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Micro-structural evolution of phenol-formaldehyde resin modified by boron carbide at elevated temperatures

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ABSTRACT

The phenol-formaldehyde (PF) resin was modified by boron carbide (B_4C). In order to investigate the modification effect of B_4C, the residue values of pure PF resin and B_4C modified PF resin were measured using thermal gravity. It was shown that the residue values of B_4C modified PF resin are 71.9% and 68.4% after being pyrolyzed at 700 and 1000 °C, respectively, which are obviously higher than those of the pure PF resin (62.9% and 60.5% at 700 and 1000 °C, respectively). The microstructure evolution of the modified resin at high temperatures was also investigated by scanning electron microscopy and energy dispersive analysis of X-rays. By means of the microstructure characterization, the modification reactions between the B_4C additives and the oxygen-containing volatiles, such as CO and H_2O, are demonstrated. The carbon and oxygen elements remained in the resin matrix in the forms of amorphous carbon and B_2O_3, respectively, resulting in the improvement of residue values and stability of the PF resin at high temperatures. The distribution of modification particles became well-proportioned gradually at the elevated temperatures, and the shape of ceramic additives changed into white spherules due to the surface tension.

1. Introduction

Organic polymer materials including synthetic resins are widely used in many fields [1–3]. But the application of organic resins in high-temperature fields is limited due to their poor heat-resistance. Drastic pyrolysis reactions of resin occurring at high temperatures release a large amount of volatiles [4], resulting in the failure of resin matrix and its composites [5]. Because the amorphous carbon derived from the pyrolysis of organic resins possesses excellent thermophysics properties, more and more synthetic resins are applied in high-temperature fields with the advancement of high-technology. For example, many synthetic resins such as phenol-formaldehyde (PF) resin, epoxy resin, furan resin, pitch and so on, are used as the matrix of thermal-ablation materials in the rockets, the impregnant of carbon/carbon (C/C) composite, and the binder of refractory materials [5–7].

PF resin is the first thermosetting resin, which was synthesized in 1907. Such material has been proved to possess many good properties, *e.g.*, thermal resistance, corrosion resistance, anti-friction, mechanics performance, satisfactory adhesive capacity. But the drastic pyrolysis leads to the loss of volatiles including CO, CH_4, H_2O and so on, and the disintegration and failure of organ polymeric structure at high temperatures. Multiple cycles of impregnation and carbonization are necessary to achieve C/C composite with high density. If the residue value of organic resin is improved, the manufacture cost of C/C will be reduced effectively. In order to meet the application requirements in high-temperature fields, the modification of existing resins and the synthesis of novel heat-resistant resins, aiming to improve the thermal stability of structure and properties of the PF resin, have become to a prime interest recently [8–11].

By synthesizing copolymer [10,11] or introducing some heat-resistant chemical bonds, *e.g.*, B–O bond, in the main chains [9], the thermal stability and application temperature of PF resin can be improved to some extent. However, the disintegration and loss of organic constituent are still inevitable problems. During the pyrolysis at higher temperatures, all non-carbon species are eliminated and a char of coalesced carbon rings is produced [4]. In addition, if the amorphous carbon combine with the volatile element, especially the oxygen in the boroc acid or the copolymer, the structure and stability of residue will be damaged. Therefore, because of the further disintegration and volatilization at higher temperatures, the properties of residue such as the residue quantity, compactness, mechanical performance and so on are skeptical. As a result, due to the inevitable disintegration of organic polymeric structures at higher temperatures, the above research approaches

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concerning the acquirement and maintaining of the heat-resistant polymeric system cannot ultimately ensure the application in high-temperature field in safety and stability.

The PF resin is virtually used as carbon precursor in high-temperature fields, and consequently the improvements of the value, integrity, and stability of the residues are of great importance. The novel modification aiming to control and adjust the ultimate residue is a valuable approach. However, although PF resin has been studied extensively, few attempts concerning the improvement of the thermal stability of residue have been carried out. In order to achieve better residue after being treated at ultra-high temperatures, the modification additives containing dangerous element like oxygen should be rejected. Boron carbide (B_4C) possesses a combination of properties which give it a leading role among materials suitable for high performance applications [12,13]. In our previous work [14], the modification effects including the improvement of residue ratio can be realized using B_4C as additives. The influences of the species and amount of the additives have also been discussed [15]. It was shown that the high-temperature adhesives prepared using PF resin as matrix and B_4C as modification additives had outstanding heat-resistance and bonding properties [16–18]. Due the crucial influence of the microstructure on the application properties, the microstructure evolutions of the PF resin modified by B_4C is emphatically investigated in this article.

2. Experimental

2.1. Raw materials

The PF resin with the trade of $213^{\#}$ was produced in Tianjin Daying Resin Company, PR China. The viscosity of the resin is 0.8–1.53 Pa s, which is determined by rotary viscosimeter at 20 °C. The content of free phenol is less than 21 wt%, and the solid content is 80 ± 3 wt%. B_4C powders with a mean particle size of 2.5–3.5 μm and a purity of 85% were used as modification additives.

2.2. The preparation of B_4C modified PF specimens

B_4C and PF resin were mixed together in beaker with a ratio of 1:19. In order to get better dispersion of B_4C particles, the mixture was stirred by a powerful motor agitator for 40 min. The gel was then obtained after being pretreated in furnace at 93 °C. For convenience, B_4C modified PF resin is abbreviated as B_4C-PF. Then, in a QLB typed vulcanizing machine, the gel was hot-pressed in a stainless steel mould at a pressure of 10 MPa and temperatures ranging from 120 to 160 °C. Finally, the thermoforming samples were heat-treated at different temperatures in the range of 300–700 °C. In order to avoid oxidation, the cured PF specimen was burned in the coke powder. They were then put into the crucible, and were heated at a given temperature for 2 h.

2.3. Testing and analysis

A SDT Q600 (TA Inc., USA) typed thermal gravity (TG) analyzer was used for the thermogravimetric analysis. These measurements were carried out under the protection of nitrogen gas and in the temperature range of 90–1000 °C at a constant heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$.

X-ray photoelectron spectroscopy (XPS) study was performed using a PerkinElmer P111-5300 ESCA apparatus (MgKa X-ray source) with a data acquisition system. The Apollo Series 3500 data system was used for data acquisition, spectra analysis, and quantification. Curve fitting of the B_{1S} band was carried out assuming a Gaussian peak: the curve fitting was made by generating and combining Gaussian samples. The heights, horizontal positions, and half-value widths of these shapes were determined so that the combined shape was in agreement with the measured one.

A SIRION (FEI. Co., Netherlands) scanning electron microscopy (SEM) was employed to investigate the microstructure morphologies of the B_4C modified PF resin. The chemical elements and their relative contents were determined by energy dispersive X-ray (EDS) detector with the type of GENESIS 60S (EDAX Inc., USA). Because of the poor conductivity of resin matrix, the surface gold spraying was carried before the SEM observation. In order to avoid the pollution of the external environment, the morphologies to be observed were the fracture section of the specimens. Before the characterization, the specimens of B_4C modified PF resin was fractured and the fracture section was immediately treated using gold spraying method. Subsequently, the samples were observed using SEM apparatus without standstill.

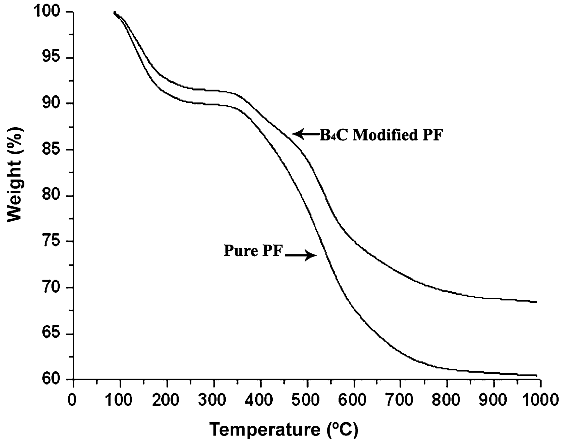

Fig. 1. TG curves of pure PF resin and B_4C-PF resin in nitrogen atmosphere.

3. Results and discussion

3.1. The elevation of residue value of B_4C-PF resin

In the past decades, many literatures concerning the pyrolysis reactions and mechanisms of PF resin had been reported elsewhere [4,5,19–21]. Now, it is well known that the drastic pyrolysis reactions occur during the heat-treatment process. Although the specimens are previously gelled at 93 °C, some condensation water and un-reacted oligomers are released out in the following thermocuring process. With the further increase of pyrolysis temperatures, many kinds of volatiles including CO, CO_2, H_2O, H_2, CH_4, C_2H_2, C_2H_6, phenol, and its methyl derivates are released out [4], resulting in the gradual decrease of weight and the failure of resin matrix and its composites [5,16–18]. The oxygen-containing molecules, including CO and H_2O, take a large proportion in the amount of decomposition volatiles [4], and provide a source of oxidizing atmosphere [21]. So B_4C is oxidized in the commencing temperature range of 560–600 °C [22–24]. It can be seen from Fig. 1 that the residue values of B_4C-PF resin are 71.9 and 68.4% after being pyrolyzed at 700 and 1000 °C, respectively. They are obviously higher than those of the pure PF resin of 62.9 and 60.5%. As discussed in Refs. [24,25], some main modification reactions are expressed as follows:

$$B_4C + 6CO = 2B_2O_3 + 7C \quad [24] \tag{1}$$

$$B_4C + (8-x)H_2O = 2B_2O_3 + xCO + (1-x)CO_2 + (8-x)H_2 \quad [25] \tag{2}$$

$$2B_2O_3 + 2H_2O = 4HBO_2 \quad [25] \tag{3}$$

To further verify the occurrence of oxidation–reduction reactions between B_4C additive and oxygen-containing volatiles, the evolution of B_4C was investigated by the XPS analysis. The XPS spectrum of B_4C modified PF matrix treated at 600 °C (Fig. 2) displays three peaks on the B_{1S} pattern: (i) peak 1 (186.50 eV): B_4C [26]; (ii) peak 2 (191.70 eV): BCO_2 (the partial oxidation product of B_4C [26,27]); (iii) peak 3 (193.92 eV): [BO_3] glass. Because B_2O_3 will melt above 450 °C and form a glass phase structure [28,29], the [BO_3] triangle is located at higher binding energy. As a result, the modification reactions effectively restrain the release of volatiles, and some carbon and oxygen elements in volatiles are consequently remained in the interior of resin matrix in the forms of amorphous carbon and B_2O_3, respectively. Therefore, the residue value of B_4C-

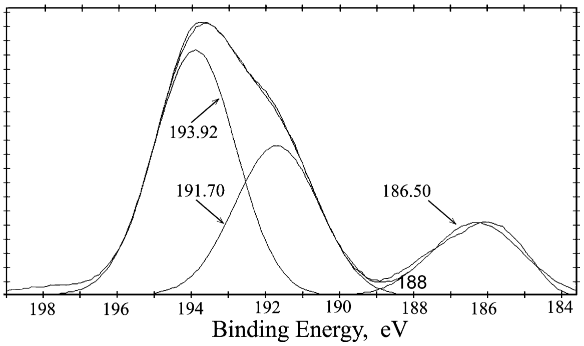

Fig. 2. B_{1S} spectra of B_4C-PF treated at 600 °C.

PF is higher than that of the pure PF resin after being pyrolyzed at high temperatures (Fig. 1).

3.2. The microstructure evolution of B_4C-PF during the heat-treatment process

3.2.1. The spontaneous homogenization and shape change at elevated temperatures

The microstructure evolution of B_4C-PF resin was investigated by SEM and EDS apparatus. As shown in Fig. 3, the distribution of additives is not well-proportioned (Fig. 3a) after being treated at 300 °C. The B_4C particles with size smaller than 5 μm accumulate together. The distinct boundary between the resin matrix and B_4C congeries could be distinguished obviously (Fig. 3b). Such phenomena indicate that homogeneous distribution of B_4C additives cannot be achieved by using simple agitation at room temperature, due to the relative high viscosity of PF resin and the physical property difference between resin matrix and B_4C particles.

It should be pointed out that the distribution of modification additives gradually becomes well-proportioned at elevated tem-

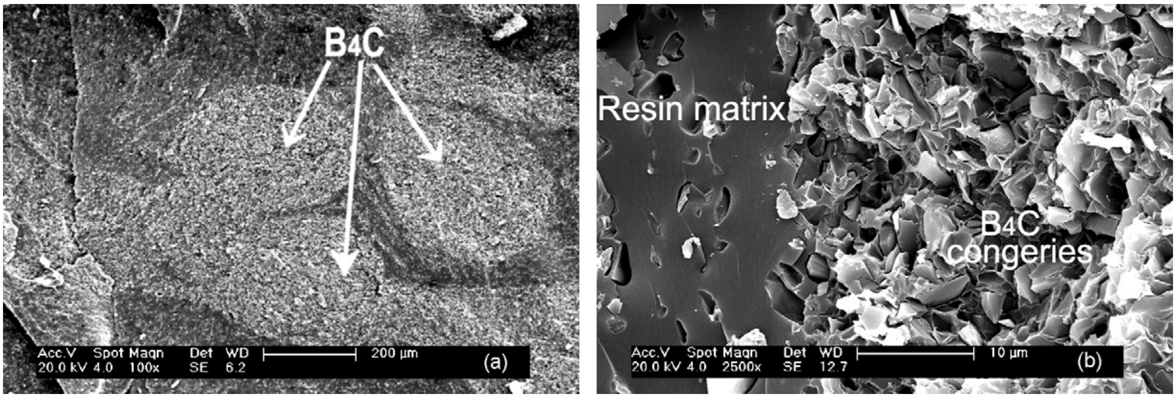

Fig. 3. SEM morphologies of B_4C-PF treated at 300 °C with different magnifications: (a) 100× and (b) 2500×.

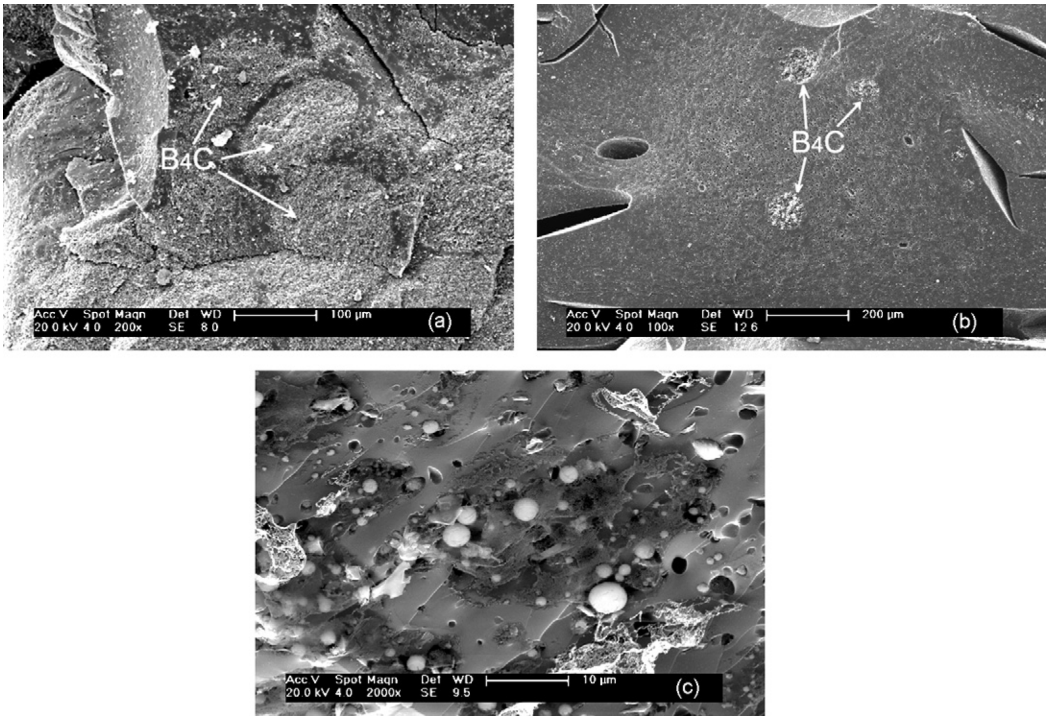

Fig. 4. The spontaneous homogenization distribution of additives in the interior of resins at elevated temperatures: (a) 600 °C; (b) 650 °C; (c) 700 °C.

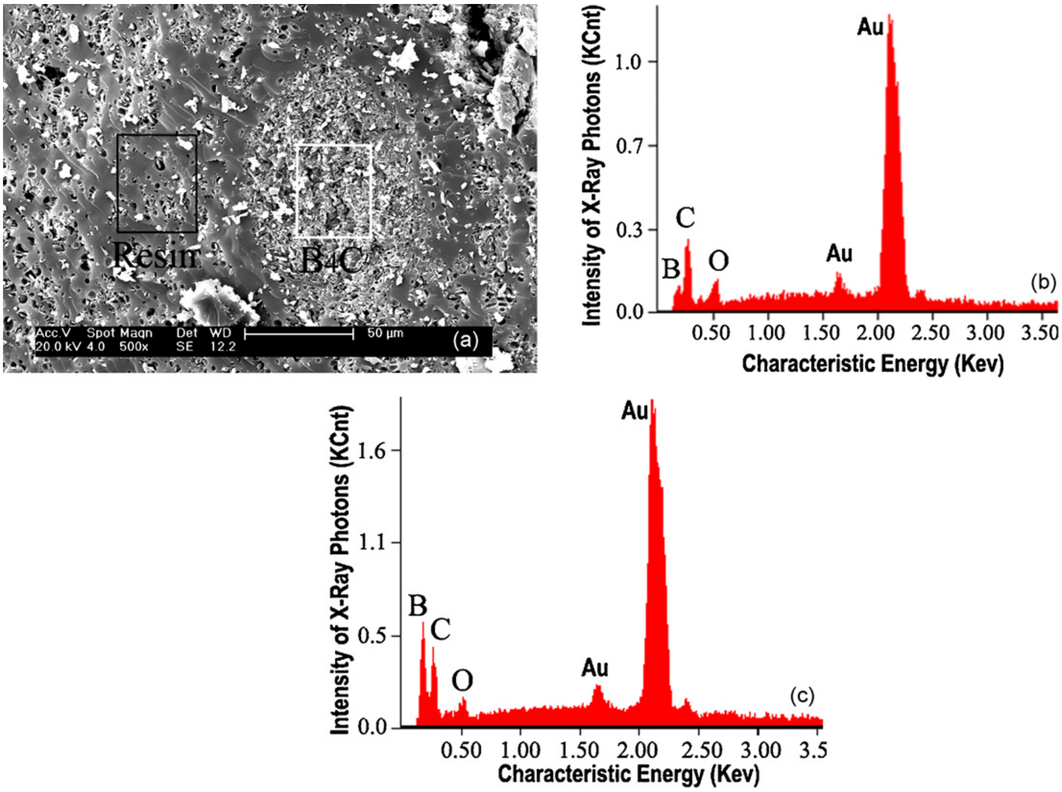

Fig. 5. SEM morphology (a), EDS spectra of PF resin matrix (b) and B_4C congeries (c) treated at 600 °C.

peratures (as shown in Fig. 4). As far as the enrichment levels are concerned, the size of B_4C congeries in the interior of B_4C-PF treated at 600 °C, is obviously smaller than that of specimen treated at 300 °C. With the further increase of heat-treatment temperature to 650 °C, the boundary between resin matrix and B_4C congeries becomes indistinct. When the heat-treatment temperature reaches 700 °C, the distribution of B_4C additives ultimately becomes well-proportioned (Fig. 4c). A spontaneous homogenization of additives occurred during the heating process.

The chemical constituents between the resin matrix and B_4C congeries are investigated and compared by using EDS detector, which is attached to the SEM apparatus. The enlarged SEM morphology and EDS results of B_4C-PF treated at 600 °C are shown in Fig. 5 and Table 1, respectively. EDS data show that the content of oxygen element is 11.51 wt% in the interior of PF resin matrix (Fig. 5b and Table 1). These results illuminate that the oxygen element still remains in the resin matrix to some extent after being pyrolyzed at 600 °C. In addition, boron element with 56.74 wt% content is also shown in the interior of resin matrix. Such boron elements are mainly derived from the B_4C particles dispersed in the resin matrix. In comparison with the oxygen content of resin matrix, the oxygen concentration in the interior of B_4C congeries (Fig. 5c and Table 1) is also found with the value of 3.72 wt%. By means of the characterization of XPS, the oxidation of B_4C at nearly 600 °C had already been demonstrated. Therefore, the appearance of oxygen in the congeries of B_4C could be interpreted by the occurrence of oxidation–reduction reactions between B_4C and oxygen-containing volatiles [22–25].

But as to the SEM morphology of B_4C-PF treated at 700 °C, drastic morphological differences of additive particles could be found. Fig. 6a is the enlarged SEM morphology of Fig. 4c. In comparison with the initial morphology of B_4C particles as shown in Fig. 3b, the shape of additive particles in the specimen treated at 700 °C changes into white spherule. It is worth noting that, the content of oxygen on the surface of additives particles increase to 27.67%, which is much higher than that of the resin matrix of 6.38% (Table 2). As already demonstrated in reference [4] that, with the elevation of heat-treatment temperature, all non-carbon species will be eliminated gradually, and a char residue characterized with the coalesced carbon rings will be produced. So the relative content of oxygen in the resin matrix keeps on decreasing. At the same time, the occurrence of the oxidization–reduction reactions between B_4C grains and the oxygen-containing volatiles had already been demonstrated using XPS that was discussed in Section 3.1. Consequently, it is conceivable that the released oxygen, which is originated from the resin matrix, migrates to the B_4C congeries. So, it is easy to understand that the content of oxygen in B_4C congeries is gradually higher that of resin matrix. Besides, the EDS

Table 1
The EDS results detected at different zones in the interior of modified resin treated at 600 °C.

Element	On the surface of PF resin matrix		Interior of B_4C congeries	
	Mass fraction %	Atomic fraction %	Mass fraction %	Atomic fraction %
B	56.74	60.95	77.40	79.87
C	31.75	30.69	18.88	17.54
O	11.51	8.35	3.72	2.59

Table 2
The EDS analysis results of specimen treated at 700 °C.

Element	On the surface of ceramic particle		On the surface of PF resin matrix	
	Mass fraction %	Atomic fraction %	Mass fraction %	Atomic fraction %
B	33.19	38.09	17.96	19.88
C	39.14	40.44	75.66	75.35
O	27.67	21.47	6.38	4.77

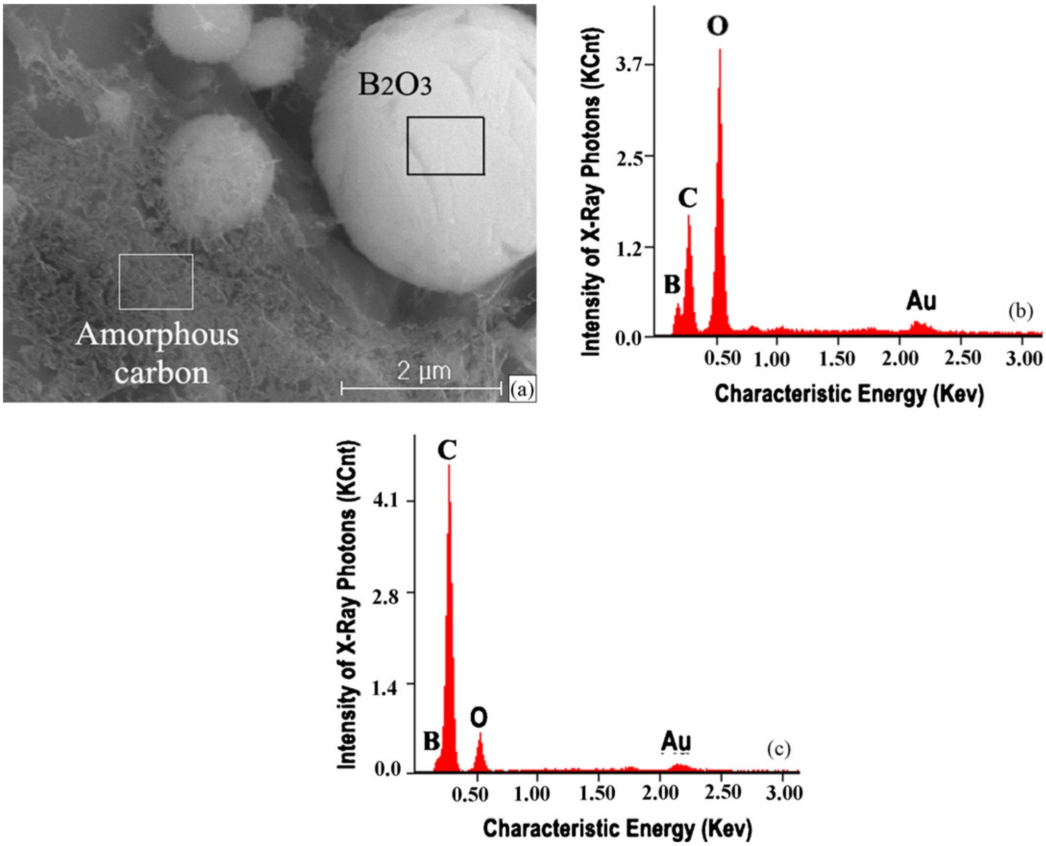

Fig. 6. SEM morphology (a), EDS spectra of ceramic particle (b) and amorphous carbon (c) treated at 700 °C.

results also illustrate that the oxidation–reduction reaction degree of B_4C is progressed with the increase of heat-treatment temperature, consequently resulting in the production of more B_2O_3 [22–25]. As mentioned before, B_2O_3 melts above 450 °C [28,29], the shape of additive particles consequently changes into spherule state driven by the surface tension (Fig. 6a).

In addition, it is also noteworthy to point out that lots of cross-linked reticulations exhibit on the SEM morphology after being treated at 700 °C (Fig. 6a). Their structures and morphologies obviously are distinguishable from those of the resin matrix and the additives. The EDS results indicate that the above reticulations are composed of carbon together with a few of boron and oxygen (Fig. 6c and Table 2). Therefore, it can be concluded that such cross-linked reticulations are amorphous carbon generated from the modification reactions occurred between B_4C and oxygen-containing volatiles.

By means of the above oxidation–reduction reactions, some carbon elements convert into amorphous carbon, and partial oxygen also remains in the resin matrix in the form of B_2O_3. As a result, the residue value of B_4C-PF is higher than that of pure PF resin, and the appearance and development of volume shrinkage are restrained effectively, which benefit in the maintaining of the stability of structure/properties of resin and its composites at high temperatures [14–18].

3.2.2. *The modification mechanism of B_4C*

As to the evolution of well-proportioned distribution at elevated temperatures, such interesting phenomena could be interpreted by the elementary-reactions of modification reactions. Among the oxygenation–reduction reactions between B_4C and CO or other oxygen-containing volatiles, some intermediate compounds are produced in gaseity. Partial detailed element-reactions can be expressed as follows [24]:

$$(1/2)B_4C(s) + 2CO(g) = B_2O_2(g) + (5/2)C(s) \tag{4}$$

$$(1/4)B_4C(s) + CO(g) = BO(g) + (5/4)C(s) \tag{5}$$

$$B_2O_2(g) + CO(s) = B_2O_3(l) + C(s) \tag{6}$$

$$BO(g) + (1/2)CO(g) = (1/2)B_2O_3(l) + (1/2)C(s) \tag{7}$$

Such gaseous intermediate compounds such as BO, B_2O_2 and so on have excellent flowability. Besides, the final oxidation product, B_2O_3, melts at above 450 °C, and its viscosity decreases with the increase of heat-treatment temperatures [30,31]. As a result, the component migration in the interior of resin matrix occurs spontaneously, driven by the difference of concentration and air pressure. Because the commencing temperatures of the oxidization of B_4C is high up to 560–600 °C [22–24], based on the TG analysis and relevant researches reported elsewhere [14–18], one can find that the temperatures around 700–800 °C might be the critical temperatures. Obvious modification effects including the elevation of char residue and the improvement of adhesive property, *etc.*, are fully exhibited when the treatment temperatures are higher than 700–800 °C.

4. Conclusion

By means of the modification reactions between B_4C and oxygen-containing volatile, some carbon and oxygen elements remain in the interior of resin matrix in the forms of amorphous carbon and B_2O_3, respectively. They are responsible for the improvement of residue value and the stability of PF resin at high temperatures. The microstructure evolution of B_4C-PF at elevated temperatures can be summarized as follow:

(i) The residue values of B_4C modified PF resin are 71.9 and 68.4% after being pyrolyzed at 700 and 1000 °C, respectively, which are obviously higher than those of the pure PF resin of 62.9 and 60.5%. In order to realize the full exertion of the modification effects, the heat-treatment temperature should reach 700–800 °C.

(ii) At high temperatures, B_4C additives are oxidized and converted into B_2O_3. The shape of ceramic additives changes into white spherules due to the surface tension.

(iii) Companied with the elevation of heat-treatment temperature and the proceeding of oxidization of B_4C, the distribution of additives spontaneously become homogeneous. It is conceivable that some intermediate compounds including of BO and B_2O_2 in gaseity are produced. Driven by the difference of concentration and air pressure, the component migration in the interior of resin matrix occurs, consequently resulting in the homogeneous distribution of additives at elevated temperatures.

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