Science Foundation' (Project No. BK2004409) and 'Education & Research Foundation for Outstanding Young Teacher by Southeast University' (Project No. 4012001003).

References

[1] R. Weiss, W. Huettner, A. Cloos, in: Proceedings of the International Conference on Carbon, Organized by Groupe Francais D'Etude Des Carbones (GFEC), France, Paris, 1990, p. 226.

[2] Y. Kubota, N. Noda, S. Sato, J. Plasma Fusion Res. 3 (2000) 246.

[3] G.R. Sheng, in: Proceeding of 21st Biennial Conference on Carbon, American Carbon Society, The State University of New York Buffalo's School of Engineering and Applied Sciences, 1993, p. 679.

[4] J.Y. Liu, S. Chen, B.A. Chin, J. Nucl. Mater. 212–215 (1994) 1590.

[5] V. Barabash, M. Akiba, A. Cardella, I. Mazul, B.C. Odegard Jr., L. Plöchl, R. Tivey, et al., J. Nucl. Mater. 283–287 (2000) 1248.

[6] M. Salvo, M. Ferraris, P. Lemoine, M. Appendino Montorsi, M. Merola, J. Nucl. Mater. 233–237 (1996) 969.

[7] S. Ishiyama, Method of joining graphite and metallic materials with a material comprising titanium, nickel and copper, US Patent 4989773, 1991.

[8] M. Salvo, P. Lemoine, M. Ferraris, J. Nucl. Mater. 226 (1995) 67.

[9] A.D. Ivanov, S. Sato, Le.G. Marois, J. Nucl. Mater. 283–287 (2000) 35.

[10] M. Merola, M. Akiba, V. Barabash, I. Mazul, J. Nucl. Mater. 307–311 (2002) 1524.

[11] B.C. Odegard Jr., C.H. Cadden, R.D. Watson, K.T. Slattery, J. Nucl. Mater. 258–263 (1998) 329.

[12] G.A. Kravetskii, L.T. Anikin, A.V. Demin, V.I. Kostikov, G.M. Butyrin, in: Proceeding of the 3rd European Workshop on High Temperature Materials, Stuttgart, Germany, 1995, p. 197.

[13] G.A. Kravetskii, L.T. Anikin, A.V. Demin, G.M. Butyrin, in: Proceeding of the 22nd Biennial Conference on Carbon, San Diego, USA, 1995, p. 798.

[14] H. Kakegawa, S. Otani, Y. Maeda, in: Proceeding of 18th Biennial Conference on Carbon, 1987, p. 231.

[15] J.G. Wang, Q.G. Guo, L. Liu, J.R. Song, Carbon 40 (2002) 2447.

[16] K.A. Trick, T.E. Saliba, Carbon 33 (1995) 1509.

[17] I. Ogawa, J. Ceram. Soc. Jpn. 94 (1986) 409.

[18] D.W. Mckee, C.L. Spiro, E.J. Lamby, Carbon 22 (1984) 507.

[19] Council of Editor (Ed.), Encyclopedia of Chemical Technology (Chinese), 12, Chemical Industry, Beijing, 1997, p. 572.

[20] Kirk–Othmer Encyclopedia of Chemical Technology, 3, Interscience, New York, 1964, p. 610.

[21] K. Kobayashi, K. Maeda, H. Sano, Y. Uchiyama, Carbon 33 (1995) 397.