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A SiC whisker reinforced high-temperature resistant phosphate adhesive for bonding carbon/carbon composites

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ABSTRACT

A SiC whisker reinforced phosphate adhesive was developed for bonding carbon/carbon composites. A kind of spine-like SiCw with a large specific surface area was synthesized at first and then was chosen as the reinforcement phase. It was found that the mechanical performance of adhesive was promoted by the appropriate amount (1 wt.%) of SiCw within the whole heat-treatment temperature range, while the excessive whisker content caused a side effect. With the temperature increasing, the variation of composition and structure of adhesive was closely related to the reinforcing effect of whiskers at different temperatures. Moreover, the reinforcement effect from 900 °C to 1500 °C was better than that below 900 °C. At 1300 °C, the fracture displacement could be extended by 100%, which was attributed to the influence of both spine-like SiCw and the newly-formed slender SiCw.

1. Introduction

Carbon/Carbon (C/C) composites have been widely studied as very promising high temperature structural materials due to their excellent properties such as low density, low coefficient of thermal expansion (CTE), good thermal shock resistance, high specific modulus and excellent mechanical properties at elevated temperature [1–5]. At present, C/C components with large sizes and complicate shapes are extensively used in the fields of aerospace, aviation and industry. However, it is difficult and expensive to prepare large size and complex structure C/C components directly because of their brittle characteristic, high cost of processing as well as long preparation cycle [6–8]. One alternative way is to join several small, simple C/C parts into the large, complicated components. In addition, the joining method is also significant for repairing damaged C/C parts after being employed for many times, making them serve long time and keeping maintenance cost low [9].

Compared to mechanical joining [10], solid reaction diffusion bonding [11,12], brazing [13,14], glass bonding [15,16] and organic precursor bonding [17,18], the inorganic phosphate adhesive bonding is the fastest, cheapest, and most practical joining method, which possesses several superior properties such as room-temperature curing, low-cost production, simple preparation technology and more stable high-temperature resistance [19–21]. Its low temperature curing and stable heat-resistant properties make it the promising joining method characterized by "one-time binding without post-treatment", thus promoting the processes feasibility, especially when the fabrication and repair of components are needed to be done onsite where the heat treatment is not allowed or not easily carried out [22]. However, the phosphate adhesive is still brittle and the bonding strength is also not strong after heat-treatment. An effective toughening and strengthening method is to add nanofibers or whiskers into adhesive [23,24].

Whiskers, nanofibers and nanotubes have generally been applied as the reinforcement phases to improve the property of ceramics, metal and polymer-matrix composites, which are also beneficial to the improvement of adhesives' bonding strength [25–27]. Short carbon fibers and carbon nanotubes have been successfully added into the organic adhesive and the reinforcement effect was obvious [23,24]. Due to the relative rich-oxygen environment in the phosphate adhesive, carbon fibers and carbon nanotubes can be preferentially oxidized while SiC whiskers (SiCw) with excellent oxidative stability can keep their original shape. In addition, SiCw possess other great properties such as high temperature strength, high elastic modulus, chemical stability and high thermal shock resistance [28,29]. What is more, SiCw have a good wettability for borosilicate glass formed in the phosphate adhesive at high temperature [9,16,30]. Therefore, a kind of SiCw with large specific surface area was prepared in this work and then chosen as reinforcement phase of phosphate adhesive. The addition of SiCw effectively enhanced the adhesive's bonding strength within the whole heat-treatment temperature range and leaded to the formation of a new slender SiCw (which was defined as NSiCw)

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at 1300 °C. The reinforcement effect and mechanism of whiskers were investigated and the adhesive's mechanical property was studied.

2. Experimental procedure

2.1. Materials

3D-C/C composites produced by chemical vapor deposition (CVD) with a density of 1.75 g/cm^3 were supplied by Yiyang Auspicious Technology Co., Ltd., China. C/C composites were cut into substrates with size of 40 × 6 × 3 mm from a plate of 300 × 300 × 3 mm by using a diamond cutter. The room-temperature bending strength and the interlaminar shear strength (ILSS) of C/C composites were over 100 MPa and 14 MPa, respectively.

Carbon black powder (d = 4.5–6.5 μm, Hebei Carter Trade Co., Ltd., China) and silica (d = ~1.6 μm, Ningbo Fumei Chemical Co., Ltd., China) were selected as reactants of carbothermal reduction for synthesis of SiC whiskers. Besides, H_3PO_4 (85 wt.%; Tianjin Kewei industrial Co., China) and $Al(OH)_3$ (analytically pure; Tianjin Kewei industrial Co., China) were used as starting materials of the adhesive; B_4C (d = 6.5–10 μm; Mudanjiang Chenxi Boron Carbide Co., Ltd., China) and Si (d = 0.5 mm; Guangzhou Tuoyi Trade Co., Ltd., China) were used as the inorganic fillers of the adhesive.

2.2. Synthesis of SiCw

SiCw were prepared via carbothermal reduction. In order to increase the efficiency of SiCw formation, the reactants were prepared with a carbon-to-silica molar ratio of 2:1 to provide extra carbon. Fe and Cu powders as catalysts (5 wt.%) and the reactants were mixed by ball milling for 1 h. The mixture was calcined at 1600 °C for 4 h in stationary argon atmosphere. The heating rate from room temperature (RT) to 1200 °C was 10 °C/min while that from 1200 °C to 1600 °C was 5 °C/min. After the first heat-treatment, the as-synthesized samples were heat-treated in air at 800 °C for 2 h to burn out residual carbon. The final products had a light green color.

2.3. Preparation of adhesive and bonding process

Firstly, 85 wt.% H_3PO_4 was diluted with water to 60 wt.%. Various amounts of SiCw were added in the dilute phosphoric acids followed by ultrasonically dispersing for 0.5 h in order to overcome whisker agglomeration. Secondly, the solution was heated up to 85 °C under mechanical agitator stirring. After a few minutes, the inorganic additions (B_4C and Si) were slowly mixed into solution using mechanical agitator and then followed by keeping stirring the synthetic matrix solution in high vacuum chamber until the phosphate adhesive reached suitable viscosity which prevented whiskers' precipitation and kept them in good dispersion. In order to study the influence of the amount of SiCw, several adhesives consisting of different content (0–4 wt.%) of SiCw were prepared. The adhesive containing no SiCw was referred as AP + Si + B_4C, which had been detailed studied in Ref. [19]. The C/C joints were bonded by the above adhesives according to the sample configuration in Ref. [19] and then cured at RT with the pressure of 0.75 MPa.

2.4. Testing and analysis

The shear strength was tested under RT by using the Universal Testing Machine (CSS-44001, Changchun, China) at a cross-head speed of 0.2 mm/min, after the bonding joints were heat-treated at different temperatures from RT to 1500 °C for 1 h in argon. Each shear strength value was obtained as the average of five specimens. The chemical composition of as-synthesized SiCw and phase variation of adhesives were analyzed by X-ray diffraction (XRD; Cu Ka radiation D/Max-2500; Rigaku, Akishima, Japan). Scanning electron microscopy (SEM; S-4800; Hitachi, Tokyo, Japan) was applied to characterize microstructures of the cross-section surfaces and fractured surfaces of adhesive. The micromorphology of newly-generated SiCw was identified by Transmission Electron Microscopy (TEM; Tecnai G2 F20; FEI, Eindhoven, Netherlands). The atomic composition of as-synthesized SiCw and newly-generated SiCw were detected by X-ray Energy Dispersive Spectrometers (EDS) equipped on TEM and SEM, respectively.

3. Results and discussion

3.1. The characteristic of as-synthesized SiCw

Fig. 1 shows the microstructure observation and composition identification of as-synthesized SiCw. It could be clearly seen from Fig. 1A that most of the formed SiC whiskers with spine-like morphology were thick and straight. There were a lot of knots formed on the whisker trunk. The dimension of SiCw ranged from 0.2 μm to 1 μm and the length was about 10–15 μm. As Fig. 1B illustrates, only carbon, silicon and small amount of oxygen elements were indentified from EDS spectrum. No elements of metal catalysts were detected by EDS because of their small amounts. Meanwhile, the ratio of atomic number between carbon and silicon was 1.2 according to the quantitative elemental analysis shown in Fig. 1B, indicating that the content of carbon and silicon conformed to the stoichiometric composition of SiC, thus implying that the whisker might be silicon carbide. Fig. 1C illustrates the XRD pattern of whisker samples, confirming the phase of 3C-SiC. The major peaks of SiC were observed at 2θ = 35.60°, 41.40°, 60.0° and 71.70°, which could be indexed as the (111), (200), (220) and (311) reflections of 3C-SiC, respectively. These diffraction peaks were sharp, indicating that the product was highly crystalline. In addition, stacking faults (SFs) on the {111} planes in cubic SiC whiskers were detected in the pattern, which was closely related to the growth morphology of spine-like whisker [31,32]. The SFs and morphology of SiC whiskers were important to the reinforcement of whiskers. The surface special area expanded with the increasing of SFs, leading to the increase of bonding surface between the matrix and whiskers. Besides, the knots which acted like hooks enhanced the interfacial adhesion, thus improving the mechanical properties of SiCw-reinforced materials. Moreover, the as-synthesized SiCw had variable diameters, as seen from Fig. 1A, which were also beneficial to the toughening properties of whisker-reinforced adhesives [33].

3.2. Results of shear strength test

Fig. 2 shows the variation of shear strength with concentration of SiCw for bonded specimens after being heat-treated at 500 °C, 900 °C and 1300 °C, wherein all data were average values. As Fig. 2 illustrates, the shear strengths at all these three curves increased firstly with the elevating concentration of SiCw: from 6.5 to 7.3 MPa at 500 °C, from 3.3 to 4.4 MPa at 900 °C and from 4.1 to 4.7 MPa at 1300 °C, respectively with the content of SiCw increasing from 0 to 1 wt.%. Similarly, the shear strengths at different temperatures all reached peak points when the concentration of SiCw was up to 1 wt.%. However, as the concentration of SiCw continued to grow, shear strengths corresponding to these three temperatures decreased. It should be noted that the decrease tendency at 1300 °C was more obvious than that at other temperatures. Also, it is found from the curves that the bonding strengths of adhesives with 4 wt.% SiCw after heat-treatment at any temperatures were even less than those of whisker-free adhesives under the same conditions. Thus, 1 wt.% was considered as the ideal concentration of SiCw and the adhesive with 1 wt.% of SiCw was referred as AP + Si + B_4C + SiCw for convenience in the paper.

Fig. 3 illustrates the shear strengths of bonded specimens after being treated from RT to 1500 °C. It could be clearly seen that the addition of SiCw enhanced the adhesive's bonding strength effectively within the whole heat-treatment temperature range. Besides, the trend of strength–temperature curve of adhesive had not been changed seriously after the addition of SiCw. In addition, the reinforcement effect from 900 °C to 1500 °C was better than that before 900 °C. The shear strengths increased by 35.1% and 15.5%, respectively, at 900 °C and 1300 °C, while the increase rate at temperatures range from RT to 700 °C was just nearly 10%. For AP + Si + B_4C + SiCw, the shear strength of bonded specimens without heat-treatment was up to the maximum of 8.8 MPa and then decreased with the temperature increasing and the value reduced to about 4.4 MPa at 1100 °C; from 1100 °C to 1300 °C, the shear strength was improved with increasing temperature and reached about 4.8 MPa at 1300 °C; Finally, from 1300 °C to 1500 °C, the value decreased again but still kept above 2.5 MPa.

Fig. 4A shows the typical shear load–displacement curves of joints bonded by AP + Si + B_4C + SiCw. It could be found from the