INTERFACIAL REACTION BEHAVIOUR AND JOINT STRENGTH OF TiC_p/Si_3N_4 COMPOSITE BONDED WITH Al FOIL①

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ABSTRACT The joints of Si_3N_4 composite bonded with Al foil were treated by metal joint becoming ceramics. Reaction behavior of the interface between Si_3N_4 and Al in joining of TiC_p/Si_3N_4 composite with Al foil was studied by means of SEM, EPMA, XRD and AES. The results show that Si, N and O diffuse from the TiC_p/Si_3N_4 composite into Al liquid phase zone to produce AlN, $Al_2O_3 \cdot SiO_2$ at 1 273 K, while at 1 173 K, only alumina is detected at interface. The thermodynamic and thermal stress analyses at the interface show that the interfacial reactions of interface are influenced not only by bonding temperature and the oxide formed at the faying surface before bonding, but also by the atmosphere of the furnace containing graphite heating elements. The effect of bonding temperature on joint strength depends on the effect of joining temperature on reaction products at the interface. The room and high temperature strengths are enhanced after metal joints have become ceramic.

Key words Si_3N_4 ceramic composite Al foil interfacial reaction metal joint ceramic joint

1 INTRODUCTION

TiC_p/Si_3N_4 composite ceramics have excellent physical, chemical and mechanical properties, and they are applied widely in several fields of industry. But due to their intrinsic brittleness and difficulty in fabrication of complex-shaped and large-sized components, the techniques of ceramics joining are required to form large-sized and complex-shaped components from small and simple-shaped parts. At present, brazing and diffusion bonding are two effective methods of Si_3N_4 ceramics joining, but joints produced by these methods have poor high temperature oxidation resistances, and are limited to application below 1 073 K. Therefore, the effective bonding techniques need to be developed further, and then the metal joint becoming ceramics is a result of the developing joining techniques for ceramics.

Previously, bonding of silicon nitride had been carried out generally with AgCuTi (NiCuTi) brazing filler metal. Due to the difficulty of Ag and Cu in joint reacting with nitrogen, the metal joints are unable to transform into ceramics. For Al system fillers, they have good wettability on Si_3N_4 ceramics when the bonding temperature is higher than 1 173 K. Moreover, because the melting point of Al is 933 K, it is no use for silicon nitride application to high temperature when Al filler remains in joint[1-7]. If the technique of metal joint becoming ceramics is taken, the free state Al and Si in joint react with nitrogen, and become AlN system reactants, which are compatible with silicon nitride, therefore, the heat-resistance of joint is enhanced greatly, which is beneficial to decreasing the cost of ceramics joining. As a result, the joints of

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Si_3N_4 composites bonded with Al foil are treated by metal joint becoming ceramics. Interfacial reaction between Si_3N_4 and Al was studied by means of SEM, EPMA, XRD and AES, and the effects of reactant on bonding strength were also analyzed.

2 EXPERIMENTAL

TiC particles reinforced Si_3N_4 ceramics (named TiC_p/Si_3N_4 or Si_3N_4 composite ceramics) of a dimension 19 mm × 19 mm × 8 mm were used. Aluminum foil is 99.8% in purity and about 0.1 mm in thickness. Prior to bonding, the surfaces of all materials to be bonded were cleaned ultrasonically in 10% sodium hydroxide solution and acetone. An aluminum interlayer was sandwiched between two Si_3N_4 composite ceramics, the sandwiched sample was fixed in a graphite jig coated with BN, and heated in a furnace containing graphite heating elements, backfilled with highly pure argon atmosphere. When the bonding temperatures reached 1 173 K and 1 273 K, the sample was first placed in a furnace under a stream of argon for 10 min, and then under a stream of nitrogen for 20 min. The bonding process was finished under a pressure of 0.16 MPa.

The microstructures and distribution of elements in the vicinity of interface were identified by SEM and EPMA. The fracture surface of joints was examined by X-ray diffraction method. The element concentration near interface was analyzed by AES.

Specimens for bending test were cut off from the joints perpendicular to the bonded interface to be of dimensions 4 mm × 4 mm × 38 mm. The four-point bending strength at room temperature and high 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.

3 RESULTS AND DISCUSSION

3.1 Microstructures at interface

According to the Ellingham diagram, the standard free energy of formation for Si_3N_4 and AlN per mol N_2 could be calculated by the formulae as follows:

$$\Delta G_f^0(Si_3N_4)/(kJ\cdot mol^{-1}) = -396.48 + 0.2066\,T \quad (1)$$

$$\Delta G_f^0(AlN)/(kJ\cdot mol^{-1}) = -600.00 + 0.1813\,T \quad (2)$$

As seen in equations (1) and (2), Si_3N_4 is not as stable as AlN. When contacted with Si_3N_4 composite at a high temperature, Al could react with N and Si decomposed from Si_3N_4 to form AlN and AlSi compound. Fig.1 shows the cross-section microstructure and the element area distribution images of TiC_p/Si_3N_4-TiC_p/Si_3N_4 joint bonded with Al foil at 1 273 K for 30 min. As seen in Fig.1(b) and Fig.1(c), corresponding to distribution layer of aluminum, there appears the distribution layer of a high silicon concentration, which indicates that there is an interdiffusion of Al and Si at the interface as Si_3N_4 composites are bonded with Al foil. As seen in Fig.1(d), the area distribution of Ti does not change, which induces that reaction between Al and TiC particles do not occur. This is identical with the thermodynamic calculation.

In order to study the reaction products and their distribution at the interface of the Si_3N_4/Al foil at 1 273 and 1 173 K respectively, we separated TiC_p/Si_3N_4-TiC_p/Si_3N_4 joint along interface, and then stripped the layer mechanically parallel to the interface to identify the phase formed in the joint. Fig.2 shows the X-ray diffraction patterns of the layer stripped at the interface bonded at 1 273 K for 30 min. The results of XRD analyses indicate that there are more AlN and a little $Al_2O_3\cdot SiO_2$ besides Si_3N_4. Among them, the diffraction peak of AlN is the highest. After mechanically removing this layer partially (the layer thickness about 5 μm), XRD (Fig.2(b)) shows that the reaction layer is composed of AlN and $Al_2O_3\cdot SiO_2$. It is notable that the peak height of the $Al_2O_3\cdot SiO_2$ increases, whilst that of the AlN decreases. After removing the reaction layer completely, as shown in Fig.2(c), XRD shows that the surface is still silicon nitride composite. From the XRD results, it can be confirmed that Al would react with nitrogen at 1 273 K and with Si_3N_4 as well, and the former metal joints are transformed into ceramics

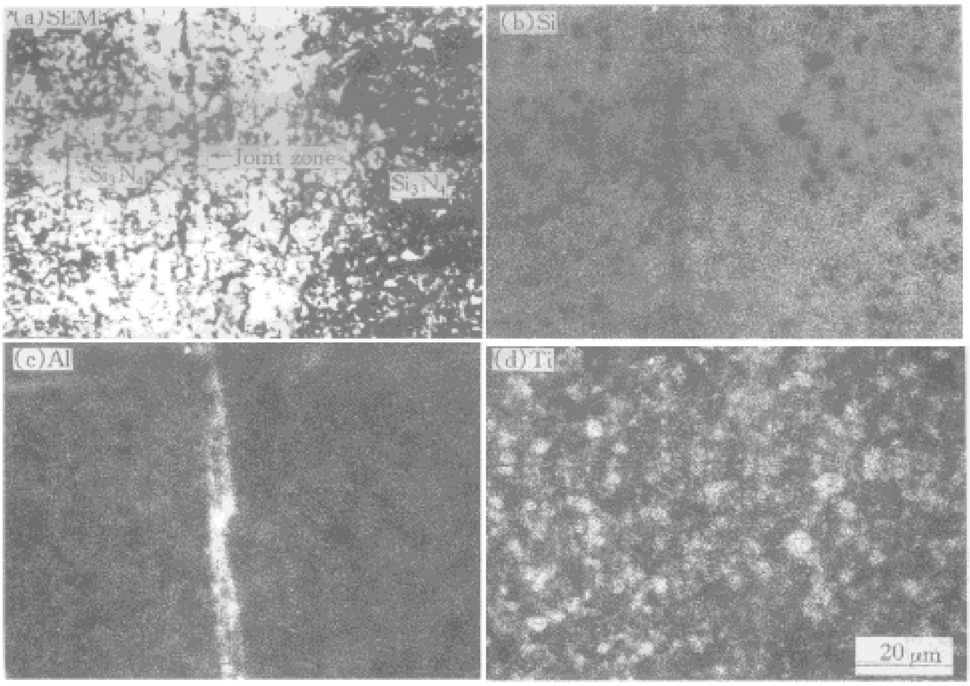

Fig.1 Microstructure and element area distribution images of Al, Si, Ti for Si_3N_4 ceramic composite joint bonded with Al foil at 1 273 K for 30 min

joint gradually, which is beneficial to improving the high temperature properties of joint.

Fig.3 shows the X-ray diffraction patterns of fracture surface joint bonded at 1 173 K for 30 min. The results of the XRD analyses indicate that there are the peaks of alumina besides the peaks of silicon nitride. Fig.4 shows the Auger patterns of the interface near the ceramics. According to the concentration analyses of these patterns, the atomic fractions of Al and O are 45.2 % and 57.5 % respectively, which is identical with the concentration of alumina. It is indicated that at 1 173 K, the alumina on aluminum surface is not reduced easily, and impedes the reaction between Al and Si_3N_4 as well as nitrogen atmosphere. Therefore, the metal joints are not transformed into ceramics joint easily.

3.2 Bonding mechanism at interface

The present work was carried out in the graphite heating element furnace, first backfilled with high purity argon atmosphere, and later with high purity nitrogen atmosphere, which would affect the reaction products and bonding mechanisms. Under the condition of low oxygen pressure fixed by CO/CO_2 and H_2/H_2O residual atmosphere of the furnance containing the graphite heating elements, first backfilled with argon atmosphere, the alumina on aluminum surface is reduced at 1 273 K[8]:

$$Al_2O_3(s) + 3CO(g) = 2Al(l) + 3CO_2(g) \quad (3)$$

When alumina is reduced in liquid aluminum, the real $SiO_2(s)/Al$ contact is observed and SiO_2 is reduced:

$$4Al(l) + 3SiO_2(s) = 2Al_2O_3(s) + 3Si(l) \quad (4)$$

$$\Delta G_T^0/(kJ\cdot mol^{-1}) = -653.5 + 0.1258\ T \quad (5)$$

Under the condition of the decomposition of protective oxide layer in metal and composite, the real Si_3N_4 composite/Al(l) contact is observed, and the following reaction between them can occur:

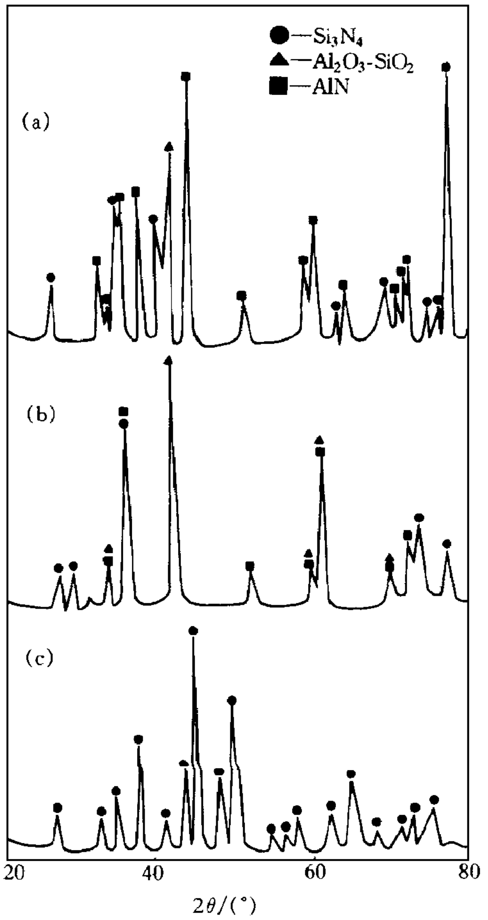

Fig.2 XRD patterns of fracture surface(1 273 K, 30 min)

(a) —Fracture surface; (b) —After mechanically removing brazing surface; (c) —After mechanically removing reaction layer completely

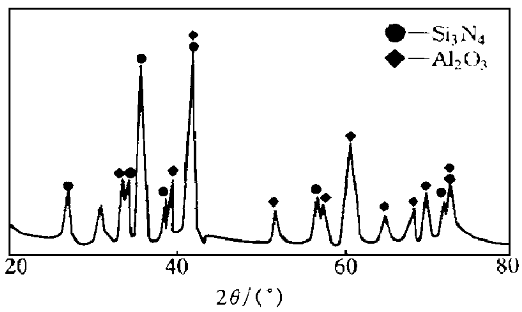

Fig.3 XRD pattern of fracture surface(1 173 K, 30 min)

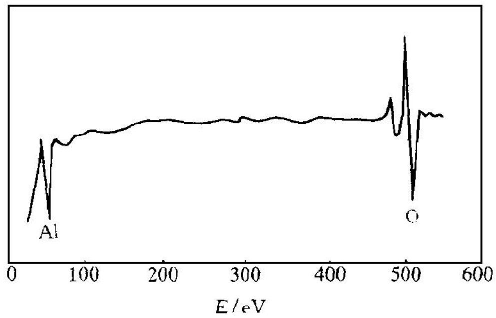

Fig.4 Auger pattern of joint (1 173 K, 30 min)

$$Si_3N_4(s) + 4Al(l) = 4AlN(s) + 3Si(l) \quad (6)$$

$$\Delta G^0_T / (kJ \cdot mol^{-1}) = -126.9 + 0.01649\,T \quad (7)$$

Meanwhile, in the absence of sufficient contents of SiO_2 and Al_2O_3 at interface, the following reaction is possible:

$$Al_2O_3(s) + SiO_2(s) = Al_2O_3 \cdot SiO_2(s) \quad (8)$$

$$\Delta G^0_T / (kJ \cdot mol^{-1}) = -8.8 + 0.00389\,T \quad (9)$$

The subscripts s, l and g in the above equations signify solid, liquid and gas states respectively. The ΔG^0_T values of reactions (4), (6) and (8) are -493.35, -105.29 and -3.85 kJ/mol respectively at 1 273 K. The negative values indicate that the reactions could occur spontaneously at the bonding temperature. As a result, a layer transition structure of Si_3N_4 composite/ $Al_2O_3 \cdot SiO_2$ + AlN + AlSi/ Al formed at the interface. Due to the fact that TiC reacts with Al difficultly, TiC particles do not change(Fig.1(d)).

Under the protection of nitrogen atmosphere, the free Al and Si in joint would react with nitrogen, and form 15R-AlN-Sialon ceramic with AlN structure[5], which is compatible with silicon nitride, and beneficial to enhancing joint strength at high temperatures. It is known that there is only 15R-AlN-Sialon at reaction-sintered Si_3N_4/ Al at 1 273 K ~ 1 473 K under the protection of nitrogen atmosphere[5]. From the results of XRD analyses, it can be confirmed that the above-mentioned reaction mechanism is of importance during the silicon nitride composite bonding.

When the bonding temperature is lower than 1 273 K, the alumina on Al foil surface is not reduced easily, and impedes the reaction between Al and silicon nitride. Aluminum atoms diffuse to the surface of Si_3N_4 through the alumina film, and react with silica as:

$$4Al(l) + 3SiO_2(s) = 2Al_2O_3(s) + 3Si(l) \tag{10}$$

which makes the film of alumina thick, and impedes the further reaction between Al and Si_3N_4. Therefore, the reaction products of AlN and Si can not be detected by AES and XRD. Meanwhile, the reaction between Al and nitrogen atmosphere is also impeded by alumina, and a layer transition structure of Si_3N_4 composite/Al_2O_3/Al forms at the interface, which is in agreement with the result of Ref.[6].

3.3 Effect of interfacial reaction on bonding strength

Table 1 shows the bonding temperature dependence of the bonding strength of Si_3N_4-Si_3N_4 joints using Al foil and Ag57Cu38Ti5 brazing filler metal[10] respectively. It is observed that the interfacial reaction products are one of the key factors that affect bonding strength. Elssner and Petzow[9] indicated that the formation of micrograin TiN at interface is beneficial to relaxing the interfacial thermal stress and improving the joint strength when Si_3N_4 ceramics are bonded with AgCuTi(NiCuTi) brazing filler metal, whilst the formation of coarse grain Ti_5Si_3 phase is harmful to joint strength due to its brittleness. On the other hand, joining strength also has something to do with the layer interface structure which may affect the thermal stress distribution in the joint. When a joint is cooled down from the bonding temperature, thermal stress develops in the joint due to the thermal expansion mismatch between two different materials. If the materials can deform only elastically with the stresses developing on both sides of the reaction layer don't interfere with each other in this layer, the stress in the close vicinity of the interface between two adjacent materials i and j is expressed roughly as follows[2]:

$$\sigma_i = -\sigma_j = \frac{E_i E_j}{E_i + E_j}(\alpha_i - \alpha_j)(T - T_0) \tag{11}$$

where E is Young's modulus, α is the thermal expansion coefficient, T is bonding temperature, and T_0 is room temperature. The calculated thermal stresses at the interface of Si_3N_4/AlN, Si_3N_4/Al_2O_3 are 241.93 and 697.5 MPa respectively(from Table 2). The thermal stress at the interface of Si_3N_4/AlN is lower than that of Si_3N_4/Al_2O_3. It is shown that the effect of temperatures on the joint strength is due to the effect of temperatures on interfacial reactant and the stress distribution in the joint, which induces the change of the joint strength. Because of large thermal stress at the interface of Si_3N_4/Al_2O_3, the microcrack initiates near the interface, and the joint strength at room temperature decreases[11].

As seen in Table 1, it is thus clear that at 1 273 K, aluminum has a good wettability on Si_3N_4 ceramics, and then the interfacial reaction is accelerated by the decomposition of protective

Table 1 Bonding strength for Si_3N_4/Al/Si_3N_4 and Si_3N_4/AgCuTi/Si_3N_4 joints

Bonding conditions T(K)/t(min)	Fillers	Interfacial reactant	Test temperature/K	Bending strength/MPa
1 273/30	Al	$AlN + Al_2O_3 \cdot SiO_2$	298	327
1 273/30	Al	$AlN + Al_2O_3 \cdot SiO_2$	1 073	250
1 173/30	Al	Al_2O_3	298	190
1 173/30	Al	Al_2O_3	673	50
1 103/5[10]	Ag57Cu38Ti5	Ti_5Si_3	298	366
1 153 to 1 203/5[10]	Ag57Cu38Ti5	TiN	298	490

Table 2 Physical properties of materials

Material	E/ GPa	α/ 10^{-6} K^{-1}
TiC_p/ Si_3N_4	300	3.3
AlN	345	4.84
Al_2O_3	372	8.1

oxide layer in aluminum. Moreover, the free Al and Si remaining in joint react with nitrogen atmosphere to form ceramic joint, which is beneficial to enhancing the joint strength at high temperatures; whilst at 1 173 K, due to the protection of oxide layer on the surface of metal, the interfacial reaction and the transformation of metal joint to ceramic joint are impeded, and then more aluminum remains in joint, which decreases the heat-resistant properties of joint, and deteriorates the high temperature strength of joint.

4 CONCLUSIONS

(1) The joints of Si_3N_4 composite bonded with Al foil at 1 273 K for 30 min were treated by metal joint becoming ceramis, which may enhance the joint strength at room and high temperature.

(2) The Si_3N_4 composite reacts with aluminum to form a reaction layer. At 1 273 K, a transition structure of Si_3N_4 composite/ Al_2O_3 · SiO_2 + AlN/ AlN forms at the interface, while at 1 173 K, that of Si_3N_4 composite/ Al_2O_3/ Al forms at the interface.

(3) The effect of bonding temperature on the joint strength is due to the effects of temperature on interfacial reactant, and hence affects the thermal stress distribution in the joint, which induces the change of the joint strength.

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