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Bonding ZrB_2-SiC-G ceramics using modified organic adhesive for engineering applications at ultra high temperatures in air

Zhengxiang Zhong[a], Huifang Xu[a], Xuanfeng Zhang[a], Baosheng Xu[b,c,*], Li Liu[a,**], Yudong Huang[a]

[a] *MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, PR China*

[b] *Beijing Key Laboratory of Lightweight Multi-functional Composite Materials and Structures, Beijing Institute of Technology, Beijing 100081, PR China*

[c] *AML, Department of Engineering Mechanics, School of Aerospace Engineering, Tsinghua University, Beijing 100084, PR China*

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ABSTRACT

It is a challenge to bond ceramics for engineering applications at ultrahigh temperatures in air. In this paper, a high temperature organic adhesive (HTOA) was prepared using methylphenylsilicone resins (MPSR) as the matrix, trisilanolisobutyl-methylsilicone resin/polyhedral oligomeric silsesquioxane (POSS) as the modifier, ZrB_2, SiO_2 and Si powders as the inorganic fillers, and γ-aminopropyltriethoxysilane (KH550) as the curing agent. The synthesized HTOA was used to bond ZrB_2-SiC-G ceramic (ZSG). The ceramic yield of MPSR was increased from 71% to 91% after being modified by trisilanolisobutyl-POSS. The average shear strength of ZSG joints bonded by HTOA was 13.2 MPa at room temperature. After 1500 °C/1 h processing, the bonding strength between HTOA and ZSG ceramic was 53.8 MPa. The inter-diffusion of elements between the HTOA and the ZSG occurred at 1500 °C and $ZrSiO_4$ compound was formed via the interface reaction. The excellent high-temperature performance of the prepared HTOA makes it one of the convenient and effective organic adhesive for joining ZSG for engineering applications at ultrahigh temperatures in air.

1. Introduction

With the development of hypersonic aircrafts and atmospheric reentry vehicles, great interests in ultrahigh-temperature ceramics (UHTC) have been increased in the past decades [1,2]. Zirconium diboride (ZrB_2)-based ceramics have attracted much attention from the research communities due to their unique properties such as high melting temperature, high hardness, high thermal and electrical conductivity, low thermal expansion coefficient and relatively low density [3–11]. However, ZrB_2-based ceramics are brittle and high rigidity that makes them difficult to directly fabricate large-sized and complex-shaped ceramic parts by traditional methods [12]. Therefore, in order to extend their applications, the joining techniques for ZrB_2-based ceramics become extremely important.

Different joining technologies have been reported for joining the ZrB_2-based ceramics to themselves or to metallic parts, such as Ni-based brazing alloys [13,14], Ag-based brazing alloys [15,16], Pd-based brazing alloys [17], inorganic glasses [18,19], and Ti based alloy [20,21]. For instance, Yuan et al. used pure Ni powers as an interlayer to join monolithic ZrB_2 ceramics and $ZrB_2 - 20$ vol% SiC composite, and the maximum shear strength of the joint was 60 MPa [13]. Yang et al. used Ti-Ni-Ti powder filler metal to braze ZrB_2–SiC ceramic. The maximum shear strength of the brazed joints reached 134 MPa with a brazing temperature of 1050 °C [14]. Sciti et al. used Ca–Al–Si–O glass as interlayers to join ZrB_2–SiC ceramics at 1437 °C, and the bonding strength of 277 MPa was obtained at room temperature [19]. Although the aforementioned methods for bonding ZrB_2-based ceramics have been proved effective, there are still many problems. For example, the stress concentration caused by heat treatment in joints greatly impaired the mechanical properties of obtained joints. Furthermore, the aforementioned joining technologies often need special equipment (i.e., vacuum furnace, heating equipment) and complex technological processes (for instance, surface treatment, component mounting), all of these are required to achieve accurate and complex treatment processes for practical applications [22,23]. More importantly, the heat-resistant temperature of the joints can hardly reach 1500 °C that restricts its practical applications in the hypersonic aerospace vehicles and reusable atmospheric reentry vehicles [1,3,23]. Thus, it is important to develop an effective bonding method for joining ZrB_2-based ceramics.

The adhesive bonding technology is low cost, high speed, convenient and it could minimize stress concentrations. Thus, many adhesives using organic resins as matrix have successfully joined many

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[*] Corresponding author at: AML, Department of Engineering Mechanics, School of Aerospace Engineering, Tsinghua University, Beijing 100084, PR China.

[**] Corresponding author.

E-mail addresses: xubaosheng211@163.com, baoshengxu@mail.tsinghua.edu.cn (B. Xu), liuli_hit1@163.com (L. Liu).

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ceramics [24–29]. For example, Zhang et al. prepared a room-temperature cured heat-resistant adhesive based on silicone resin and epoxy resin that could be used in air surroundings, but the maximum strength of the joints was only 9.44 MPa [26]. Wang et al. joined various engineering ceramics and composites by the modified preceramic polymer, and the shear strength could reach 33 MPa after heating at 1300 °C in air [27]. Qin et al. prepared ceramizable heat-resistant organic adhesive using preceramic polymer polysiloxane as matrix, and the shear strength of the joints was 21 MPa when treated at 1200 °C for 2 h in air [28]. Luan et al. joined Al_2O_3 ceramic by using polyborosilazanes resin as the matrix, and the strength of the joints was 15.73 MPa after treatment at 1500 °C [29]. Thus, such characters as low-temperature curing, low-cost, simple preparation technology and more stable high-temperature resistance of the adhesive bonding makes it a promising candidate for bonding ZrB_2-SiC-Graphite ceramics (ZSG).

In this work, a trisilanolisobutyl-polyhedral oligomeric silsesquioxane (POSS)-modified methylphenylsilicone resins (MPSR) adhesive was prepared and used to bond ZSG. This high temperature organic adhesive (HTOA) was prepared using MPSR, trisilanolisobutyl POSS, Si, SiO_2, ZrB_2 powders and γ-aminopropyltriethoxysilane (KH550). The interfacial microstructure of ZSG joints was characterized by scanning electron microscopy (SEM) and inter-diffusion of elements was analyzed by energy dispersive spectroscopy (EDS). Furthermore, the reaction mechanism between HTOA and ZSG, and the formation mechanism of $ZrSiO_4$ were proposed according to X-ray diffractometry (XRD) results. The shear strength of ZSG joints at room temperature and 1500 °C was investigated by universal testing machine.

2. Experimental

The ZrB_2-20 vol% SiC-10 vol% graphite flake (ZSG) composite ceramic was fabricated by uniaxial hot pressing at 2000 °C/30 MPa for 1 h. The raw ZSG was cut into pieces with the size of 10 mm × 10 mm × 7 mm and the joining surfaces of samples were polished using SiC paper (< 1000 grit). The ZSG pieces were ultrasonically cleaned in acetone and then dried at 80 °C for 30 min 5 wt% of TriSilanolIsobutyl-POSS (TriSilanolIsobutyl-POSS was purchased from Hybrid Plastics, Inc, USA) was blended into silanol-terminated methylphenylsilicone resins (MPSR) (Hydroxyl-terminated MPSR in toluene (received from ShangHai Chemicals Co. resin content: 50 wt%, viscosity: 25 cSt, and molecular weight: 2400)) before end linking and a small portion of anhydrous ethanol (amounting to 10 wt% MPSR) was added to dissolve the POSS before it was mixed with MPSR. The mixture was stirred vigorously, and the solvent was removed at 55 °C by evacuation [25]. SiO_2 powder (5 μm, 99.9%, Connaught Qinhuangdao new materials development Co. Ltd., China), Si powder (5 μm, 99.9%, Connaught Qinhuangdao new materials development Co. Ltd., China), ZrB_2 (2 μm, purity > 99.5%, Northwest Institute for Non-ferrous Metal Research, China) and γ-aminopropyltriethoxysilane (KH550, purity > 99.0%, Alfa Aesar, MA, USA) were added into the POSS-MPSR to form a novel high temperature adhesive. The adhesive was applied to ZSG surfaces with a uniform thickness using a doctor blade method. Specimens were superposed and bonded to the configuration (Fig. 1) and then placed into the muffle to cure at 150 °C in an air condition for 2 h. Subsequently, the samples were heated up to 1500 °C at 25 °C/min in air condition and held for 1 h.

The un-cured and cured POSS-MPSR resins were measured on a Nicolet FT-IR spectrophotometer using KBr pellets with a spectral resolution of 1 cm^{-1} at room temperature. The thermogravimetric analysis (TGA) of pure MPSR resin and POSS-MPSR were carried out through TGA. Differential scanning calorimetry (DSC) of MPSR resin and POSS-MPSR were carried out on a NETZSCH STA449C thermogravimetric analyzer at a heating rate of 10 °C/min with an air flow rate of 100 cc/min. The morphology and crystalline structure of the obtained samples were characterized by scanning electron microscope (SEM, Helios Nanolab600i) coupled with back scattered electron(BSE), energy dispersive spectrometer (EDS) and X-ray diffraction (XRD, Rigaku D/max-3C). The shear strength of the joints was measured with a universal mechanic test machine with a load rate of 0.2 mm/min at 25 °C in air. At least five specimens were tested for each experimental condition.

3. Results and discussion

3.1. Structure and thermal properties of POSS-MPRS

Fig. 2 shows the FTIR spectra of POSS-MPSR before and after curing. For the uncured POSS-MPSR (Fig. 2(a)), the main absorption peaks, 3725 cm^{-1} (Si-OH), 2970 cm^{-1} (C-H), 1408–1270 cm^{-1} and 767–690 cm^{-1} (Si-C, Si-Ph), 1112–1038 cm^{-1} (Si-O-Si) were observed [25]. After the curing treatment (Fig. 2(b)), the stretching vibration of Si-OH disappeared, while the width peak intensity of Si-O-Si, and the width and intensity strengthening of Si-O-Si, Si-CH_3 and Si-Ph were significantly increased, suggesting that the Si-OH of silicone resin would have an interaction with POSS through condensation reaction to form hydrogen bonds for eliminating the effect of terminated Si-OH. FTIR analysis indicate that POSS-MPSR could be crosslinked through polycondensation reactions.

The thermal properties of pure MPSR and POSS-MPSR are also evaluated by TGA and DTG, as shown in Fig. 3. The ceramic yield of MPSR and POSS-MPSR after curing in air up to 1000 °C was 74% and 91%, respectively (Fig. 3(a)). Introducing POSS cages through polycondensation reaction caused the formation of crosslinking network structure, which is favorable for improving the thermal stability and ceramic yield of POSS-MPSR [25]. The temperature of peak degradation following the same change trends as the thermal stability is shown in the DSC curves (Fig. 3(b)). For MPSR, two endothermic peaks are identified at 217 and 484 °C, which can be explained by the existence of a two-stage decomposition mechanism. However, there is only one obvious exothermic peak at 576 °C for POSS-MPSR and it is 92 °C higher than the second decomposition temperature of MPSR. The introduced POSS can contribute to the following two aspects. On one hand, the first degradation process of POSS-MPSR is suppressed after the incorporation of POSS. On the other hand, the thermal stability of the main chain of POSS-MPSR was improved. In short, through the analysis of TGA and DSC results, we can conclude that the introduced trisilanolisobutyl-POSS have the ability to improve the decomposition temperatures and oxidation resistance. Hence, the POSS-MPSR is a desired matrix serving for high temperature adhesive.

3.2. Structure evolution and shear strength of ZSG joints

The cross-section SEM images of ZSG joints before and after heat-treatment at 1500 °C in air can be seen in Fig. 4(a) and (e). Good joints were formed after curing and heat-treatment. After curing, the joint was achieved through cross-linking reaction between Si-OH of POSS-silicone resin and Si-OH of ZSG substrates. The wettability of HTOA on ZSG was very excellent and the HTOA was well adherent to ZSG with no obvious cracks (Fig. 4(a)). After heat-treatment, the thickness of adhesive was reduced from 100 to 70 μm, which could be attributed to the shrinkage engendering from the pyrolysis of silicone resin and the reaction of the inorganic filler [24,25]. Furthermore, the adhesive presented a very compact structure without obvious cracks and pores (Fig. 4(e)). As seen from Fig. 4(b), that interface between HTOA and ZSG was obvious and the distribution map of Si elements has a smooth interface. Compared with the Si element distribution map in Fig. 4(b) and (f), the interface shape between HTOA and ZSG has changed from smooth sharp into the saw tooth shape after heat-treatment at 1500 °C. At the same time, the Si element transports across the interface and the reaction layer with 6 μm width was formed (Fig. 4(f)).

The EDS line scanning results of Zr and Si across joining interfaces show obvious difference before and after heat-treatment at 1500 °C for