www.elsevier.com/locate/ijadhadh

A self-healing strategy for inorganic fillers: Toward practical applications of silicone resin treated at high temperatures for bonding ceramic joints

Lege Wang, You-Fen Li, Shi-Hai You, Liangliang Sun, Yaoyao Tong

PII: S0143-7496(18)30218-5
DOI: https://doi.org/10.1016/j.ijadhadh.2018.09.014
Reference: JAAD2271

To appear in: *International Journal of Adhesion and Adhesives*
Accepted date: 20 September 2018

Cite this article as: Lege Wang, You-Fen Li, Shi-Hai You, Liangliang Sun and Yaoyao Tong, A self-healing strategy for inorganic fillers: Toward practical applications of silicone resin treated at high temperatures for bonding ceramic joints, *International Journal of Adhesion and Adhesives,* https://doi.org/10.1016/j.ijadhadh.2018.09.014

A self-healing strategy for inorganic fillers: Toward practical applications of silicone resin treated at high temperatures for bonding ceramic joints

Lege Wang, You-Fen Li*, Shi-Hai You, Liangliang Sun, Yaoyao Tong

Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, P.R. China

*Corresponding authors. College of Materials Science and Engineering, Beijing University of Chemical Technology, 15 Beisanhuan East Rd., Chaoyang District, Beijing 100029, P.R. China. Fax: +86 10 64436736. E-mail addresses: yfli@mail.buct.edu.cn (You-Fen Li).

Abstract

A high-temperature adhesive composed of a silicone resin (SR) matrix was prepared for bonding ceramic joints. The adhesive primarily consists of boehmite sol as the modifier and B_4C, Al and fumed SiO_2 powders as inorganic fillers. In this study, the ceramic yield of the adhesive was determined to reach 138 % after heat treatment at 1100 °C. The bonding strength of ceramic joints heated at 200 °C was measured as 6.25 MPa and increased to 41.67 MPa after heat treatment at 1000 °C. According to mechanistic analysis, the volume shrinkage induced by the pyrolysis of SR was effectively restrained, and the micro-pores and cracks resulting from the oxidation process of the inorganic fillers can be self-healed by introducing borate. In addition, chemical bonds were introduced at the interfaces, thereby further improving the adhesive strength at elevated temperatures.

Keywords

Adhesive strength; Silicon resin; Self-healing; Inorganic fillers; Ceramic yield

1. Introduction

Ceramic materials are widely applied in high-temperature environments, such as aerospace, electronics, nuclear and automotive environments. However, difficulty arises when large and complex shapes of ceramic materials are used directly due to their brittle nature, which restricts their applications. Thus, the joining of ceramic structures is necessary for extending their applications. There have been various methods reported, the most promising and appropriate of which is the adhesive bonding technique [1-4].

High-temperature adhesives have found widespread application in bonding materials at elevated temperatures [4]. There are two major types: inorganic adhesives and organic adhesives. Inorganic adhesives, which are usually prepared with metal phosphate and alkali silicate components, have excellent heat resistance but can be brittle with low bonding strength and require unconventional joints (muff-coupling, groove, tongue, etc.). Organic adhesives are primarily based on various polymers; however, even though they exhibit an excellent bonding strength at room temperature, their thermal resistance is weak [3]. The pyrolysis of organic adhesives produces high-temperature residues, which are then converted into carbonaceous char with outstanding thermophysical properties [5]. Therefore, organic adhesives can be applied to bond materials used at elevated temperatures. With phenol-formaldehyde resin as a raw material, different fillers are used to join C/C composites, graphite materials and ceramic materials; the resulting adhesives possess satisfactory bonding strength at extreme temperatures but cannot be used in air [4, 6, 9].

Silicone resin (SR) is a preceramic polymer based on Si-O-Si chains, and when heated at high temperatures, it can be pyrolyzed to produce amorphous silicon oxycarbide (SiO_mC_n) in an inert atmosphere or produce amorphous silica in an oxidizing environment with superior yield [10,11]. The pyrolysis products will then further react with inorganic additives, forming a new mixture of ceramics and glass phases with good bonding properties to ceramic materials [12]. Therefore, SR is regarded as a promising material for the connection of ceramics [11]. SR was first used to join SiC ceramics by Yajima et al [13], and this report was followed by numerous investigations. Yuan et al [10,11] and Narisawa et al [14-16] joined SiC or SiOC ceramics using SR with satisfactory bonding strength. Luo et al [3,17,18] prepared several heat-resistant adhesives based on SR and inorganic fillers for C/C composite bonding; however, the maximum bonding strength was only approximately 10 MPa after treatment between 200 and 1000 °C. Additionally, there are still many unresolved issues with the addition of inorganic fillers: 1) the decreased strength arising from the volume shrinkage and micro-cracks caused by resin pyrolysis during the high temperature process; 2) the compatibility between and distribution of the inorganic fillers in the organic resin; and 3) the inability to use inorganic fillers at high temperatures in an oxygen environment. Considering the potential applications of ceramics, advanced joining techniques are crucial for the fabrication of ceramic parts that are large and complex in shape. Therefore, developing novel high-temperature adhesives with outstanding bonding strength through simple routes is important.

The purpose of this paper is the development of an adhesive that can be applied in a high-temperature environment through a simple and inexpensive ceramic bonding process. In this study, boehmite sol-modified SR (M-SR) was chosen as the matrix, in which, boehmite sol is utilized for its peptization ability [19]. Moreover, the properties of the composites can be improved by adding coupling agents into inorganic fillers and organic materials due to molecular bridges with winding covalent bonds and molecular chains to link two kinds of relatively inert materials [20–22]. Liang et al. [23] illustrated that the adhesion of the aggregate and asphalt can be improved by the addition of KH570. Therefore, we chose a silane coupling agent (KH560) to modify the surface of fillers. The metallic Al and B_4C were utilized as the main adhesive fillers. Al_2O_3, which is generated in situ within the organic resin matrix during the oxidation process at elevated temperatures, further reacts with the organic resin pyrolysis products to form a dense ceramic/glass phase. The volume expansion induced by the oxidation process of the inorganic fillers will compensate for the volume shrinkage caused by the densification of the adhesive, leading to micro-defect healing and a consequent significant improvement in the bonding strength.

2. Materials and methods

2.1. Raw Materials

SR, with a solid content of 50 % and viscosity of 85-225 MPa·s at 25 °C (industrial grade, Wujiang City Heli Resin Co., Ltd., China), was selected as the adhesive matrix. Al (500 mesh, 95 %), B_4C (2.5-3.5 μm, 90 %) and fumed SiO_2 (20-40 nm, 99.8 %) powders were used as inorganic fillers. A corundum plate (17.5 × 17.5 × 5 mm) was employed as the adherend.

2.2. Experimental processes

2.2.1. Preparation of the boehmite sol-modified SR and adhesive

Aluminum isopropoxide (A.R.) was dissolved using isopropyl alcohol (A.R.) and gradually added to a mixture of deionized water and HNO_3 solution (1 mol/L) with constant stirring in a three-necked glass reactor. The mixed solution was maintained at 80-90 °C for 3-4 h in air, and the pH controlled at 3-4 to synthesize the boehmite sol. SR was mixed with the boehmite sol in the mass ratio of 8:2 to form M-SR. B_4C and Al powders were surface modified with a silane coupling agent (KH560), followed by ultrasonic dispersion in ethanol for 30 min. The inorganic filler suspension was then uniformly blended with M-SR with mass ratio of 50 % at 70-80 °C to prepare the high-temperature adhesive. All of samples with different mass ratios between the matrix and fillers are listed in Table 1.

2.2.2. Preparation of ceramic joints

Corundum plates with an arithmetic average of roughness surface Ra ≈ 1.549 μm were ultrasonically cleaned in ethanol for 30 min and then dried. The adhesive was evenly brushed on the pretreated corundum plate surfaces. Two corundum plates were bonded together to establish a ceramic joint. The bonding area was 17.5 × 8 mm with a bonding thickness of approximately 10-20 μm. The ceramic joints were treated at 70 °C for 24 h to volatilize the solvent and then cured at either 120 °C for 5 h or 200 °C for 3 h under the application of a pressure of 0.1 MPa. All ceramic joints were then heated at different temperatures ranging from 200 to 1200 °C in a muffle furnace in air and maintained at each given temperature for 3 h.

2.3. Characterization and bending strength tests

The bonding strength of ceramic joints was evaluated using a universal mechanical testing machine (SGW, Xiangtan Xiangyi Instrument Co., Ltd., China) with a load rate of 1.5 mm/min at room temperature. The thermal stability of the adhesive was tested by a thermogravimetric analyzer (ZRY-2P, Shanghai Instrument Factory Co., Ltd., China) at a heating rate of 10 °C/min in the open air. Microstructures of cross-sections of the ceramic joints were observed by using a scanning electron microscope (S-4700. Hitachi). Phase structures of the surfaces of broken joints after adhesive treatment at different temperatures were identified via X-ray diffraction (D/Max-2500. Rigaku) with Cu K_α radiation. The working voltage was 35 KV with a 20 mA tube current. The scanning range was 10-90°C with a scanning speed of 2 °C/min.

3. Results and discussion

3.1. XRD analysis and phase formation

Fig. 1 shows XRD patterns of the adhesive, and all phase structures at different heating temperatures are presented in Table 2, in which crystalline phases of B_4C and Al can be identified. The relatively high background is attributed to the presence of SR (Fig. 1(a) and (b)). As the treatment temperature rose to 600 °C (Fig. 1(c)), B_2O_3 and SiO_mC_n were generated, forming new amorphous phases of $xSiO_mC_n \cdot yB_2O_3$. The reactions that occurred were as follows [2, 3, 7]:

$$B_4C + 4O_2 \rightarrow 2B_2O_3 + CO_2 \quad [1]$$

$$B_4C + 6CO \rightarrow 2B_2O_3 + 7C \quad [2]$$

$$xSiO_mC_n + yB_2O_3 \rightarrow xSiO_mC_n \cdot yB_2O_3 \quad [3]$$

The XRD pattern of the adhesive treated at 800 °C (Fig. 1(d)) indicates that some additional phases occurred, such as Si, Al_2O_3 and $2Al_2O_3 \cdot B_2O_3$, which are produced through reactions between the inorganic fillers and pyrolysis products of SR, as given below [3, 9, 24-26]:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \quad [4]$$

$$4Al + (6/(m-n))\ SiO_mC_n \rightarrow 2Al_2O_3 + (6n/(m-n))CO + (6\ m/(m-n))Si \quad [5]$$

$$2Al_2O_3 + B_2O_3 \rightarrow 2Al_2O_3 \cdot B_2O_3 \quad [6]$$

Above 1000 °C, the peak intensity of Al_2O_3 and $9Al_2O_3 \cdot 2B_2O_3$ was enhanced. However, the B_2O_3 peaks weakened, and the peaks of Si that formed in Equation [5] disappeared, which was attributed to the oxidation of Si to amorphous SiO_2. The $9Al_2O_3 \cdot 2B_2O_3$ phase was generated through the reaction between Al_2O_3 and $2Al_2O_3 \cdot B_2O_3$ expressed below [3, 9]:

$$2(2Al_2O_3 \cdot B_2O_3) + 5Al_2O_3 \rightarrow 9Al_2O_3 \cdot 2B_2O_3 \quad [7]$$

3.2. SEM images of the cross section and EDS analysis

Fig. 2 shows SEM cross-sectional images of the interfacial areas for ceramic joints treated at temperatures ranging from 200 to 1200 °C. The thickness of the adhesive layer is within 10-20 μm. As shown in Fig. 2(a), the adhesive layer cured at 200 °C is continuous and dense without obvious cracks and pores, and the inorganic fillers are scattered uniformly in the M-SR matrix. When the treatment temperature rose to 400 and 600 °C, some pores and cracks appeared in the adhesive layer due to the pyrolysis of M-SR, as shown in Fig. 2(b) and (c) with the circles for pores and the boxes for cracks. After treatment at 800 and 1000 °C (Fig. 2(d) and (e)), the adhesive layer became much denser due to the oxidation of the inorganic fillers and formation of M-SR pyrolysis products. We also observed that some parts of the adhesive interfaces disappeared (as seen in Fig. 2(e)) which can arise from the volume expansion due to the oxidation process of the inorganic fillers, resulting in the healing of micro-defects. When the treatment temperature was continuously increased to 1200 °C, some cracks formed along the bonding interface as a result of volume shrinkage caused by the densification of the adhesive (Fig. 2(f)).

To obtain better insight into the interfacial areas, the energy dispersive spectroscopy (EDS) line scanning spectra for Si and Al elements were acquired (Fig. 3). Interdiffusion occurred between the bonding interfaces after heat treatment. In this process, the Si atoms are diffused from the bonding layer to the alumina ceramic. Conversely, Al atoms spread to the adhesion layer, and the thickness of the interdiffusion layer was approximately 2 μm. The phenomenon of interdiffusion indicates that the formation of a chemical force at the adhesion interface plays an important role in improving the adhesive strength [27]. In addition, with the increase in the heat treatment temperature, the diffusion rate of each element will accelerate, and more chemical bonds will be introduced, thereby further enhancing the adhesion strength of the adhesive.

3.3. TG and FTIR analysis

Fig. 4 presents TG curves of SR, M-SR and the prepared adhesive of M-SR-5. As revealed in Fig. 4(a), the mass loss of SR primarily occurred at temperatures from 380 to 650 °C due to its pyrolysis. Above 650 °C, there was no significant mass loss even up to 1100 °C, at which the ceramic yield obtained was 55 %. The TG curve of M-SR was similar to that of SR, but its ceramic yield increased by 60 % due to the addition of the boehmite sol. As shown in Fig. 4(c), the ceramic yield is 88 %, which is far greater than those of the SR and M-SR at 573 °C; with a treatment temperature greater than 1100 °C, its production greatly increased to 138 %, which can be attributed to the oxidation of the B_4C and Al inorganic fillers. Lower mass loss and higher ceramic yield will result in smaller volume contractions, increasing the density in the structure, which will allow the adhesive to exhibit superior bonding strength [2].

Fig. 5 shows the infrared spectra of the SR and adhesives at different heat treatment temperatures. The FTIR spectrum of methyl phenyl silicone resin is shown in Fig. 5(a). The wide absorption band at 1000-1134 cm^{-1} is the peak of the stretching vibration absorption of Si-O-Si, which is a characteristic absorption peak of SR [28]. The characteristic absorption peaks of $Si\text{-}CH_3$ in SR were at 1260, 845 and 804 cm^{-1}. The stretching vibration peaks of the benzene ring in $Si\text{-}C_6H_5$ can be observed at 1594 and 1430 cm^{-1}, and the broad and weak absorption peaks at 3200~3700 cm^{-1} belong to the stretching vibration of Si-OH.

Compared to the spectrum in Fig. 5(a), the spectra in Fig. 5(b) and (c) are similar to the spectrum of M-SR. The definite bands of B_4C at 1507, 843, 702 and 605 cm^{-1} were not observed. This can be explained by the peaks of M-SR covering the weak absorption peak of B_4C [29]. Notably, the characteristic peaks of $Si\text{-}CH_3$ and $Si\text{-}C_6H_5$ are weaker and will disappear, as shown in Fig. 5(d) to (g), suggesting that the pyrolysis of M-SR begins at high temperatures.

In Fig. 5(d), the wide and strong peaks located at 1000~1134 cm^{-1} are replaced by the sharp absorption peak for the Si-O-Si bridging oxygen vibration. In addition, the absorption peak of Si-C is present at 795 cm^{-1} [25], which shows that the matrix has been completely pyrolyzed and has formed amorphous SiO_2 and SiO_mC_n at 800 °C. The sharp absorption peaks located at 2260, 1468 and 1196 cm^{-1} are assigned to the characteristic absorption peaks of B-H, B-O-B and B-OH in H_3BO_3, respectively. At 883 and 674 cm^{-1}, the absorption peaks belong to Si-O-B, with the borosilicate glass bridging oxygen peak appearing at approximately 460-650 cm^{-1} [29, 30]. Here, it can be assumed that the reaction between B_2O_3 and amorphous SiO_2 or SiO_mC_n occurs, forming the Si-O-B and Si-O-B-C groups. The different phases detected by XRD and reported in Fig. 1 are consistent with the FTIR results. The borosilicate glass phase remains until the treatment temperature reaches 1200 °C, with only a small amount of change in the composition and inorganic crystalline phases formed at high temperatures.

3.4. Bonding strength of samples containing B_4C/Al

Fig. 6(a) is the curve of the bonding strength of Al_2O_3 ceramics adhered using M-SR filled with Al and B_4C and treated at various temperatures. It shows that the adhesive performance of Al powder and B_4C are well improved, especially for treatment temperatures in the range of 800 ~ 1200 °C. The bonding strength of Al-filled M-SR is up to 6.25 MPa at 200 °C and reaches 20.07 MPa below 1000 °C, an increase of almost 5.52 times. Furthermore, the bonding strength of B_4C-filled M-SR ranges from 3.81 MPa to 41.67 MPa as the temperature increases from 200 °C to 1000 °C. It is obviously that within 600 ~ 1000 °C, the bonding strength of the -filled samples was improved more than that of the Al-filled samples, suggesting that B_4C is the more effective modified filler within this temperature range. However, after heat treatment at 1200 °C, the bonding strength of B_4C-filled M-SR is rapidly reduced to 11.77 MPa, which means that boron glass can play a certain role in low temperature. Borate glass has a very low viscosity thus making the joined components susceptible to failure by shear. M-SR with Al powder and B_4C can improve its high-temperature bonding performance. However, M-SR filled with a single species has certain advantages and disadvantages at different temperature stages. To further investigate the function of the inorganic filler, co-adopted M-SR adhesives were discussed.

Fig. 6(b) shows the bonding strength of ceramic joints with different ratios of inorganic fillers heated at different temperatures. The bonding strength of ceramic joints is lowest at 400 °C but increases with increasing temperature, reaching the maximum value at 1000 °C. Combined with the phase evolution from the XRD results, these results indicate that the bonding mechanism might be different from 200 to 1200 °C. Below 600 °C, there are no obvious inorganic filler reactions, and the bonding strength is attributed to the outstanding adhesive properties of the M-SR matrix in the adhesive [3]. When the treatment temperature increased above 600 °C, the adhesive bonding strength began to greatly improve due to the B_2O_3 and amorphous $xSiO_mC_n \cdot yB_2O_3$ species generated in the adhesive layer, as shown in Fig. 7(a). B_2O_3 has good wettability for ceramics that melt at high temperature and can expand to 250 % of its volume with the conversion from B_4C to B_2O_3 [2, 3, 7]. Consequently, the volume shrinkage brought about by the pyrolysis of SR can be effectively restrained, and micro-pores and cracks can be self-healed, particularly at 1000 °C (as seen in Fig. 2(e)); the simulated processes are shown in Fig. 7(b). At 1200 °C, some cracks were established at the bonding interface owing to the densification of the adhesive structure, resulting in decreased bonding strength.

4. Conclusions

With M-SR as the matrix and B_4C and Al powders as inorganic fillers, high temperature adhesives were prepared and successfully employed for joining Al_2O_3 plates. The bonding strength of ceramic joints was 6.25 MPa after curing at 200 °C. When the treatment temperature increased to 1000 °C, the bonding strength increased and reached a maximum value of 41.67 MPa. According to the XRD analysis and structural evolution of the adhesive layer, the increasing adhesion strength was mainly attributed to two factors: (1) inorganic fillers in the resin matrix were oxidized at elevated temperatures and then further reacted with the pyrolysis products to form a dense, ceramic/glass phase, such as B_2O_3, $xSiO_mC_n \cdot yB_2O_3$, $2Al_2O_3 \cdot B_2O_3$ and $9Al_2O_3 \cdot 2B_2O_3$, effectively restraining the volume shrinkage and healing micro-defects caused by the pyrolysis of SR. (2) Under extreme temperature conditions, chemical bonds were introduced at the bonding interface through reactions between the adhesive and corundum substrate. In addition, the thermal stability of the adhesives is excellent, and the ceramic yield reached 138 % at temperatures above 1100 °C. As a result, inorganic filler-modified silicone adhesives have a superior bonding strength and will have prospective applications at elevated temperatures.

References

[1] W. Guin, J. Wang, Theoretical model of adhesively bonded single lap joints with functionally graded adherends, Eng. Struct. 124 (2016) 316-332.

[2] X. Wang, J. Wang, H. Wang, Preparation of high-temperature organic adhesives and their performance for joining SiC ceramic, Ceram. Int. 39 (2) (2013) 1365-1370.

[3] J. Zhang, R. Luo, M. Jiang, et al, The preparation and performance of a novel

room-temperature-cured heat resistant adhesive for ceramic bonding, Mat. Sci. Eng. A. 528 (6) (2011) 2952-2959.

[4] J. Wang, N. Jiang, H. Jiang, Effect of the evolution of phenol-formaldehyde resin on the high-temperature bonding, Int. J. Adhes. Adhes. 29 (7) (2009) 718-723.

[5] J. Lefebvre, V. Mamleev, M.L. Bras, S. Bourbigot, Kinetic analysis of pyrolysis of cross-linked polymers, Polym. Degrad. Stabil. 88 (1) (2005) 85-91.

[6] SA. Haddadi, M. Mahdavianahadi, F. Abbasi, Effect of Nanosilica and Boron Carbide on Adhesion Strength of High Temperature Adhesive Based on Phenolic Resin for Graphite Bonding, Ind. Eng. Chem. Res. 53 (53) (2014) 11747-11754.

[7] J. Wang, Q. Guo, L. Liu, J. Song, The preparation and performance of high-temperature adhesives for graphite bonding, Int. J. Adhes. Adhes. 25 (2005) 495-501.

[8] S. Li, Y. Luo, L. W, C. Xu, Polyborosilazane preceramic as matrix resin of high temperature adhesive for graphite bonding, Int. J. Appl. Ceram. 14 (2017) 999-1005.

[9] J. Wang, N. Jiang, H. Jiang, The high-temperatures bonding of graphite/ceramics by organ resin matrix adhesive, Int. J. Adhes. Adhes. 26 (7) (2006) 532-536.

[10] X. Yuan, H. Chen, Residual thermal stress analysis of SiC joint by polysiloxane silicon resin YR3187, J. Adhes. Sci. Technol. 27 (14) (2013) 1525-1534.

[11] X. Yuan, B. Xu, Fabrication and life prediction of SiC ceramic joint joined with silicon resin YR3370, Chinese Journal of Aeronautics. 20 (1) (2007) 81-85.

[12] E. Bernardo, P. Colombo, S. Hampshire, Advanced ceramics from a preceramic polymer and nano-fillers, J. Eur. Ceram. Soc. 29 (5) (2009) 843-849.

[13] S. Yajima, K. Okamura, T. Shishido, et al, Joining of SiC to SiC using polyborosiloxane, Am.

Ceram. Soc. Bull. 60 (2) (1981) 253-253.

[14] M. Narisawa, Y. Abe, Microstructure of SiC-Si-Al_2O_3 composites derived from silicone resin-metal aluminum filler compounds by low temperature reduction process, Mater. Sci. Eng. 18 (2011) 042003.

[15] H. Tian, Q. Ma, Effects of exterior gas pressure on the structure and properties of highly porous SiOC ceramics derived from silicone resin, Mater Letter. 66 (1) (2012) 13-15.

[16] H. Tian, Q. Ma, Y. Pan, W. Liu, Structure and mechanical properties of porous silicon oxycarbide ceramics derived from silicone resin with different filler content, Ceram. Int. 39 (2013) 71-74.

[17] J. Li, R. Luo, Y. Bi, et al, The preparation and performance of short carbon fiber reinforced adhesive for bonding carbon/carbon composites, Carbon. 46 (14) (2008) 1957-1965.

[18] J. Zhang, R. Luo, C. Yang, A multi-wall carbon nanotube-reinforced high-temperature resistant adhesive for bonding carbon/carbon composites, Carbon. 50 (2012) 4922-4925.

[19] B. Kindl, D.J. Carlsson, Y. Deslandes, A.J. Hoddenbagh, Preparation of γ-alumina ceramics: the use of boehmite sol as dispersion agent, Ceram. Int. 17 (1991) 347–350

[20] X.L. Wang, B. Zhang, Y. Zhao, Y. Xu, B.S. Xu, Dispersion and Behavior of Silane Coupling Agent to Surface Modification of n-Cu Particles, Powder Technol. Appl. 92 (2010) 73–78.

[21] H.Q. Chen, B.M. Tang, Surface Modification of Fire-retardant Asphalt with Silane Coupling Agent, J. Wuhan. Univ. Technol. Sci. Edi. 27 (2) (2012) 310–315.

[22] B.G. Wei, Q. Chang, C.X. Bao, L. Dai, G.Z. Zhang, F.P. Wu, Surface modification of filter medium particles with silane coupling agent KH550, Colloids Surf. A-Physicochem. Eng. Asp. 434 (2013) 276–280.

[23] X. Liang, X.D. Guo, H. Wang, X.S. Yu, The Effect and Characterization of Modified Asphalt by Coupling Agent, Struct. Eng. Meas. 105 (2012) 1773–1778.

[24] X. Wang, J. Wang, H. Wang, Synthesis of a novel preceramic polymer (V-PMS) and its performance in heat-resistant organic adhesives for joining SiC ceramic, J. Eur. Ceram. Soc. 32 (12) (2012) 3415-3422.

[25] J. Anggono, B. Derby, Mullite formation from the pyrolysis of aluminum-loaded polymethylsiloxanes: the influence of aluminum powder characteristics, J. Eur. Ceram. Soc. 26 (7) (2006) 1107-1119.

[26] J. Anggono, B. Derby, Intermediate phases in mullite synthesis via aluminum-and alumina-filled polymethylsiloxane, J. Am. Ceram. Soc. 88 (8) (2005) 2085-2091.

[27] Z. Ma, W. Wang, J. Zou, Preparation and properties of flame-sprayed Mo-FeB-Fe cermet coatings, Trans. Nonferrous Metals Soc. China. 21 (6) (2011) 1314-1321.

[28] J. Zhang, R. Luo, M. Jiang, The preparation and performance of a novel room-temperature-cured heat-resistant adhesive for ceramic bonding, Mater. Sci. Eng. A. 528 (6) (2011) 2952-2959.

[29] X. Wang, J. Wang, H. Wang. Performance and structural evolution of high-temperature organic adhesive for joining Al_2O_3 ceramics, Int. J. Adhes. Adhes. 45 (2) (2013) 1-6.

[30] X. Wang, J. Wang, H. Wang. Joining of Al_2O_3 ceramics via preceramic polymer and inorganic additives, Mater. Sci. Eng. A. 576 (8) (2013) 1-5.

Fig. 1 XRD patterns for adhesives treated at (a) 200, (b) 400, (c) 600, (d) 800, (e) 1000 and (f) 1200 °C.

Fig. 2 SEM images of the cross-section for ceramic joints treated at different temperatures. (a) 200, (b) 400, (c) 600, (d) 800, (e) 1000 and (f) 1200 °C.

Fig. 3 EDS spectra of the cross-section of Al_2O_3 joints treated at 600 (a) and 800 °C (b).

Fig. 4 TG curves for (a) SR, (b) M-SR and (c) the adhesive of M-SR-5 in air.

Fig. 5 FTIR spectra of SR and adhesives treated at different temperatures.

(a) SR, (b)-(g) the adhesive treated at 200, 400, 600, 800, 1000 and 1200 °C.

Fig. 6 The bonding strength of an Al_2O_3 joint bonded by (a) Al- or B_4C-filled M-SR and (b) ratios of B_4C/Al.

Fig. 7 Simulation diagrams of the adhesive interface with (a) ceramic joints bonded and (b) the self-healing process.

Fig. 1

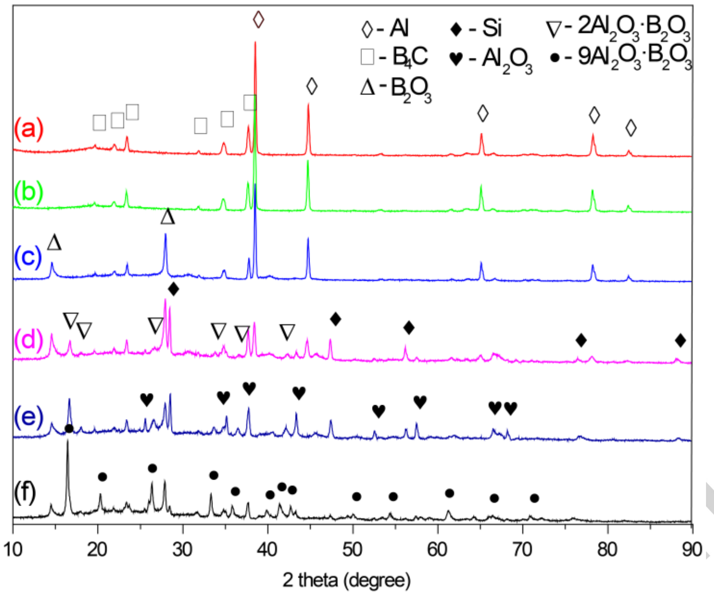
◊ - Al
♦ - Si
▽ - 2Al2O3·B2O3
□ - B4C
♥ - Al2O3
● - 9Al2O3·B2O3
Δ - B2O3
(a)
(b)
(c)
(d)
(e)
(f)
10
20
30
40
50
60
70
80
90
2 theta (degree)

Fig. 2

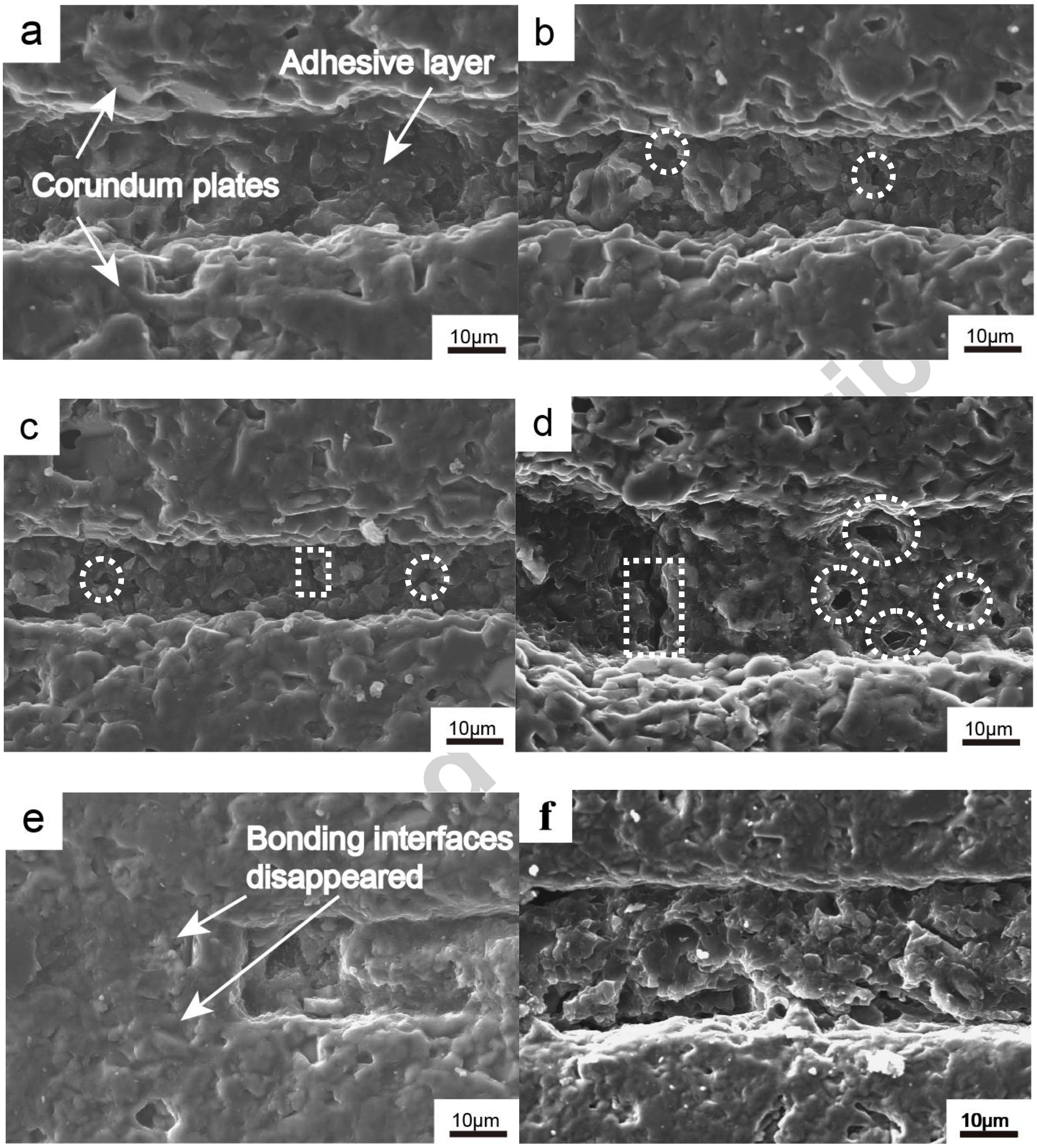
a
Adhesive layer
Corundum plates
10μm
b
10μm
c
10μm
d
10μm
e
Bonding interfaces disappeared
10μm
f
10μm

Fig. 3

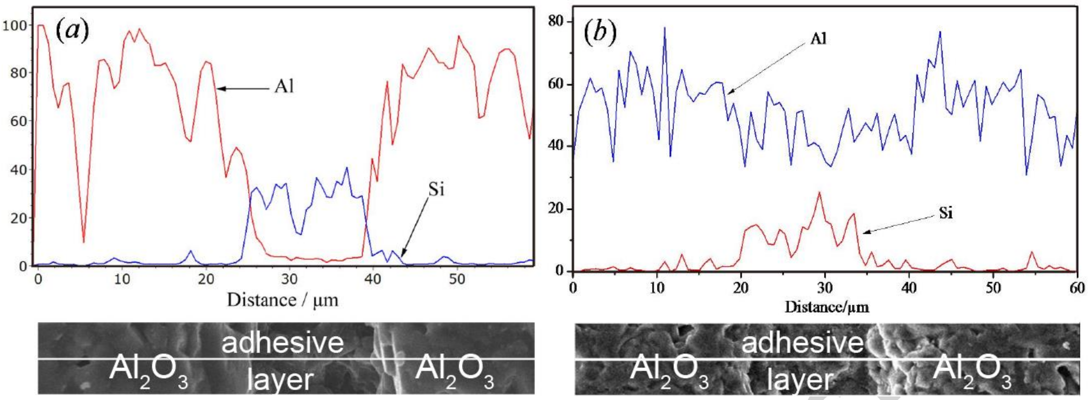
(a)
100
80
60
40
20
0
Al
Si
0
10
20
30
40
50
Distance / µm
Al2O3
adhesive
layer
Al2O3
(b)
80
60
40
20
0
Al
Si
0
10
20
30
40
50
60
Distance/µm
Al2O3
adhesive
layer
Al2O3

Fig. 4

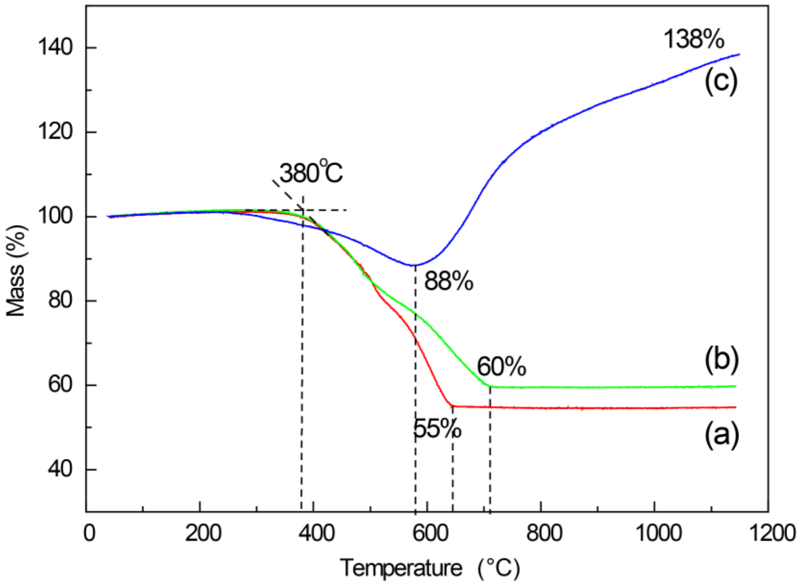
Mass (%)
140
120
100
80
60
40
0
200
400
600
800
1000
1200
Temperature (°C)
380°C
138%
(c)
88%
60%
(b)
55%
(a)

Fig. 5

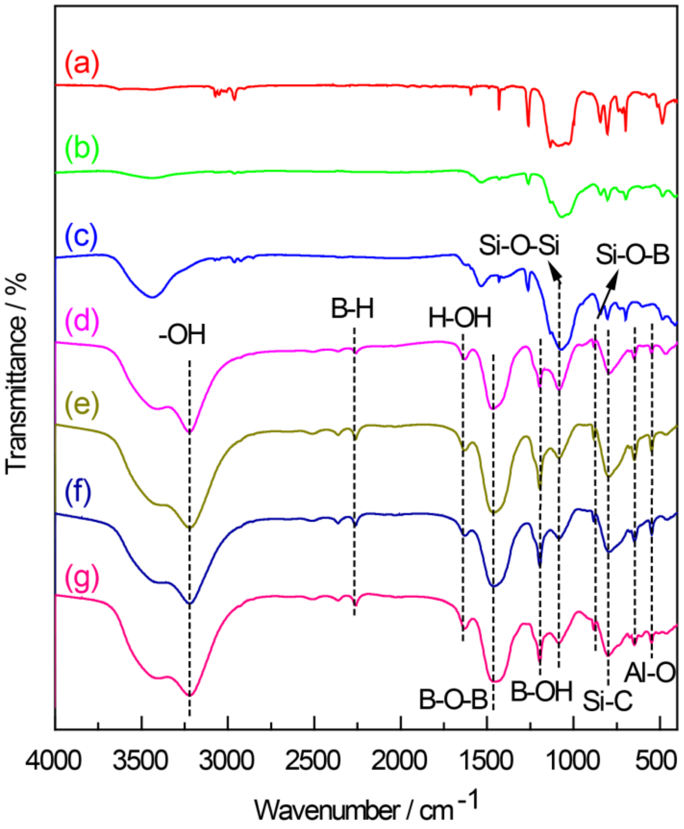
(a)
(b)
(c)
(d)
(e)
(f)
(g)
Si-O-Si
Si-O-B
-OH
B-H
H-OH
B-O-B
B-OH
Si-C
Al-O
Transmittance / %
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm^{-1}

Fig. 6

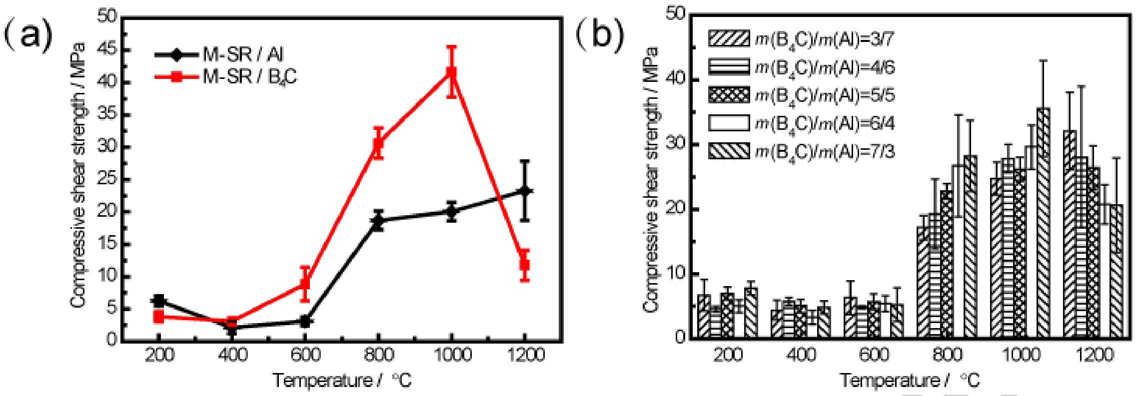
(a)
Compressive shear strength / MPa
0
5
10
15
20
25
30
35
40
45
50
M-SR / Al
M-SR / B4C
200
400
600
800
1000
1200
Temperature / °C
(b)
Compressive shear strength / MPa
0
10
20
30
40
50
m(B4C)/m(Al)=3/7
m(B4C)/m(Al)=4/6
m(B4C)/m(Al)=5/5
m(B4C)/m(Al)=6/4
m(B4C)/m(Al)=7/3
200
400
600
800
1000
1200
Temperature / °C

Fig. 7

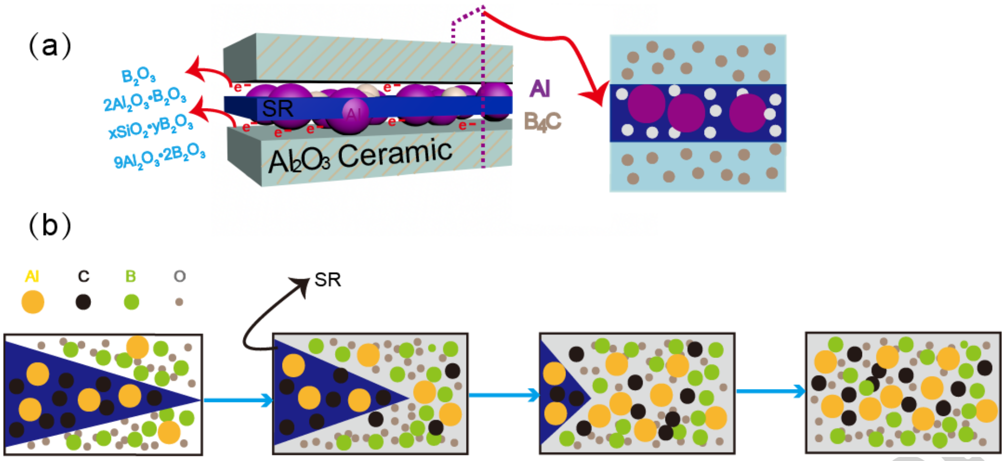
(a)
B_2O_3
$2Al_2O_3$•B_2O_3
$xSiO_2$•yB_2O_3
$9Al_2O_3$•$2B_2O_3$
e⁻
SR
Al
Al
B_4C
Al_2O_3 Ceramic
(b)
Al
C
B
O
SR

Table 1 The mass ratio of the matrix and fillers for adhesives.

Name	Matrix / mass%		Filler / mass%	
	SR	Boehmite sol	B_4C	Al
SR	100			
M-SR	80	20		
M-SR-1	40	10	50	
M-SR-2	40	10		50
M-SR-3	40	10	35	15
M-SR-4	40	10	30	20
M-SR-5	40	10	25	25
M-SR-6	40	10	20	30
M-SR-7	40	10	15	35

Table 2 Phase compositions of the adhesives treated at different temperatures.

T/°C	Phase structures
200	SR, B_4C, Al,
400	SR, B_4C, Al
600	SiO_mC_n, B_4C, B_2O_3, $xSiO_mC_n\cdot yB_2O_3$, Al
800	SiO_mC_n, B_4C, B_2O_3, $xSiO_mC_n\cdot yB_2O_3$, Al, Al_2O_3, $2Al_2O_3\cdot B_2O_3$, Si
1000	SiO_mC_n, B_4C, B_2O_3, $xSiO_mC_n\cdot yB_2O_3$, Al_2O_3, $2Al_2O_3\cdot B_2O_3$, Si
1200	SiO_mC_n, B_4C, B_2O_3, $xSiO_mC_n\cdot yB_2O_3$, $9Al_2O_3\cdot 2B_2O_3$