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Preparation of high-temperature organic adhesives and their performance for joining SiC ceramic

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Abstract

Two kinds of high-temperature organic adhesives were prepared and successfully applied to join SiC ceramic. One adhesive was composed of preceramic polymer (V-PMS) and B_4C powder (HTA-1), and the other was composed of V-PMS, B_4C powder and low melting point glass powder (HTA-2). The properties of the obtained adhesives were investigated by TGA, XRD, bonding test and SEM analysis. The results show that the obtained adhesives exhibit outstanding heat-resistant property and excellent bonding strength. The bonding strength of HTA-1 treated at 200 °C, 400 °C, 600 °C were 26.8 MPa, 18.9 MPa, 7.3 MPa, respectively. When the temperature increased to 800 °C or even higher, the shear strengths of the joints were enhanced to over 50 MPa. Moreover, by adding glass powder as the second filler, it was found that the minimum shear strength of HTA-2 was enhanced to 16.4 MPa. The excellent performances of the obtained adhesives make them as promising candidates for joining SiC ceramics for high-temperature applications.

Keywords: A. Joining; C. Strength; C. Thermal properties; D. SiC

1. Introduction

Silicon carbide is an artificial ceramic material of great importance for advanced technological applications, particularly for high-temperature purposes [1,2]. However, its brittleness and high rigidity restrict its application in directly fabricating structures of large dimensions and complex shapes. In order to meet the fabrication demands of various structures, effective joining methods are needed. The traditional methods such as riveting, bolting and threading are not suitable to be applied in joining of SiC ceramic materials due to the inevitable problem of stress concentration, while the commonly used techniques, diffusion bonding, metal brazing and diffusion welding, need accurate and complex treatment processes. Moreover, the joints achieved by the above techniques still have certain limitations such as porosity, mismatch of thermal expansion coefficients, and low strength at joining sites [3–6]. Therefore, many works are still focusing on the research for the joining of SiC ceramics.

Up to date, the most convenient and promising method for joining SiC ceramic is the use of high-temperature adhesive (HTA). There are two kinds of high-temperature adhesives, i.e. inorganic and organic adhesives. Although inorganic adhesives possess outstanding heat resistance, their brittleness and low bonding strengths restrict their application in the bonding of structural components. Thus, novel high-temperature adhesives using organic resins as matrix have been developed to join SiC ceramic and composite materials [7–13]. In our previous work [14], a novel preceramic polymer (V-PMS) has been synthesized by modifying polymethylsilane with D4Vi (1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, $[CH_3(CH_2{=}CH)SiO]_4$) and used as a high-temperature organic adhesive. In order to improve the bonding strength of this adhesive, B_4C powder and glass powders were used as fillers to modify the adhesive in this work. The properties of the modified adhesives and the modification mechanism of the fillers were investigated.

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2. Experimental

2.1. Preparation of V-PMS and adhesives

V-PMS was synthesized as described in our previous report [14,15]. Two adhesives were prepared, One was abbreviated as HTA-1 was prepared by V-PMS and B_4C powder (Mudanjiang Qianjin Boron Carbide Co., Ltd., 3–5 μm, 95%). The other adhesive was prepared by V-PMS, B_4C powder and low melting glass power (Foushan Glass materials Co., Ltd., 99%) with a size of 1250 mesh was abbreviated as HTA-2.

2.2. Characterization and bonding strength test

Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449C thermogravimetric analyzer at a heating rate of 10 °C/min with air flow rates of 100 cc/min. Scanning electron microscopy (SEM) images of joint sections were obtained using a JEOL JSM-5600 LV electron microscope. The phase structure of the samples was characterized by X-ray diffraction analysis with CuK_α radiation and a nickel filter.

The bonding properties of the adhesive were tested by joining pieces of sintered SiC (Weifang Huamei Fine Ceramic Company) with a size of $20 \times 10 \times 5\ mm^3$. Specimens were prepared and tested as described in the literature [16]. After joining, all of the bonded samples were cured at 200 °C for 2 h in air. To obtain satisfactory bonding properties, 0.1 MPa pressure was applied on the joints until the specimens were cured. The cured samples were then placed in a muffle furnace and heat-treated at different temperatures ranging from 400 to 1200 °C. Each bonded sample was heat-treated at a given temperature for 2 h. Five specimens were tested under the identical conditions. The average value of the shear strength was calculated for each case.

3. Results and discussion

3.1. Ceramic yields of preceramic polymer and HTAs

The ceramic yields of HTAs are crucial parameters to determine the strength of the joints. The amount of residual porosity, presence of cracks, joint thickness and shrinkage stresses are affected by the ceramic yields of HTAs [8]. Fig. 1 shows TGA curves of V-PMS, HTA-1 and HTA-2. The ceramic yield of V-PMS treated in air at up to 1200 °C reached 90.6%. Lower mass loss will lead to smaller volume shrinkage and less amount of volatiles, which will make the adhesive exhibit high bonding strength. By adding B_4C and glass powders as fillers, HTA-1 and HTA-2 samples displayed less mass loss. It can be seen from Fig. 1 that as the temperature increased to 740 °C, the modified adhesives exhibited a maximum mass loss of about 6%. The specimens then showed a mass increment due to oxidation reaction between B_4C and oxygen or oxygenic volatiles derived from V-PMS. It should be noticed that the mass increment of HTA-2 was lower than HTA-1, which could be attributed to the volatilization of low melting point glass. The lower the variation in mass, the higher the bonding strength can be expected. Therefore, the bonding strengths of HTAs should be larger than that of V-PMS.

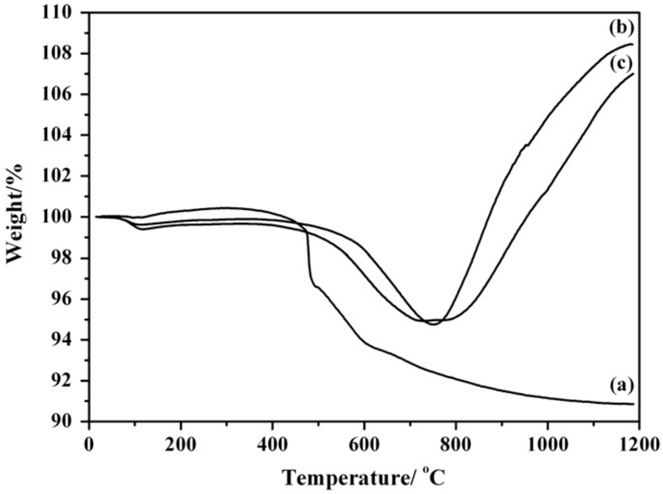

Fig. 1. TGA curves of (a) V-PMS, (b) HTA-1 and (c) HTA-2.

3.2. Bonding strengths of HTAs

Table 1shows the bonding strengths of HTA-1 and HTA-2 at different treated temperatures in air atmosphere. After cured at 200 °C for 2 h, the shear strengths of HTA-1 and HTA-2 were 26.8 MPa and 18 MPa, respectively. The good bonding strengths at low treated temperature can be attributed to the outstanding adhesive property and strong cohesive force of organic matrix (V-PMS) in HTAs. The shear strengths of HTA-2 treated at low temperature (< 400 °C) were lower than HTA-1 treated at the same temperature, which was caused by reduction of the effective adhesive area caused via adding low melting glass as the second additive.

When the temperature increased to 600 °C, the shear strength of HTA-1 decreased to a minimum value, 7.3 MPa. The decrease of the shear strength could be attributed to volume shrinkage of the adhesive caused by decomposition of the organic structure and the release of volatiles. In Fig. 1, it could be found that HTA-1 exhibited weight loss when the temperature increased before 740 °C. This resulted from the decomposition of preceramic polymer (V-PMS). Thus, volume shrinkage would be brought into the bonding layer if many volatiles released out during the heat-treatment process. Consequently, the SiC joints were weakened because of stress concentration and the shear strength of the joints decreased.

In addition, when the treated temperature was higher than 800 °C, the bonding strengths of the joints bonded by

Table 1
Bonding strengths of SiC ceramic joints treated at different temperatures for 2 h.

Samples	Strengths of samples treated at different temperatures (MPa)					
	200 °C	400 °C	600 °C	800 °C	1000 °C	1200 °C
HTA-1	26.8	18.9	7.3	> 50	> 50	> 50
HTA-2	18	17.3	16.4	26.2	20.3	19.5

HTA-1 increased to above 50 MPa. It was shown by Fig. 1 that the modified adhesives showed a mass increment as the temperature increased to over 740 °C, which should due to oxidation reaction between B_4C and oxygen or oxygenic volatiles derived from V-PMS. It is reported that the production of the oxidation reaction, B_2O_3, melts at 450 °C and displayed good wettability and chemical compatibility on ceramic surfaces [16]. Thus, the excellent bonding strengths might come from the good chemical compatibility between B_2O_3 converted by B_4C filler in HTA-1 at high treated temperature in air and SiC ceramic substrates. Therefore, a strong chemical joining force, the high bonding strength in this case, is successfully introduced at the interface between the cement and the SiC ceramic substrate.

Moreover, it should be noticed that the shear strength of HTA-2 reached 16.4 MPa after being heat-treated at 600 °C, which was remarkably enhanced comparing with HTA-1. Low melting point glass plays an important role in elevating the bonding strength at this treated temperature, as the low viscosity of glass melt at 600 °C make it propitious to flow in the ceramic joints, leading to the formation of strong joining force, densification of the cement, and thus higher shear strength. As the temperature farther increased, the shear strengths of HTA-2 were also enhanced which was most resulted from the modification of B_4C powder. However, the shear strengths of HTA-2 treated at 800, 1000, 1200 °C were 26.2, 20.3, 19.5 MPa, much lower than HTA-1 treated at the same temperature. This should be owed to the volatilization of low melting point glass which will form cracks and flaws. Additionally, the amount of volatile will increase when the temperature increases. Thus, the cracks and pores will also increase with elevating the treated temperatures, which will cause the strengths of the joints decrease. This result was in good consistent with the TGA analysis.

3.3. SEM analysis of the cross section of SiC ceramic joints

The SEM cross section micrographs of the interfacial area of the joints bonded by HTA-1 and HTA-2 are presented in Figs. 2 and 3, respectively. The thickness of the bonding layer of HTA-1 were among 10–20 μm, while that of HTA-2 were more than 20 μm at different treated temperatures. The bonding layers of both HTA-1 and HTA-2 were uniform and intact with no obvious cracks or pores when the temperatures were lower than 600 °C. As the treated temperature increased, some cracks or pores appeared in the bonding layer due to decomposition of the organic structures and release of volatiles. It could be observed that the interfaces between SiC substrate and the bonding layer of HTA-1 were almost disappeared when the temperature were above 600 °C, indicating the occurrence of chemical reactions at the interface. Consequently, the high chemical bond force formed between SiC substrate and HTA-1 made the joints exhibit excellent bonding strength.

Compared with HTA-1 treated at high temperature (> 800 °C), the bonding layers bonded by HTA-2 were much looser and showed much more pores as shown in Fig. 3((d)–(f)) which might be due to volatilization of low melting point glass. Thus, the shear strengths of HTA-2 treated at high temperature were lower than that of HTA-1. However, the minimum shear strength of HTA-2 (16.4 MPa) treated at different temperatures was much higher than that of HTA-1 (7.3 MPa), which enables HTA-2 a more promising high-temperature adhesive for application. The SEM cross section micrographs of the interfacial area of the joints bonded by HTA-1 and HTA-2 are in very good accordance with the results of bonding strengths test in Table 1.

3.4. XRD analysis of the HTAs

X-ray diffraction patterns of the HTA-1 heat-treated for 2 h in air at different temperatures are shown in Fig. 4. The identified phase of the HTA-1 at 200 °C, 400 °C and 600 °C was B_4C. When the treated temperatures were over 800 °C, a new phase of H_3BO_3, a product of reactions between the oxidizing atmosphere and B_4C, appeared. The reactions can be expressed as follows [16,17]:

$$B_4C+8O_2=2B_2O_3+CO_2 \quad (1)$$

$$B_4C+6CO=2B_2O_3+7C \quad (2)$$

$$B_4C+(8-x)H_2O=2B_2O_3+xCO+(1-x)CO_2+(8-x)H_2 \quad (3)$$

$$B_2O_3+3H_2O=2H_3BO_3 \quad (4)$$

It is reported that the conversion of B_4C to B_2O_3 could result in a 250% volume increase [16]. B_2O_3 melted at 450 °C and displayed good wettability on the surface of SiC ceramics. Once microcracks were formed, B_2O_3 melts will migrate to the crack tips to stop their propagation. As a result, the shrinkage was effectively restrained and

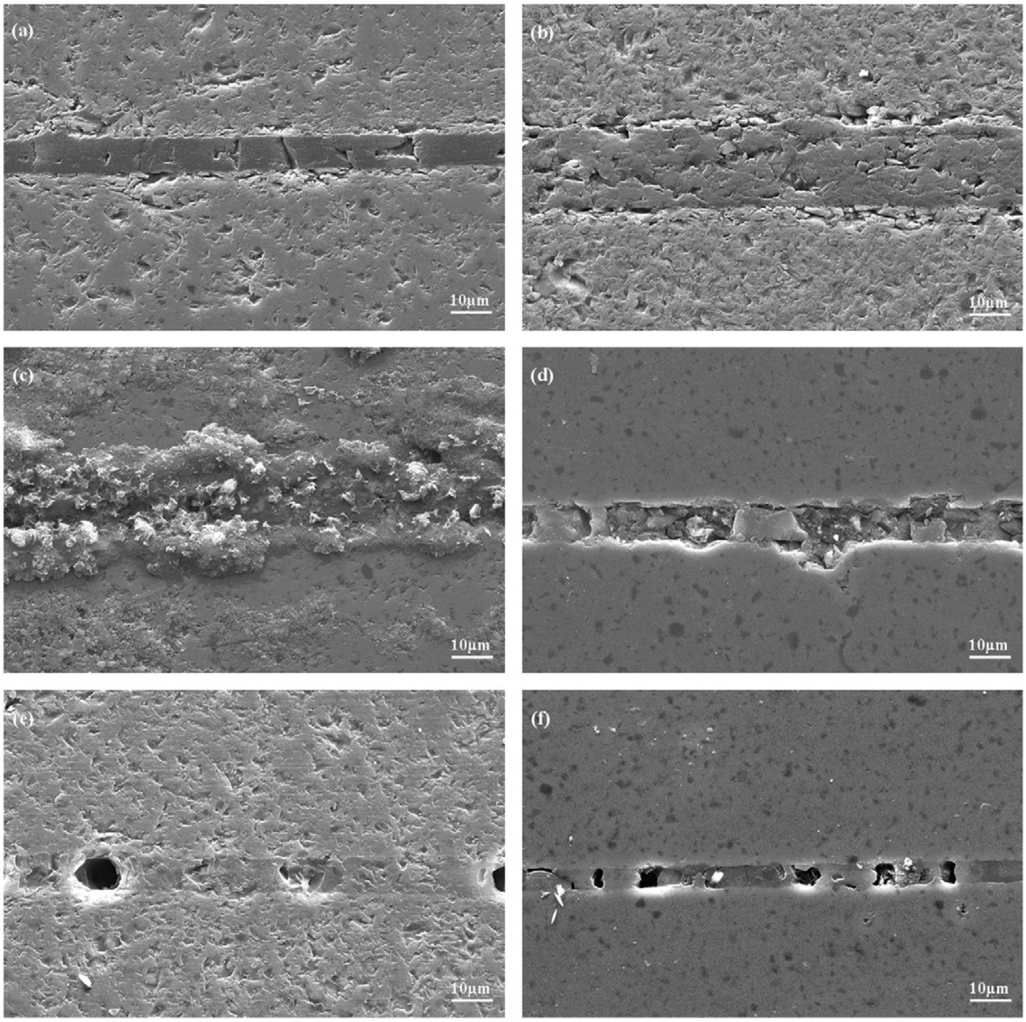

Fig. 2. SEM cross section micrographs of SiC ceramic joints bonded by HTA-1 heat-treated for 2 h in air at different temperatures: (a) cured at 200; (b) 400; (c) 600; (d) 800; (e) 1000; and (f) 1200 °C.

cracks were healed. Thus, the bonding strength would be enhanced as proved by the bonding strength test and SEM analysis.

Fig. 5 shows the X-ray diffraction patterns of HTA-2 heated for 2 h in air at different temperatures. Comparing with HTA-1, the patterns exhibit additional phases such as SiO_2 and Pb which come from the glass powder. The peak of Pb appeared when the treated temperature increased to 400 °C, and enhanced dramatically when treated at 600 °C. In addition, the peak of SiO_2 appeared when the treated temperature increased to 800 °C, which may be caused by crystallization of low melting point glass.

4. Conclusion

Two kinds of high-temperature organic adhesives were prepared by using preceramic polymer (V-PMS) as matrix and B_4C powder, glass powder as fillers. The obtained adhesives exhibited outstanding heat-resistant properties and excellent bonding strengths. The shear strength of HTA-1 treated at 200 °C, 400 °C, 600 °C were 26.8 MPa, 18.9 MPa, 7.3 MPa, respectively. When the heat-treated temperature increased to 800 °C or even higher, the shear strengths of the joints were enhanced to more than 50 MPa. The enhanced shear strength could be caused by the wetting property of the newly formed B_2O_3 and the strong chemical bonds between B_2O_3 and the SiC ceramic substrates under high treated temperatures. By adding glass powder as the second filler, the bonding strength treated at moderate temperature (600 °C) was remarkably enhanced and the minimum shear strength treated at different temperatures was increased from 7.3 MPa to 16.4 MPa. This may be due to the modification of low melt glass powder which dramatically densified the bonding layer and repaired the cracks. In conclusions, the excellent performances of the obtained adhesives make them as promising candidates for joining SiC ceramics for high-temperature applications.

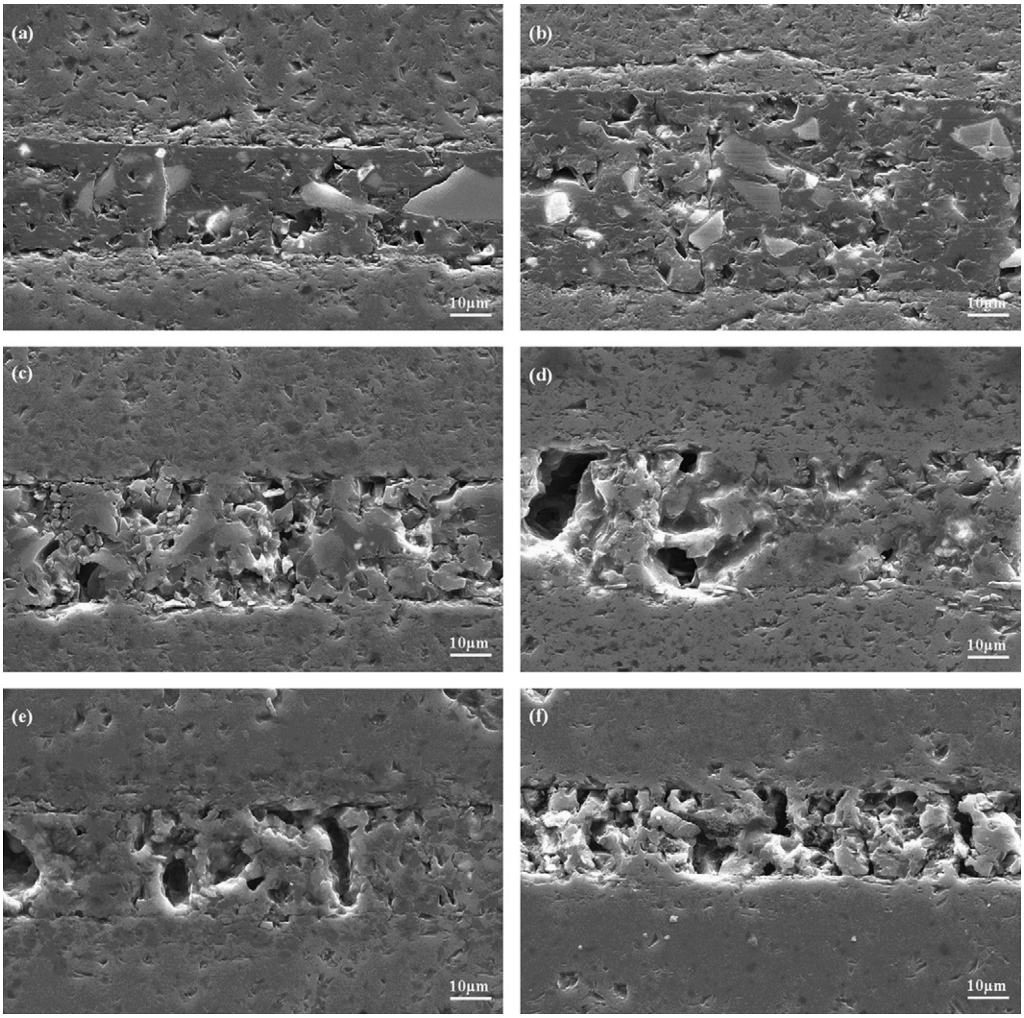

Fig. 3. SEM cross section micrographs of SiC ceramic joints bonded by HTA-2 heat-treated for 2 h in air at different temperatures: (a) cured at 200; (b) 400; (c) 600; (d) 800; (e) 1000; and (f) 1200 °C.

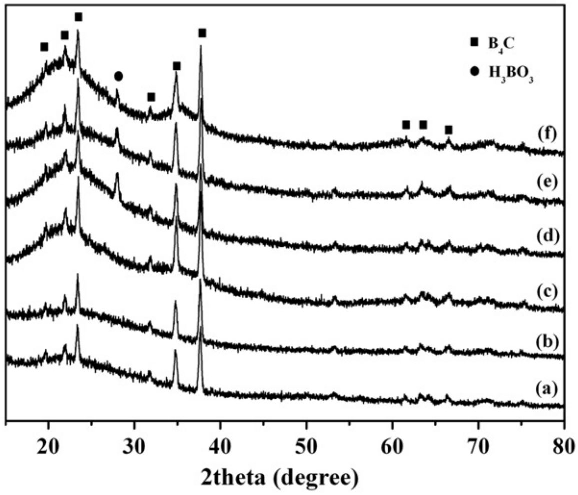

Fig. 4. X-ray diffraction patterns of HTA-1 heat-treated for 2 h in air at different temperatures: (a) 200; (b) 400; (c) 600; (d) 800; (e) 1000; and (f) 1200 °C.

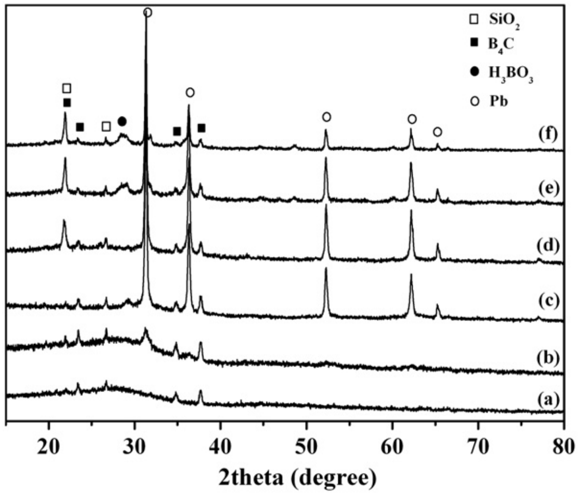

Fig. 5. X-ray diffraction patterns of HTA-2 heat-treated for 2 h in air at different temperatures: (a) 200; (b) 400; (c) 600; (d) 800; (e) 1000; and (f) 1200 °C.

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