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Effect of adhesive composition on bonding of silicon nitride ceramic

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Abstract

Si_3N_4–Si_3N_4 ceramics were bonded by using Y_2O_3–Al_2O_3–SiO_2, Y_2O_3–La_2O_3–Al_2O_3–SiO_2, Y_2O_3–CeO_2–Al_2O_3–SiO_2 solders. Joining was carried out at 1823 K for 15 min at atmospheric pressure. The effects of adhesive composition on interfacial wetting and joint strength were investigated. The microstructure and chemistry of joints were characterized by scanning electron microscopy, electron probe microanalyses and X-ray diffraction. The results show that some elements of the solder diffuse into silicon nitride to form a diffusion layer. As compared with the joint strength of silicon nitride bonded with Y_2O_3–Al_2O_3–SiO_2 solder, the joint strength with Y_2O_3–La_2O_3–Al_2O_3–SiO_2 solder increased, while the one with Y_2O_3–CeO_2–Al_2O_3–SiO_2 solder decreased. The results indicate that the effect of adhesive composition on joint strength is related to interfacial wetting and joint thickness.

Keywords: D. Silicon nitride; Bonding; Y_2O_3–Al_2O_3–SiO_2; Joint strength; Interface reaction

1. Introduction

Up to now, the most common methods for joining silicon nitride are active metal brazing, diffusion bonding and oxide glass sealing [1]. The joints produced by active metal brazing have high bending strength at room temperature, but are limited to apply below about 1073 K. High joint strength can be obtained by diffusion bonding. However, this method requires an elevated bonding temperature, long joining time and smooth contacting surfaces so it is inadequate for mass production. Satisfactory bonding of silicon nitride with oxide glass solder has been developed [2–9]. However, the elevated temperature strength of joint is limited owing to the lower softening temperature of residual glass in joint. In order to improve the joint strength at elevated temperature, high refractory adhesives must be developed.

It is known that the elevated temperature properties of silicon nitride with additives from the Y–Al system are better than those with additives from the Mg–Al system [10]. To enhance the elevated temperature properties of silicon nitride ceramic, rare earth oxides such as La_2O_3 etc. have been added to the oxide additives of the Y–Al system [11]. Therefore, the bonding of silicon nitride ceramic was carried out with Y_2O_3–Al_2O_3–SiO_2, Y_2O_3–La_2O_3–Al_2O_3–SiO_2, Y_2O_3–CeO_2–Al_2O_3–SiO_2 mixtures at 1823 K for 15 min, and the effect of adhesive composition on interfacial wetting and joint strength was investigated.

2. Experimental procedure

Hot-pressure sintered silicon nitride ceramics, which were provided by Tsinghua University, with bending strength of 700–800 MPa and 19 mm×19 mm×8 mm in size were used. Before bonding, the bonded surfaces of all materials were diamond ground, and cleaned ultrasonically in acetone. La_2O_3 and CeO_2 powders were added to the Y_2O_3–Al_2O_3–SiO_2 (YA) mixture, the molar ratio between Y_2O_3 and the other rare earth oxide being 1:1.The compositions of YA, YL and YC mixture are listed in Table 1.

The wetting angle of the solder on the ceramic was determined by the sessile drops method. Disks (ϕ5 mm×2 mm) of the three kinds of glass solders were

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Table 1
Composition of rare earth oxide glass (percent mass fraction)

Glass solder	La_2O_3	Y_2O_3	Al_2O_3	SiO_2	CeO_2
YL	23.63	16.37	20	40	0
YA	0	40	20	40	0
YC	0	22.7	20	40	17.3

placed on the Si_3N_4 ceramic, and heated in a graphite furnace filled with pure N_2 gas at atmospheric pressure at 1823 K for 15 min. The wetting angle measurement was carried out at room temperature.

The YA, YL and YC mixtures were mixed with acetone to form a homogenous slurry. Then a 0.5 mm thick coating was applied onto a silicon nitride ceramic polished surface by dipping in the slurry. After two coated surfaces were placed together and fixed in a graphite jig coated with boron nitride. The joining was carried out at 1823 K for 15 min in a graphite furnace filled with pure N_2 gas at atmospheric pressure.

The 4 mm×4 mm×38 mm specimens were cut off from the joint perpendicular to the bonded interface for microanalyses and bending tests. The specimen surface for microanalyses was diamond ground and cleaned ultrasonically in acetone. The microstructures and distribution of elements in the joint were identified by JXA-840A scanning electron microscopes (SEM) and electron probe microanalyses (EPMA), respectively. The fracture surfaces of tested samples were examined by X-ray diffraction (XRD). Four-point bending strength at room temperature was measured with an upper span of 10 mm, a lower span of 30 mm and a cross-head speed of 0.5 mm min^{-1}.

3. Results and discussion

3.1. Interface microstructure

Fig. 1 shows microstructure and elements distribution in the cross section of Si_3N_4/Si_3N_4 joints bonded with YA mixture at 1823 K for 15 min. The thickness of joint is 40 μm. Some elements of solder (Y^{3+}, Al^{3+}, O^{2-}) diffuse into Si_3N_4 to form a diffusion layer, while Si^{4+} diffuse into the molten glass. This shows that the YA molten glass diffuses into the Si_3N_4 ceramic along its grain boundary, resulting in Si_3N_4 dissolution and formation of Y-Sialon glass at the interface. According to XRD analyses of the fracture surface (Fig. 4a), the β-Si_3N_4 near the interface turned into Si_2N_2O gradually at 1823 K, indicating its dissolution into the molten Y-Sialon glass. With the increase of the dissolved Si_3N_4

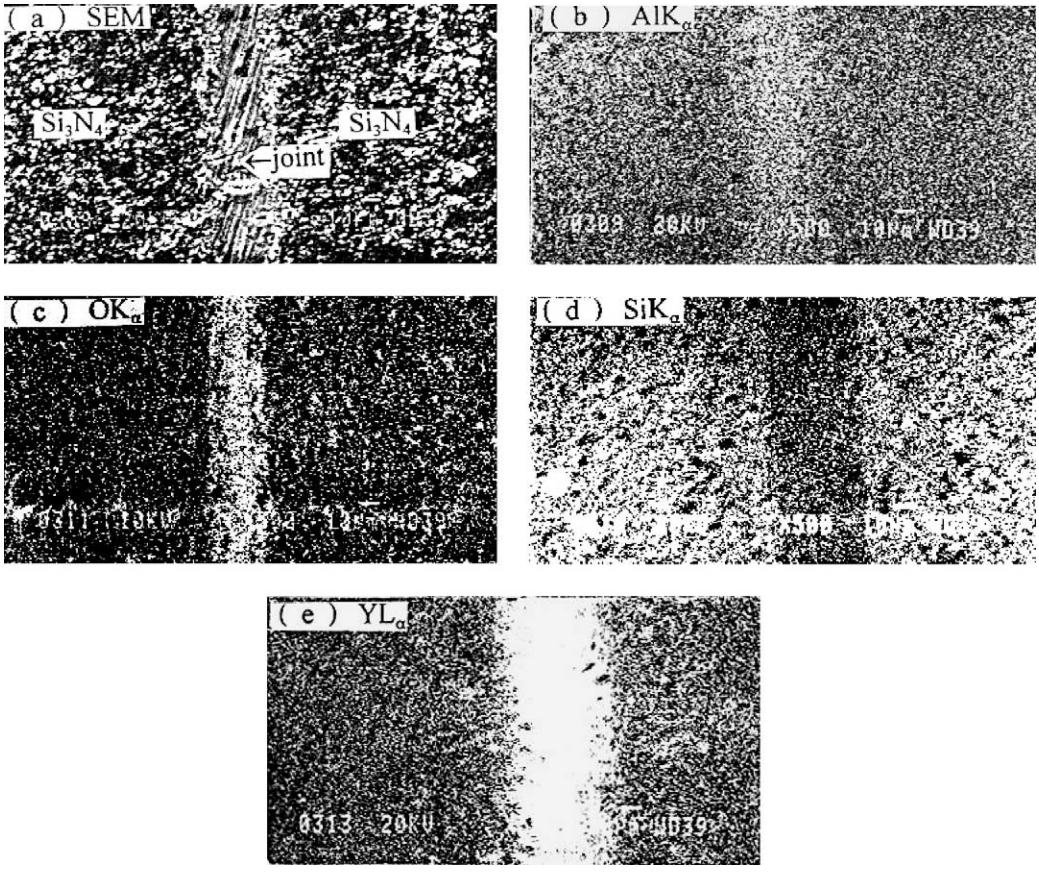

Fig. 1. Microstructure and element distribution images of Al, O, Si, Y for the Si_3N_4/Si_3N_4 joint bonded with YA glass solder at 1823 K for 15 min.

content, the number of non-bridging nitrogen beneficial to crystallization in Y-Sialon glass increases, and thus Si_2N_2O particles are precipitated from interfacial glass.

Figs. 2 and 3 show microstructure and elements distribution in the cross section of Si_3N_4/Si_3N_4 joint bonded with YL and YC mixtures at 1823 K for 15 min, respectively. The thickness of joint bonded with YL mixture is 20 μm, while that of YC mixture is 50 μm. Some elements of solder (Y^{3+}, Al^{3+}, La^{3+-}, Ce^{4+}, O^{2-}) diffuse into Si_3N_4 to form a diffusive layer at interface. The results of XRD analyses on the fracture surface (Fig. 4b and c) show that there are $LaYO_3$,Y_2-Ce_2O_7 phases in joint bonded with YL and YC mixtures, respectively, besides β-Si_3N_4 and Si_2N_2O.

In fact, YA, YL and YC liquid glasses diffuse along grain boundary of silicon nitride, penetrate into ceramics, and remain at the triple junctions of grains at 1823 K. This will decrease nitrogen concentration at the grain boundary, which results in the dissolution of β-Si_3N_4 in the glass. The mean length of Si–N bond in silicon nitride and that of Si–O bond in silica are 0.174 and 0.162 m respectively [12]. In silicon oxynitride characterized by $Si(O,N)_4$ tetrahedra, the mean length of Si–N bond and Si–O bond are 0.172 and 0.162 nm respectively [12]. It can be seen that the length of corresponding bonds in silicon nitride and silicon oxynitride are equal. This implies that at the interface, the thermodynamically stable Si_2N_2O crystal can easily precipitate from molten glass. Thus, interfacial reaction could be described as: (a) dissolution of Si_3N_4 in molten glass at interface, (b) transfer of Si and N into liquid, (c) precipitation of Si_2N_2O crystal from liquid.

3.2. Effect of solder composition on wetting angle and joint strength

As compared with YA solder, YL solder wetting angle and joint thickness are smaller, but its joint strength is higher. While YC solder wetting angle and joint thickness are larger, but its joint strength is lower

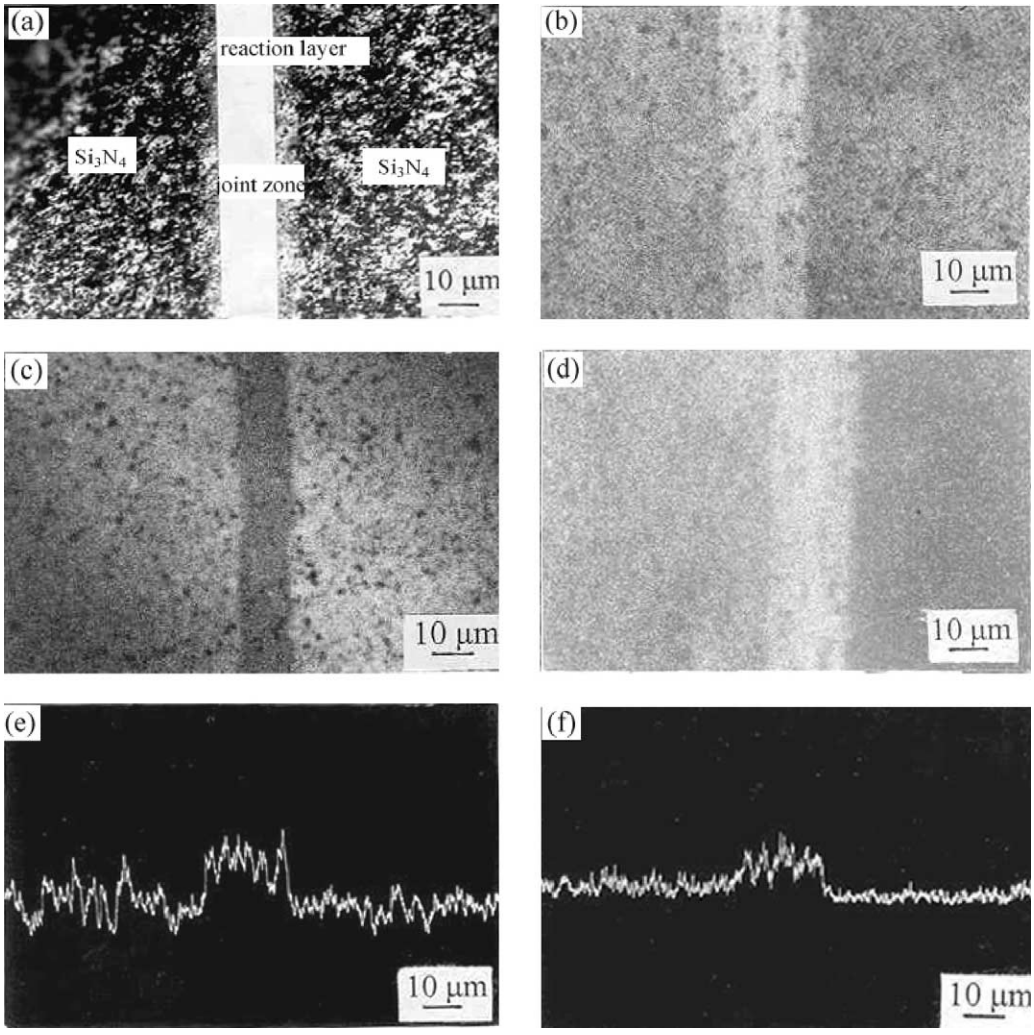

Fig. 2. Microstructure and element distribution images of Al, Ti, Si, La and line distribution images of O,Y for the Si_3N_4/Si_3N_4 joint bonded with YL glass solder at 1823 K for 15 min: (a) SEM, (b) AlK_α, (c) SiK_α, (d) $LaL_{\&alpha}$, (e) OK_α, (f) YL_α.

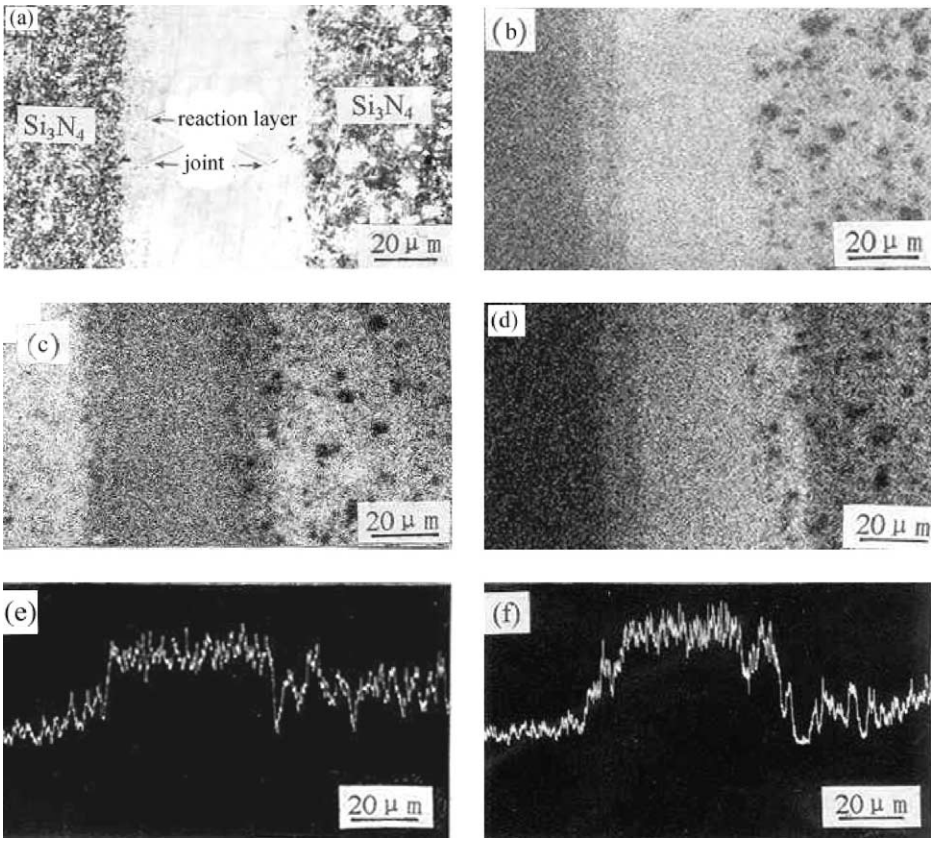

Fig. 3. Microstructure and elements distribution images of Al, Ti, Si, Ce and line distribution images of O,Y for the Si_3N_4/Si_3N_4 joint bonded with YC glass solder at 1823 K for 15 min: (a) SEM, (b) AlK_α, (c) SiK_α, (d) CeL_α, (e) OK_α, (f) YL_α.

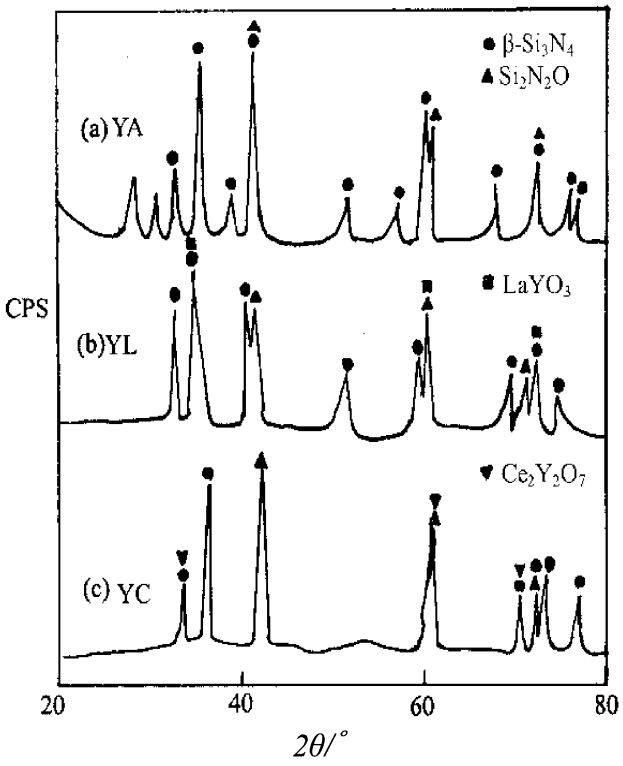

Fig. 4. XRD patterns of fracture surface after bending test.

(as seen in Table 2). The results indicated that La_2O_3 addition could improve the wetting behavior of YA glass solder on Si_3N_4 ceramic, decreases joint thickness and increases the joint strength. On the contrary CeO_2 addition would deteriorate the wetting ability of YA glass solder on Si_3N_4 ceramic, and joint thickness increases will decrease joint strength.

It is evident from Table 2 that YL liquid solder diffusion and infiltration into Si_3N_4 ceramic is easier than for YA liquid solder, while YC liquid solder diffuses and infiltrates into Si_3N_4 ceramic more difficultly than YA liquid solder does. In fact, the migration of solid/liquid interface is governed by the grain-boundary capillary effect of ceramic when the bonding of ceramic is carried out with glass solder at atmospheric pressure [7], and the joint thickness is expressed as [13]:

$$w_t = w_0 - \sqrt{2} f_v \left(\frac{\gamma \cos\theta}{\eta} rt \right)^{\frac{1}{2}} \quad (1)$$

where w_0 is initial joint thickness at bonding temperature T, w_t is joint thickness as holding time is t at bonding temperature T, f_v is capillary area fraction on the bonding surface of ceramic, r is radius of the grain-boundary capillary, γ is interface energy between liquid solder and ceramic, η is viscosity of liquid solder, θ is

Table 2
Effect of solder composition on wetting angle, joint strength and thickness

Glass solder	Wetting angle (°)	Joint strength (MPa)	Joint thickness (μm)
YA	18±2	315±10	40±2
YL	5±0.5	350±15	20±1.2
YC	38±3	280±10	50±2.5

wetting angle of liquid solder on ceramic at bonding temperature T for holding time t. In the case of the same bonding technique and ceramic, the joint thickness is mainly related to the viscosity and wetting angle of liquid solders and interface energy.

Menon and Chen [14] indicated that the wetting behavior of oxide glass on nitride ceramic is affected by the basicity of oxide glass. It is easy for strong basicity oxide glass to wet silicon nitride ceramic. For rare earth aluminosilicate glass, its basicity is related to the basicity of rare earth metal oxide [14]. According to Wen's theory [15], the basicity of rare earth metal oxide is judged by the formation energy parameter of rare earth metal ion. The higher the formation energy parameter of metal ion, the stronger the basicity of metal ion. As seen in Table 3, it is clear that the basicity of La_2O_3 and Ce_2O_3 is stronger than that of Y_2O_3 and CeO_2, respectively. If another rare earth metal oxide is added to YA glass solder, the mean parameter of formation energy for rare earth metal ions in glass is [13]:

$$\overline{w_f} = \frac{\sum_{i=0}^{n} x_i n_i w_{fi}}{\sum_{i=0}^{n} x_i n_i} \quad (2)$$

where x_i is the molar fraction of i rare earth metal oxide in all rare earth metal oxide of glass, n_i is the number of rare earth metal ion in i rare earth metal oxide, w_{fi} is the formation energy parameter of rare earth metal ion in i rare earth metal oxide. When CeO_2 is added to YA glass solder, the mean formation energy parameter for rare earth metal ions in glass is 15. Then YC glass solder wetting ability is not improved, which is in agreement with the results of the wetting test (as seen in Table 2). Moreover, In Y_2O_3–RE_2O_3 (REO_2) system, Y_2O_3 easily reacts with RE_2O_3 (REO_2) to form compounds if the ion radius difference between Y^{3+} and $RE^{3+(4+)}$ is small [16]. The ion radius of Ce^{4+}, Y^{3+} and Ce^{3+} being 0.092, 0.090 and 0.101 nm, respectively, CeO_2 more easily reacts with Y_2O_3 to form $Ce_2Y_2O_7$ than Ce_2O_3 although CeO_2 may be transformed into Ce_2O_3 at elevated temperature [17]. Therefore, the poor wetting ability of YC glass solder and the high viscosity of liquid solder caused by the phase formation would make the joint thickness increase, and then a tensile stress was formed easily at midplane of joint [19], which led to a joint strength decrease.

Table 3
Formation energy parameters for rare earth metal ions w_f [16]

Metal ions	La^{3+}	Ce^{3+}	Y^{3+}	Ce^{4+}
w_f	28	27	15	15

As La_2O_3 is added to YA glass solder, the mean formation energy parameter for rare earth metal ions in glass is 21, which shows that the basicity of YL glass solder is stronger than that of YA glass solder. Then the YL glass solder wetting ability on silicon nitride ceramic is better than for YA glass solder, which is consistent with the results of the wetting test. Moreover, after La_2O_3 is added to YA glass solder, it will expand the glass formation region, and decrease the viscosity of the molten glass [18]. As a result, the better wetting ability of YL glass solder on silicon nitride ceramic and the lower viscosity of glass solder will make the joint thickness decrease, and then the residual thermal stress at joint is relaxed [19], which is beneficial to joint strength.

4. Conclusions

1. Interfacial reaction could be described as: (a) dissolution of Si_3N_4 in molten glass at interface, (b) transfer of Si and N into liquid, (c) precipitation of Si_2N_2O crystal from liquid.
2. La_2O_3 addition could improve the YA glass solder wetting behavior on Si_3N_4 ceramic, and then enhance the joint strength, while CeO_2 addition would deteriorate the YA glass solder wetting ability on Si_3N_4 ceramic, and then lead to the decrease of the joint strength.

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