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The improvement in thermal and mechanical properties of TiB_2 modified adhesive through the polymer-derived-ceramic route

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ABSTRACT

An air stable high temperature adhesive synthesized via the polymer-derived-ceramic route had received increased attention in the last two decades. To improve the thermal stability and adhesion strength of a polysilazane (PSNB) adhesive, TiB_2 was added as active filler to join SiC ceramic discs. The thermal stability, phase composition and microstructure were investigated by using TGA, XRD, FT-IR, BSE and SEM measurements. Effects of the pyrolysis temperature and active filler TiB_2 on the microstructure and adhesion strength have been investigated. After curing and heat-treating at 120 °C and 1000 °C in air for 2 h, respectively, the adhesion strength of the modified adhesive reached up to 10.07 MPa (3 times higher than that of pure PSNB) at room temperature, and, more importantly, retained a strength of 8.0 MPa at 800 °C in air. It should be noted that the formation of a glass comprised of SiO_2-B_2O_3-TiO_2 and the emergence of the hexagonal and granular TiB_2 in the adhesive layer are mainly responsible for the enhanced high temperature strength.

1. Introduction

The silicon carbide (SiC) ceramics are widely used in the automotive, aerospace, electronics and other fields because the excellent heat, wear and corrosion resistance properties [1]. However, the brittleness and high stiffness have limited their use in structural components with the large dimensions and complex shapes [2,3]. Therefore, the connection technology is a particular important factor in the application of ceramic materials. Traditional ceramic connection technologies, such as mechanical connection, solid-phase diffusion and high-temperature brazing, inevitably leads to the problems of thermal expansion coefficient mismatch, stress concentration and poor mechanical property. Nevertheless, the PDC (polymer derived ceramic) route had been used to connect ceramics, which was a good solution to the above problems [4].

Previously, it has been reported that good performance was acquired by using polysiloxane (PSO), polycarbosilane (PCS) and polysilazane (PSN) as adhesive matrix to join SiC ceramic discs [5–7]. However, higher pyrolytic temperature (above 1200 °C) leads to a high demands on the experimental equipment and a damage on SiC ceramic discs, besides, the protection of inert atmosphere limits the heat treatment of large dimensions and complex shapes components. In addition, titanium diboride (TiB_2) has been extensively studied as an reinforced phase due to the high melting point, high chemical stability and high hardness [8,9]. And the mechanical properties of the materials are obviously improved, due to the strengthening effects of TiB_2 particles [10–13]. Typically, Qin et al. [14] successfully joined Al_2O_3 ceramic discs using TiB_2 and glass powder modified PSO, Luo et al. [15] prepared an adhesive based on TiB_2, SiC and B_4C modified PSNB to connect graphite, the lower pyrolysis temperature and the simpler process make engineering applications possible. But, a comprehensive study on the toughing and reinforcing effects of TiB_2 on SiBCN ceramic has not been conducted.

Herein, PSNB adhesive will be modified with TiB_2 to join SiC ceramic discs and be pyrolyzed at 600–1200 °C in air. The oxidation product B_2O_3 is good for reducing the oxidation temperature of SiC (the pyrolytic products of PSNB), which is beneficial to improve the wettability of SiBCN and SiC ceramic discs, and increase the effective load-bearing area [16]. Besides, the formation of $[TiO_4]$ and $[BO_4]$ can strengthen the $[SiO_4]$ network structure by connecting the broken silicon-oxygen networks, which is favorable for improving the thermal stability of SiO_2-B_2O_3-TiO_2 glass [17,18].

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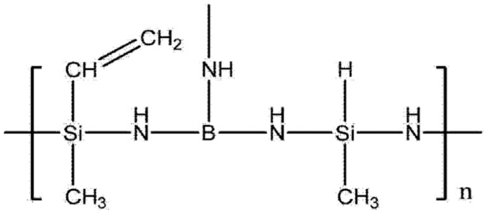

Fig. 1. Molecular structure of PSNB.

2. Experimental procedures

2.1. Materials and synthesis

SiC ceramic discs with dimensions of 20 mm * 20 mm* 2 mm and porosity of 0.39% were provided by Hangzhou Beilong company. The PSNB was provided by the Institute of Chemistry, Chinese Academy of Sciences in Beijing, with room temperature viscosity of 2400 cp and the cross-linking temperature of 120 °C. The TiB_2 was provided by the China New Metal Materials Technology Co., Ltd, with particle size of 5 µm and purity of 99.99%.

The modified adhesive was prepared by using PSNB (molecular structure of PSNB is shown in Fig. 1) as matrix and TiB_2 as additives. The mass ratio of PSNB and TiB_2 is 4:3 according to the reaction yield of active filler and the density change before and after reaction [19]. The control experiment without TiB_2 addition was also carried out.

The prepared adhesive was stored in vacuum for 30 min. The SiC ceramic discs were ultrasonically cleaned, in ethanol for 1 h, and dried in oven before use. The adhesive was brushed on the surface and two ceramics discs were single lapped. The lapped sample was cured in air, at 120 °C for 2 h, under the pressure of 9.0 kPa, then pyrolyzed at 600, 800, 1000 and 1200 °C in air for 2 h, respectively.

2.2. Characterization

The adhesion strength of the joint was tested by using an universal testing machine with the loading rate of 0.5 mm/min at room temperature (named RT strength) and with the loading rate of 0.582 mm/min, the heating rate of 20 °C/min and kept warm at 800 °C for 5 min in air (named as HT strength). The specimen specification and testing protocol has been described elsewhere [20]. The thermal decomposition behavior of pure PSNB and TiB_2 modified adhesive was analyzed using a high temperature simultaneous thermal analyzer (STA429CD/3/7; Gerätebau GmbH, Netzsch, Germany) with a heating rate 20 °C/min from room temperature to 1200 °C in air and inert atmosphere. The phase compositions of PSNB and PSNB-TiB_2 were analyzed by X-ray diffraction (XRD, Rigaku-D/max-2400; Tokyo, Japan). The chemical bonds of the adhesion layer were characterized by FT-IR spectrometer (EQUINOX55, Bruker, Germany) with spectral range of 4000–500 cm^{-1}. The microstructures of the fracture surface and cross-section of joint were observed by scanning electron microscopy (SEM, S-2700; Hitachi, Japan) and back scattered electron (BSE, S-2700; Hitachi, Japan).

3. Results and discussion

3.1. Thermal stability of adhesive

Adhesives for high temperature applications must have high ceramic yields and good temperature-resistance. As revealed by the TGA curves shown in Fig. 2, in the first stage (from 600 °C to 800 °C), the quick mass loss for PSNB in air and Ar, as well as PSNB-TiB_2 in Ar atmosphere, attributes to the breakage and rearrangement of polymer chains and release of large number of small molecular in form of gaseous by-products. While the mass of PSNB-TiB_2 in air starts to increase at 650 °C, because TiB_2 was oxidized into TiO_2 and B_2O_3, and SiBCN (the pyrolysis products of PSNB) also was oxidized into SiO_2 and B_2O_3. In the second phase (from 800 °C to 1200 °C), the mass continues to decrease for pure PSNB, and the ceramic yield of pure PSNB in air is higher than that in Ar, due to the reaction of SiBCN and oxygen in air. For PSNB-TiB_2, the ceramic yield is higher than pure PSNB both in air and Ar, owing to the percentage of PSNB is lower with the addition of TiB_2. In addition, mass increase of PSNB-TiB_2 in air is higher than in Ar atmosphere, owing to the more amount of oxidation product TiO_2 inhibits the evaporation of B_2O_3 and SiO_2 at high temperature [17,18].

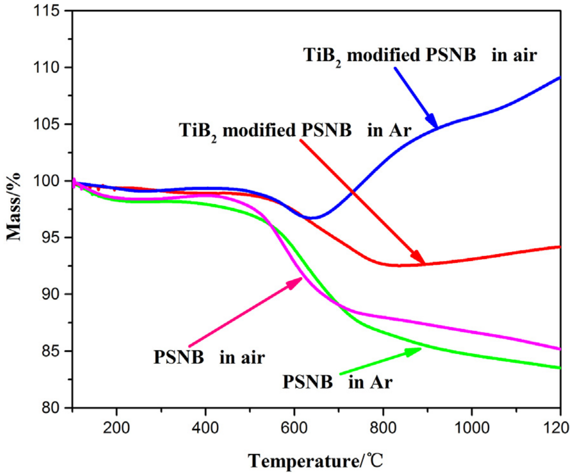

Fig. 2. TGA curves of pure PSNB and TiB_2 modified PSNB in air and Ar atmosphere.

3.2. Adhesion strength

Table 1 shows eight different kinds of samples by varying the component and pyrolysis temperature, besides, the adhesion strength of all samples have been discussed. Without presence of TiB_2, the adhesion strength increased from 0.84 MPa to 2.53 MPa (S13) as the pyrolysis temperature increased. However, adhesion strength decreased to 1.21 MPa when pyrolysis temperature elevated to 1200 °C. After the addition of TiB_2, the room temperature strengths increased 14.5, 10.8, 3.9 and 1.8 times after pyrolyzed in air at different temperatures, respectively. The adhesion strength of S23 reached up to 10.07 MPa at room temperature and retained a strength of 8.0 MPa at 800 °C in air, this means that the adhesion strength improved significantly with the addition of TiB_2.

3.3. Microstructure of pure PSNB and TiB_2 modified adhesive at room temperature

Room-temperature fracture topographies of pure PSNB adhesive layers are shown in Fig. 3, breakage happens at the adhesive layer, indicating the cohesive strength is not high enough.

Table 1
The adhesion strength of pure PSNB and TiB_2 modified adhesive.

Samples	Component	Pyrolysis temperature/℃	RT strength/MPa /MPa	HT strength/ MPa /MPa
S11	PSNB	600	0.84 ± 0.26	
S12		800	1.19 ± 0.53	
S13		1000	2.53 ± 0.81	
S14		1200	1.21 ± 0.39	
S21	PSNB:TiB_2 = 4:3	600	12.25 ± 1.25	2.4 ± 0.5
S22		800	12.85 ± 1.34	5.4 ± 1.3
S23		1000	10.07 ± 0.56	8.0 ± 1.5
S24		1200	2.20 ± 0.83	7.6 ± 1.8