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Effect of the evolution of phenol–formaldehyde resin on the high-temperature bonding

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ABSTRACT

The novel high-temperature adhesives (HTAs) were prepared using phenol–formaldehyde (PF) resin as matrix and elemental silicon or boron carbide as modification additives. The bonding properties of the above adhesives were investigated by the bonding experiment on graphite substrate. The graphite joints were heat treated at high temperatures ranging from 200 to 1500 °C. It was shown that the degradation and the content of PF resin had important influences on the bonding properties of the HTAs. The pyrolysis and degradation of the organic resin led to the drastic volume shrinkage and the decrease of mechanical strength of resin matrix. It is the main reason leading to the failure of the joints treated at high temperatures, especially in the range of 400–650 °C. It is concluded that the satisfactory bonding property of the novel organic resin matrix HTAs lies in two aspects: (i) the selection of additives with good modification effect, and (ii) the optimized ratio between resin matrix and modification additives.

1. Introduction

The joining qualities of the joints are extremely important for the application of instruments in safety. With the increasing application of materials in some severe environments such as high-temperature high-speed, high-pressure, high-erosion, etc., more and more strict performances of the joints are required. To realize the joining of some special materials including heat-resistant metals and ceramics employed at high temperatures, many methods have been attempted in the past decades [1–8]. However, some joining results are not satisfactory, especially for the joining of carbon/carbon (C/C) composite which has inert surface [6–8]. Dadras and Mehrotra investigated the joining of C/C composite using manganese (Mn), magnesium (Mg), and aluminum (Al) as joining interlayer [6]. Although the heat-treatment temperature was high up to 2000 °C, the produced double notching shear strength using Mn interlayer was very low, ranging from only 0.15 to 1.61 MPa at test temperatures of 1200–1400 °C. The joints with Al and graphite interlayer were even weaker, with strength of only 0.11 MPa or less. The usage of Mg interlayer to join C/C composite was also unsuccessful. The usage of adhesive is a popular joining technique and has wide applications in many fields. In the past, the high-temperature bonding has to depend on the inorganic adhesives due to their outstanding heat-resistance. But their plane adhesive strength is not satisfactory, especially for the materials with inert surface. So, the design and application of some special joining modes including bell and spigot joint are required. In addition, the deficiency in functional joining of inorganic high-temperature adhesives (HTAs) made against the exertion of thermal or electrical conductivity of the materials.

In the recent years, some novel HTAs using organic resin as matrix were developed [3–5]. Usually, the application temperatures of organic resins are limited below 300 °C due to their poor heat-resistance. Even for some heat-resistant resins, the application temperatures are still limited below 600 °C. The inevitable pyrolysis reactions occurring at high temperatures result in the disintegration and degradation of organic resin. But the residue derived from the pyrolysis of organic resin tends to conserve the cross-linked structure and possesses outstanding thermophysical properties [9]. So, the organic resin also can be successfully employed in high-temperature fields. For examples, they can be used as the impregnants of carbon/carbon composites, as well as the matrix of thermal ablation materials [10]. On the basis of the above research and application, some HTAs composed of organic synthetic resins and modification additives were prepared. The above mentioned high-resistant materials including ceramics and carbon materials could be successfully joined by the novel HTAs [3–5].

In the period table of elements, boron, carbon, and silicon are the closest adjacent elements. The substances containing of boron or silicon are the common additives used in the modification of carbon materials. In our previous works [11,12], an organic HTA

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composed of phenol–formaldehyde (PF) resin and boron carbide (B_4C) had been investigated. Such adhesive possessed satisfactory high-temperature bonding properties for carbon materials and ceramics. But for the joints after being treated at temperatures ranging from 400 to 650 °C, there exists an obvious decrease of adhesive strength. In this paper, the HTAs are prepared using PF resin as matrix and using elemental silicon or boron carbide as modification additives. As shown in many references, the high-temperature joining of C/C composite is quite difficult [6–8]. The graphite has the similar physicochemical properties to C/C composite. In this work, the bonding properties of the above HTAs were investigated by the bonding experiment on graphite substrate. Because the PF resin was the matrix of HTA and worked as the framework of adhesive cement, the microstructure evolution of PF resin and its influences on the bonding properties were especially discussed.

2. Experimental

2.1. The preparation of HTAs and test specimens

The novel HTAs were prepared by directly mixing the PF resin and ceramic fillers (elemental silicon or boron carbide) with different weight ratio. As the matrix of adhesive, a PF resin with thermosetting properties and trade of $213^{\#}$ was provided by Tianjin Resin Factory (PR China). The viscosity of the resin was 1.53 Pa s, which was determined by rotary viscosimeter at 20 °C. The solid content was $80 \pm 3\%$. At high temperatures, through pyrolysis, PF resin tends to eliminate all non-carbon species and produce a char of coalesced carbon rings [13]. The char constitutes the adhesive cement. Therefore, the integrity and stability of the residue have a critical effect on the bonding properties, namely the char ratio of the PF resin is of great importance. The char ratio of PF resin after being treated at 900 °C was 46.5%. The determination of the char ratio was carried out under isolating air condition. The detailed procedures were expressed as follows: (i) 1 g liquid PF resin was placed in a 10 ml crucible; (ii) the small crucible was placed in a 150 ml crucible, in which the coke powder was filled with for isolating air; (iii) the crucibles were placed in a muffle furnace for 7 min. The muffle furnace has already been heated to 900 °C; (iv) finally, the char ratio was calculated according to the following equation:

$$\text{Char ratio} = \frac{\text{Weight of char}}{\text{Weight of resin}} \times 100\% \tag{1}$$

In this work, there are two kinds of modification additives: (i) the silicon powder with size smaller than 74 μm and with analysis purity; (ii) boron carbide (B_4C) powder, which had the size of 2.5–3.5 μm and purity of 85%. For convenience, the HTAs were abbreviated as PF+Si and PF+B_4C, respectively.

In order to investigate the high-temperature bonding properties of the above HTAs, the bonding experiment were carried out on the graphite substrate. The density of the isotropy graphite to be bonded was 1.8 g/cm^3. The flexural strength and compressive strength of graphite were 25 and 46 MPa, respectively. Graphite materials were cut into specimens with sizes of $20 \times 10 \times 10$ and $10 \times 10 \times 10$ mm^3. The surface to be bonded was ultrasonically cleaned in water and then dried. The bonding area was 10×10 mm^2. The adhesives were brushed on the surface and the graphite specimens were bonded together at room temperature. Then all the joints were treated at different temperatures ranging from 400 to 1500 °C in a muffle furnace at a constant heating rate of 2 °C/min and were maintained at each given temperature for 2 h. The treatment process was controlled by a PTC-2 type intelligent temperature-control instrument (Institute of Coal Chemistry, Chinese Academy of Sciences). During the bonding and heating process, no extra pressure was applied to the joints. For comparison, the pure PF resin was also used to bond graphite substrates, and the treatment process of pure resin and modified resins were the same.

2.2. Testing and analysis

The bonding strength of graphite joints was tested by a universal testing machine at room temperature with a loading rate of 1.5 mm/min under shear condition (Fig. 1) [11]. Ten replicates treated at the same temperature were employed in the testing of bonding strength, and the final bonding strength was the average value.

A SIRION typed scanning electron microscope (SEM, FEI Ltd., Netherlands) system was employed to investigate the structural morphology of the modified resin. The chemical analysis was performed by GENESIS 60S typed energy dispersive X-ray spectroscopy (EDS) microprobe (EDAX Co., USA) attaching to the SEM instrument.

3. Results and discussion

3.1. Effect of the content of additive on the bonding properties

Table 1 shows the bonding strength of the joints bonded by PF+Si adhesive treated at different temperatures. When the treatment temperature reaches 200 °C, both the pure PF and PF+Si will exhibit satisfactory bonding strength due to the outstanding wettability and adhesive properties of PF resin. And the failures locate in the graphite substrates. But as to the joints bonded by pure PF resin, the bonding strength rapidly decrease to 1.6 and 1.2 MPa at 800 and 1500 °C, respectively. Because of the pyrolytic decomposition of the PF resin, considerable volatiles are

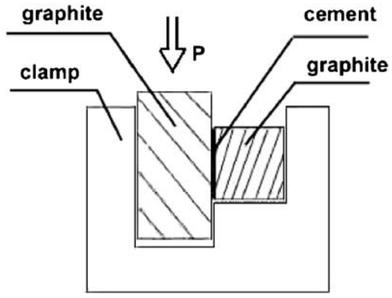

Fig. 1. Schematic representation of the test of shear strength for the bonded graphite joints.

Table 1
Bonding strength of graphite joints bonded by PF+Si treated at different temperatures [11].

PF:Si (weight ratio)	Bonding strength of joints treated at different temperature (MPa)		
	200 °C	800 °C	1500 °C
100:0	Failure of graphite substrate (>20 MPa)	1.6	1.2
100:23		3.7	0.8
100:35		5.1	0.7
100:47		7.8	0.3
100:59		7.4	0.2
100:71		5.4	0.2

released during the heat-treatment process [13], and consequently resulting in a large number of volume shrinkage defects such as voids and cracks (Fig. 2) [14]. Therefore, the joints bonded by pure PF resin would fail quickly at elevated temperatures, and the individual organic resin cannot be applied to high-temperature bonding due to the stress concentration.

Data in Table 1 indicate that the content of modification additive also has an important effect on the bonding strength. For the joints treated at 800 °C, when the addition ratios of silicon are lower than 100:47, the bonding strength keeps on increasing with the elevation of silicon content. However, a reverse happens with higher addition ratios. On the other hand, the bonding strength of the joints treated at 1500 °C is decreasing with increasing silicon content.

At 800 °C, the bonding strength keeps on increasing from 1.6 to 7.8 MPa with the content of silicon powders gradually increase from 100:0 to 100:47. It is not only the reduced volatile content (coming from the reduced level of PF resin), but also the presence of the Si filler, reduces the overall shrinkage level. So the volume shrinkage appearing at high temperatures can be controlled and benefits in overcoming the stress concentration effectively. Once the silicon's content further keeps on increasing to 100:71, the bonding strength reversely drops to 5.4 MPa. At the heat-treatment temperatures below 800 °C, no chemical reactions occur between silicon powders and PF resin matrix or the volatiles released from the pyrolysis of PF resin. So the effect of silicon powders is only physical modification, namely working as the stuffing to reduce the content of resin (or reduce the amount of volatiles) besides particle-reinforcement effect. With the further addition of silicon, the content of PF resin is excessively reduced. As a result, the stability and integrity of the adhesive's framework derived from PF resin matrix are impaired, which result in the decrease of bonding strength.

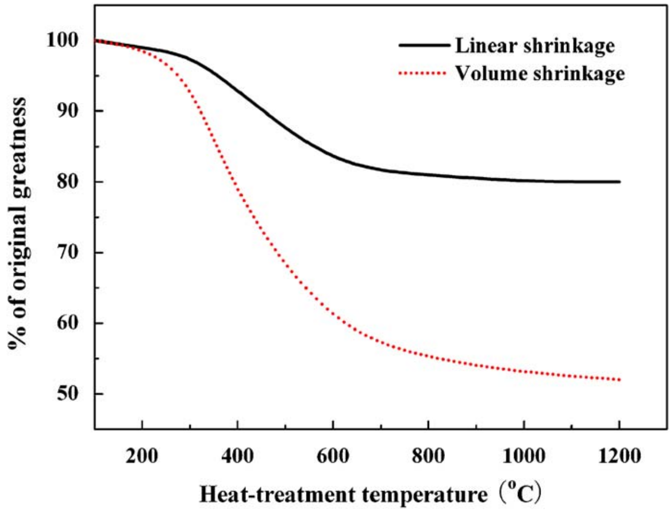

Fig. 2. The volume shrinkage curves of PF resin during heat-treatment process under pure N_2 protection (based on Ref. [14]).

When the heat-treatment temperature reaches 1500 °C, it is worth noting that all the bonding strength of PF+Si adhesive are lower than that of pure PF resin. In addition, for the joints bonded by pure PF resin treated at 800 and 1500 °C, their bonding strength are comparable to each other. When the heat-treatment temperature reaches 800 °C, the pyrolysis of PF resin nearly finishes and most non-carbon elements are released out [13,14]. The amorphous carbon (namely the residue) derived from the pyrolysis reaction of PF resin, still remains cross-linked structure like the primary un-carbonized PF resin [9]. The amorphous carbon possesses excellent thermophysics property including the structural stability. It is also shown in Fig. 2 that there is a further volume shrinkage at the temperatures above 800 °C. So, as to the joints bonded by pure PF resin, the bonding strength is relatively stable during the heat-treatment process at 800–1500 °C. Due to the structure defects produced in the pyrolysis process, the bonding strength of joints treated at 1500 °C (1.2 MPa) is slightly lower than that of joints treated at 800 °C (1.6 MPa).

But as to the joints bonded by PF+Si adhesive treated at 1500 °C, their bonding strength is obviously lower than that of pure PF resin (1.2 MPa). And the bonding strength of PF+Si adhesive keeps on decreasing with the increase of silicon content, which is unlike to its' evolution tendency at 800 °C. When the heat-treatment temperature reaches 1250 °C and even higher, silicon will react with amorphous carbon. Consequently, silicon carbide (SiC) is formed. Some SiC in celadon color could be found at the bonding interface by the naked eye. Although SiC is ceramic materials with outstanding heat-resistance and mechanical property, it is difficult to be sintered into a whole [15]. So, the integrity and cross-linked structure of amorphous carbon, which works as the framework of the adhesive cement, is destroyed. The destroy level increases with the increasing of the silicon content. As a result, when the heat-treatment temperature reaches 1500 °C, a step-down tendency of the bonding strength of PF+Si will be shown.

3.2. *The influence of resin's structure evolution on the bonding properties*

Table 2 shows the satisfactory joining properties of joints bonded by PF+B_4C. Even if the heat-treatment temperature reaches 1500 °C, the bonding strength is still 9.3 MPa. But it is should be pointed out that the bonding strength are 6.3 and 13.2 MPa at 600 and 800 °C, respectively. These results indicate that the starting temperature of modification reactions is rather high. It begins at temperature above 600 °C [16], and fully exerts the modification effect at nearly 800 °C. So, at temperatures below 600 °C, the evolution of resin's structure and property play a quite important role in the bonding performance. At 400 °C, the pyrolysis level of the PF resin is relatively low, and the polymeric system can be remained in a well integrated level. As shown in Fig. 2 that the volume shrinkage at 400 °C is insignificant. So the bonding strength of 7.7 MPa is achieved for the pure PF resin. As to the joints bonded by PF+B_4C, it can be seen that the distribution of B_4C additives in the resin matrix appears as agglomerates (Fig. 3a). A distinguishable boundary between

Table 2
The bonding strength of graphite joints treated at different temperatures (MPa) [8].

PF:B_4C (weight ratio)	The bonding strength of joints treated at different temperatures (MPa)						
	200 °C	400 °C	600 °C	800 °C	1000 °C	1200 °C	1500 °C
100:0	Failure of graphite (>20 MPa)	7.7	2.8	1.6	–	–	1.2
100:100	Failure of graphite (>20 MPa)	8.6	6.3	13.2	15.8	13.2	9.3

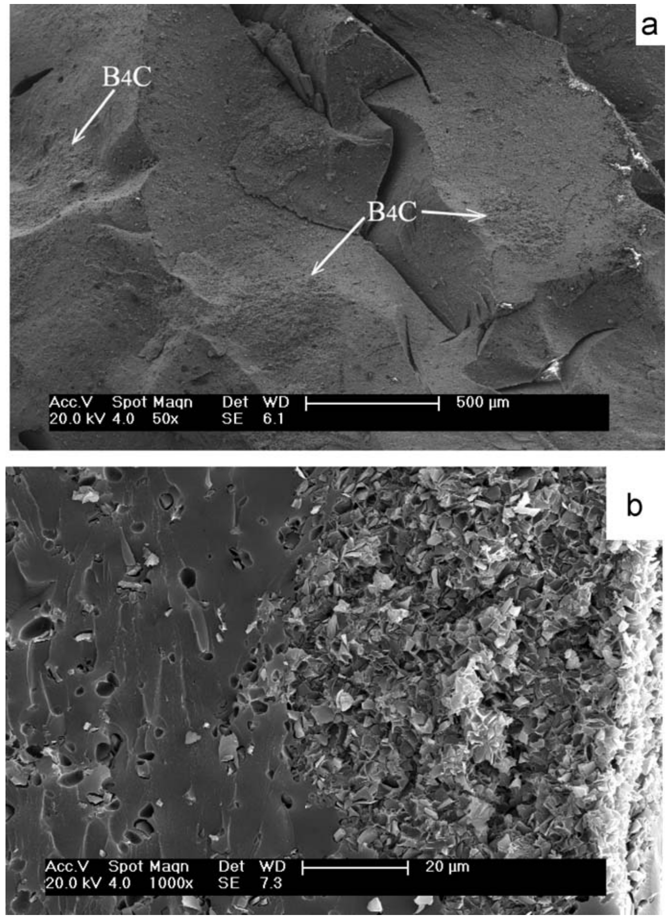

Fig. 3. The failure morphology of B_4C modified PF resin treated at 400 °C: (a) the agglomeration state of B_4C in the resin matrix (50 ×); (b) the agglomeration state of B_4C particles in the PF resin matrix treated at 400 °C (1000 ×).

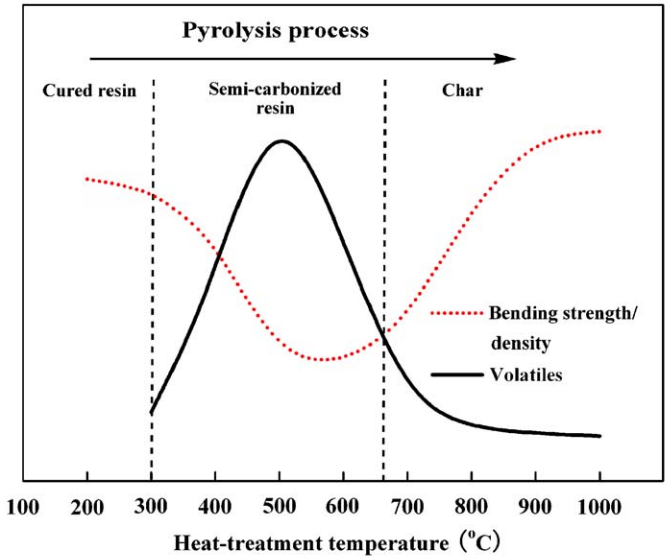

Fig. 4. The strength level and emissions during pyrolysis of PF resin (based on Ref. [17]).

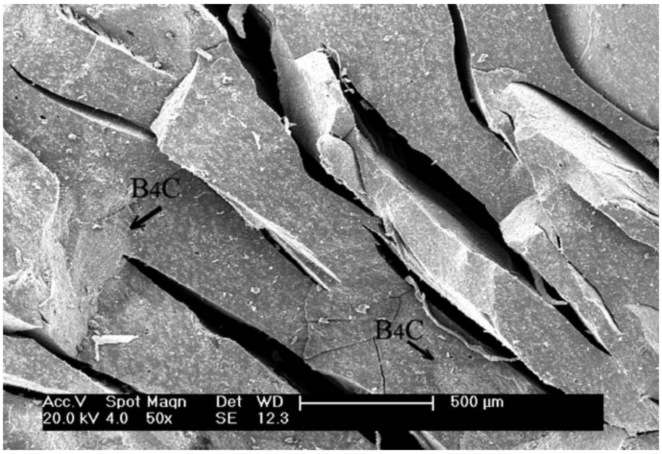

Fig. 5. The morphology of B_4C modified PF resin treated at 600 °C.

resin matrix and B_4C agglomerates is clearly shown in Fig. 3b. One can find that all the B_4C particles stack together with smooth crystal planes. As a result, the particle-reinforcement could not be fully exerted out. The bonding strength of PF+B_4C is 8.6 MPa, just a little higher than that of pure PF at 400 °C. When the heat-treatment temperature reaches 600 °C, the bonding strength of pure PF resin and PF+B_4C keep on decreasing to 2.8 and 6.3 MPa, respectively. It is well known that drastic degradation or pyrolysis reactions of PF resin occur at high temperatures, especially in the range of 400–650 °C. At this stage, most of small molecules release out in the forms of CO, CO_2, H_2O, CH_4 and so on [13,14,17] (Fig. 4). The release of small molecules results in the drastic volume shrinkage (Fig. 2). As a result, the bonding strength of pure PF resin is only 2.8 MPa.

Although it is shown in references that some chemical reactions between B_4C and oxygen-containing molecules occur above 600 °C [16], the bonding strength of PF+B_4C is just only 6.3 MPa. It can be seen from Fig. 5 that the distribution of B_4C powders in the resin matrix is still shown in the agglomeration state. Besides, by analyzing the energy spectrum, little oxygen atom is found in the B_4C agglomerate zone (Fig. 6 and Table 3). These results demonstrate that the degree of the modification reactions between B_4C and oxygen-containing volatile is quite low, and the joining properties still mainly depend on the properties of PF resin matrix at 600 °C. As a result, at the heat-treatment temperatures below 600 °C, the bonding strength of PF+B_4C keeps on decreasing because of the degradation and failure of resin matrix (Figs. 2 and 4). It can be found in Fig. 5 that there are many failure cracks in the resin matrix.

When the heat-treatment temperature further increases to 700 °C and even higher, satisfactory bonding strength of PF+B_4C is achieved (Table 2). It is also worth noting that the B_4C particles disperse in the resin matrix in a well-distribution (Fig. 7), which is obviously different from the morphologies shown at 400 °C (Fig. 3) and 600 °C (Figs. 5 and 6). In addition, the morphologies of B_4C particles are in spherical shape. All this results demonstrate the occurrence of the modification reactions between B_4C and volatiles. Some main modification reactions can be expressed as follows [11,18,19]:

$$B_4C + 6CO = 2B_2O_3 + 7C \; [11,18]$$

$$B_4C + (8-x)H_2O = 2B_2O_3 + xCO + (1-x)CO_2 + (8-x)H_2 \; [19]$$

$$2B_2O_3 + 2H_2O = 4HBO_2 \; [19].$$

B_2O_3, one of the modification products of the above reactions, possesses good wettability and adhesive property to the carbon materials. And 250% volume expansion occurs during the transformation from B_4C to B_2O_3 [20]. So, because of the

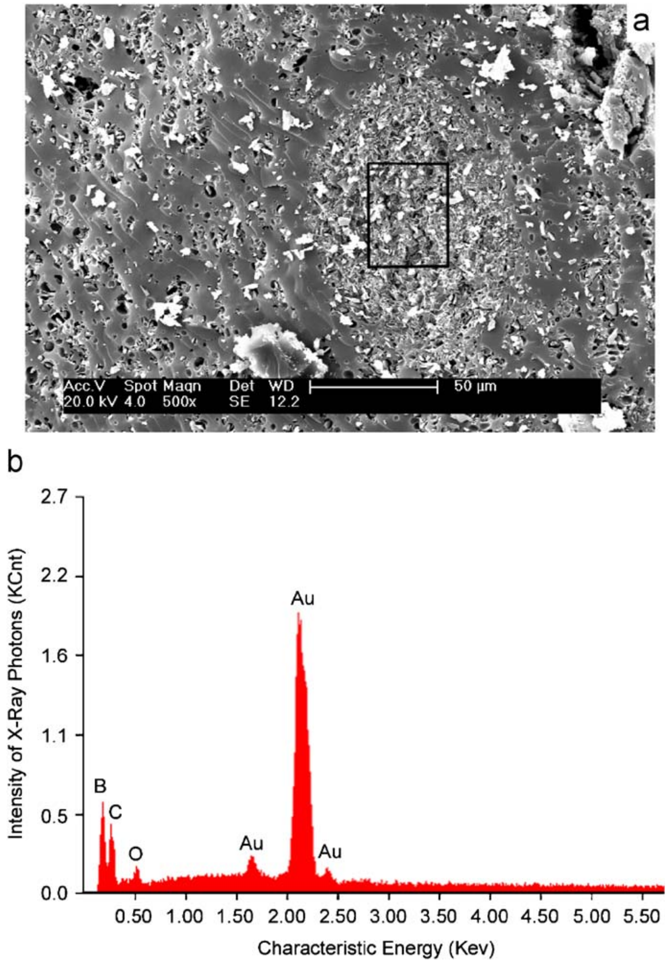

Fig. 6. The micro-morphology and energy spectrum analysis of the adhesive cement treated at 600 °C: (a) the agglomeration state of B_4C in the resin matrix (500 ×); (b) energy spectrum in the B_4C agglomerates treated at 600 °C.

Table 3
Element contribution in the B_4C agglomerates treated at 600 °C.

Element	Wt%	At%
B	77.40	79.87
C	18.88	17.54
O	03.72	02.59

complex modification reactions between B_4C and the volatiles released from PF resin, the volume shrinkage is restrained and chemical bonding force is introduced at the adhesive interface [20]. It is responsible for the satisfying high-temperatures bonding strength [11,12]. Besides, it's also worth noting that the mechanical strength of PF resin matrix picks up again when the heat-treatment temperature reaches 800 °C (Fig. 4). As a result, satisfactory bonding strength for the graphite joints bonded by PF+B_4C is achieved at higher temperatures (Table 2). For the joints treated at high temperatures, especially above 800 °C, the constituent of adhesive cement is actually carbon/ceramic composite. According to the characteristics of carbon materials, the mechanical property is increasing with the elevation of temperature. So, one can presume that the bonding strength achieved at room temperature is similar to that tested at high temperature.

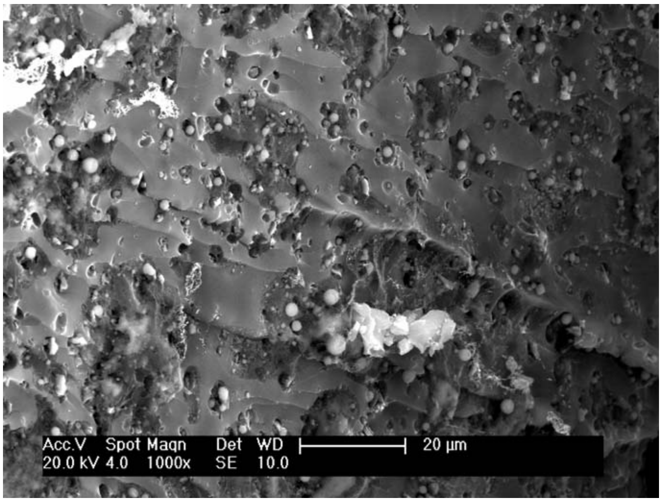

Fig. 7. The morphology of the B_4C in the resin matrix treated at 700 °C (1000 ×).

4. Conclusion

By means of the addition of ceramic fillers, phenol–formaldehyde resin can be successfully applied in high-temperature bonding. At high temperatures, the organic resin converts into amorphous carbon and works as the framework of adhesive cement. The integrity of the framework of adhesive cement is key to the bonding properties.

(1) Drastic volume shrinkage and the degradation of mechanical properties of resin matrix lead to the rapid decrease of bonding strength at high temperatures. The organic resin could not be single-handedly applied to high-temperature bonding.
(2) The appropriate content of modification additives benefits in the restraining of volume shrinkage caused by the pyrolysis of resin. But the excess addition of fillers will lead to the degradation of the framework of adhesive cement at high temperatures.
(3) The additive's property is another important factor for the high-temperature bonding. The reaction between silicon and amorphous carbon will destroy the integrity of adhesive cement. The bonding strength of PF+Si is even lower than that of pure PF resin after being treated at 1500 °C. Boron carbide is a satisfactory modification additive for the organic resin matrix HTAs. By means of the modification effects of B_4C, the adhesive of PF+B_4C can be applied to high-temperature bonding. But the joining performance of joints below 600 °C is still not satisfactory due to the degradation of resin matrix.

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