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Solid-liquid state pressure bonding of Si_3N_4 ceramics with aluminum based alloys and its mechanism①

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[Abstract] Solid-liquid state pressure bonding of Si_3N_4 ceramics with aluminum based alloys, which contain a small amount of intermetallic compounds Al_3Ti or Al_3Zr, was investigated. With this new method, the heat resistant properties of the bonding zone metal are improved, and the joints' strengths at high temperature is increased. The joints' shear strength at room temperature and at 600 ℃ reach 126~ 133 MPa and 32~ 34 MPa, respectively, with suitable bonding pressure. The reaction between aluminum and Si_3N_4 ceramics, which produces Al-Si-N-O type compounds is the dominant interfacial reaction, while the reactions between the second active element Ti or Zr in the aluminum based alloys and Si_3N_4 ceramics also occur to some extend.

[Key words] solid-liquid state pressure bonding; Si_3N_4 ceramics; intermetallic compounds; high temperature properties
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1 INTRODUCTION

Aluminum is in common use as active element to bond ceramics. Joints with high room temperature properties can be easily obtained when aluminum and its alloys such as Al-Si, Al-Mg and Al-Cu are selected as brazing filler metals or diffusion bonding interlayers with adequate technologies. The strength of joint with the microstructures consisting of pure aluminum or aluminum based solid solution, however, can be drastically degraded because of the softening of bonding zone metal with increasing test temperature. Thus the service temperature of the joints can not be higher than 300 ℃[1~ 4].

While choosing aluminum and its alloys as active bonding materials, the bonding temperature is lowered significantly due to the low melting point of aluminum. But, generally, by lowering the bonding temperature, the joint's high temperature performance becomes worse. In this case, desirable design of aluminum based alloy compositions and bonding technologies is an essential solution to this problem. If the microstructures of the original aluminum based alloy contain a large amount of aluminum based solid solution and a small number of heat resistant phases, at the same time the content of the heat resistant phases can be increased in the process of bonding by a certain method, better high temperature performance of joint can be achieved at relatively lower bonding temperature.

From the phase diagrams[5], the microstructures of aluminum based alloy are composed of a large amount of aluminum based solid solution and a small number of Al_3Ti or Al_3Zr phases when the alloy contains a little Ti or Zr. If the above mentioned aluminum based alloy is of solid-liquid state at bonding temperature, and enough pressure is exerted on the bonding couples, the proportion of the aluminum based liquid extruded out from the bonding zone may be higher than that of the intermetallic compounds Al_3Ti or Al_3Zr in the process of bonding because of the great difference in physical properties and strength between them. As a result, the content of intermetallic compounds in the bonding zone metal after bonding is higher than that in the original alloy, which will lead to improving the performance of the bonding zone metal. Up to now, this kind of solid-liquid state pressure bonding (SLSPB) has not been reported in the available literature, but it may be a practical method to enhance the ceramic joint's high temperature performance.

In the present study, the bonding of Si_3N_4 ceramics is conducted with Al-3% Ti and Al-4% Zr (mass fraction) alloys, and the effects of bonding pressure on the microstructures and room temperature performance of the joint are investigated. The strength change trends with testing temperature of both the joints bonded with aluminum based alloys and the joint with pure aluminum are examined and analyzed for the sake of comparison.

2 EXPERIMENTAL

Ceramic joints were produced from a pressureless sintered Si_3N_4 ceramics block with a size of 10mm × 5 mm × 4 mm, whose the three-point bend strength is 300~ 500MPa, with Al_2O_3 and Y_2O_3 as sintering additives. Prior to being bonded, the surfaces of the

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Si_3N_4 ceramics blocks were polished with SiC paste. Al-Ti and Al-Zr alloys were smelted into a block with tungsten arc in Ar atmosphere, then the block was sliced into sheets with demension of 10 mm × 5 mm × 0.4 mm, and at last the dunghill at the surfaces of sheets were removed by chemical and mechanical ways. Just before assembling block/sheet/block sandwiches, the oxide layers at the surfaces of the alloy sheets were eliminated with mechanical method.

The bonding of block/sheet/block assembly was performed in a semi-closing die placed in a vacuum chamber to reduce the oxidation of the alloys. The temperature was raised to the bonding temperature at a rate of 20 ℃/min. During the thermal cycle, the vacuum in the chamber was in the range of 5~ 20 mPa, and a bonding pressure was exerted on the bonding couples. After keeping at the bonding temperature, the joint cooled together with chamber.

The microstructures of the joint were observed by electron scanning microscope (SEM), while their chemical compositions were examined by using electron probe microanalysis(EPMA). The phase compositions were determined by X-ray diffraction analysis (XRD). The strength of the joint was evaluated by fracture shear loading in air at a displacement rate of 1 mm/min. The specimen for high temperature strength testing was heated at a rate of 15 ℃/min, and was held at the desired temperature for 10 min prior to loading.

3 RESULTS AND DISCUSSION

3.1 Procedure of SLSPB and effects of pressure on joint's microstructures

The brazing of ceramics with pure aluminum as filler metal, according to the available data[1~3], was usually performed at 800~ 1 000 ℃ for 20~ 60 min. In order to shorten the bonding cycle, 800 ℃, 20 min for aluminum and Al-3%Ti alloy, and 850 ℃, 20 min for Al-4%Zr alloy were used in this study.

The microstructures of the bonding zone metals with different bonding pressure are shown in Fig. 1. There are intermetallic compounds Al_3Ti or Al_3Zr and aluminum solid solution with Al-3%Ti or Al-4%Zr as bonding alloys, respectively. The width of bonding zone metal decreases, while the content of intermetallic compounds increases as the pressure rises, and, in particular, the intermetallic compounds become dominant microstructures when the pressure reaches 7 MPa. Thus, the content of intermetallic compounds is higher than that of the original alloy (as shown in Fig. 2) by exerting pressure on the couples in the process of bonding, which results in improving the heat stability of the bonding zone metal.

It is well known that the ductility of the aluminum based alloy, such as Al-Ti, Al-Zr, is close to that of pure aluminum. When the heating temperature of the assembly is below the peritectic point, which is 665 ℃ for Al-Ti alloy and 660.5 ℃ for Al-Zr alloy, respectively, the plastic deformation of the bonding zone metal under pressure becomes increasingly larger as the temperature rises, and, at the same time, the amount of the metal extruded out from the bonding zone increases. In the above case, the composition of extruded metal is the same as that of the original alloy. At the peritectic point temperature, aluminum solid solution dissolves into aluminum liquid and intermetallic compounds. Furthermore, when the temperature rises continuously, a small amount of inter metallic compounds begin to dissolve into aluminum liquid, which contributes to increasing the content of the second alloying element in the alu-

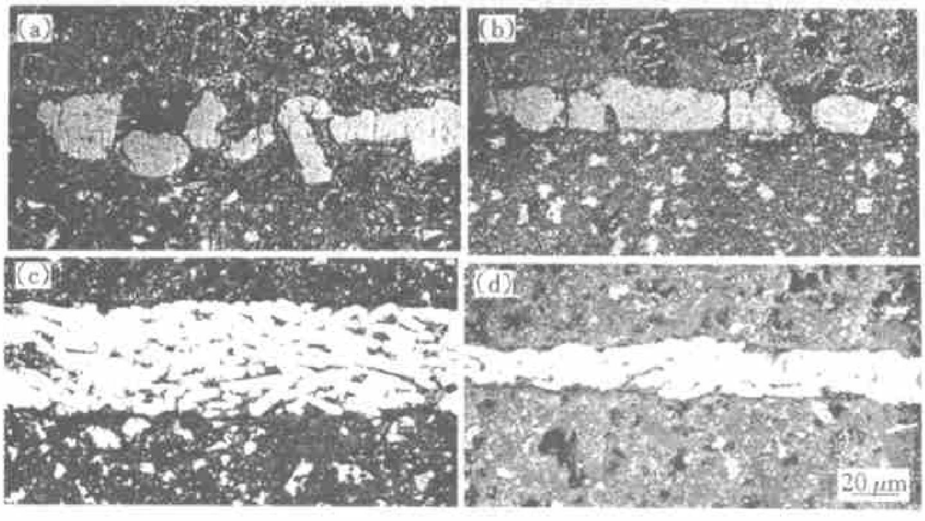

Fig. 1 Effects of bonding pressure on microstructures of joint's bonding zone metal

(a) —Al-3%Ti as bonding material, θ_B= 800 ℃, t_B= 20 min, p_B= 3 MPa;

(b) —Al-3%Ti as bonding material, θ_B= 800 ℃, t_B= 20 min, p_B= 7 MPa;

(c) —Al-4%Zr as bonding material, θ_B= 850 ℃, t_B= 20 min, p_B= 3 MPa;

(d) —Al-4%Zr as bonding material, θ_B= 850 ℃, t_B= 20 min, p_B= 7 MPa

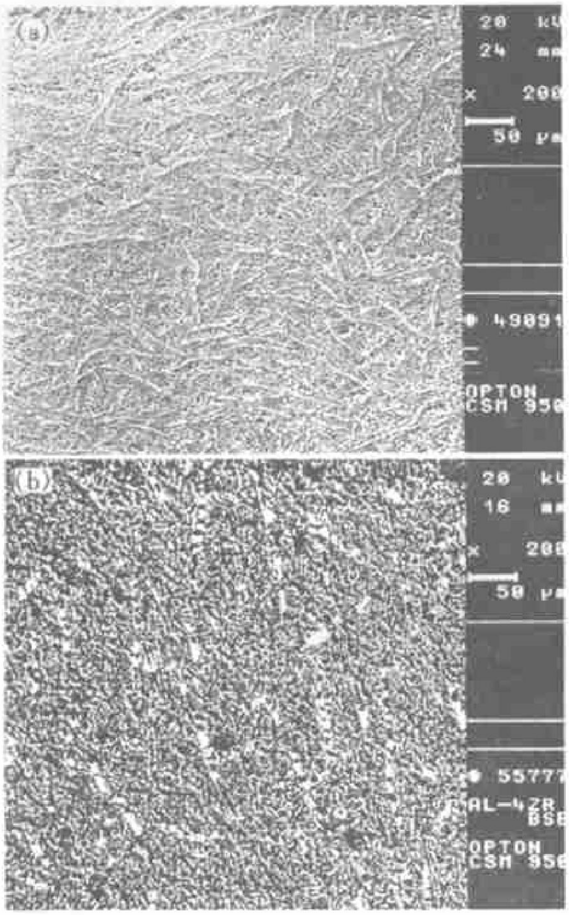

Fig. 2 Microstructures of original aluminum based alloys
(a) —Al-3%Ti; (b) —Al-4%Zr

minum liquid. Since the aluminum liquid flows more easily out of bonding zone under pressure than solid-state intermetallic compounds do, at the temperature in which the alloy is in solid-liquid phase status, the content of intermetallic compounds in the bonding zone metal increases gradually with time, temperature and pressure. It is also found that, by comparing Fig. 1 with Fig. 2, exerting enough pressure coarsens the intermetallic compounds to some extent. The possible reason is that a part of the intermetallic compound grains can contact with each other when their contents in the bonding metal reach a certain degree, then the contacting grains can interdiffuse to become into more coarse grains.

From the formation mechanism of bonding zone metal described above, it can be concluded that SLSPB is also suitable for bonding ceramics with Al-V, Al-Cr, Al-W alloys, which are quite similar to Al-Ti, Al-Zr alloys in properties.

As an active element, solid-state aluminum in the bonding zone metal can slightly react with Si_3N_4 ceramics when the temperature is in the range from 550 ℃ to the peritectic point[4]. Further increasing temperature, in which the bonding alloy exists at solid-liquid state, can promote the reactions between the aluminum solution containing a little second active element Ti, Zr and Si_3N_4 ceramics. Naturally, the higher the bonding temperature and the longer the bonding time, the more sufficient the interfacial reactions, which results in stronger bond of bonding zone metal/Si_3N_4 ceramics interfaces[6, 7]. The joint's formation with SLSPB is similar to that of non-complete isothermal solidification transient liquid phase diffusion bonding (TLPB) in that the low melting point aluminum in the bonding zone metal is reduced little by little during bonding. Therefore the SLSPB can be essentially called as a special TLPB.

3.2 Strength and fracture feature of joint

The effect of bonding pressure on the strength of joints is presented in Fig. 3. When aluminum is used as bonding material, the joints' strength first increases as the pressure rises, then, when the pressure is greater than 3 MPa, the joints' strength increases very slowly with pressure. However, when Al-3%Ti and Al-4% Zr are used as bonding materials, the joints' strength reaches the maximum at 7 MPa, then decreases gradually with pressure. If aluminum is used as the bonding material, the compositions of bonding zone metal remain unchanged in the bonding process, while its width decreases drastically with the pressure when it is below 3 MPa; and when the pressure is higher than 3 MPa, the width decreases very slowly. Thus the constraining strengthening of joint by pressure is consistent with changing of bonding zone metal width by pressure. That is, it changes first drastically then very slowly. If Al-3%Ti and Al-4%Zr are used as bonding materials, both constraining strengthening and the intermetallic compounds strengthening increase the joint's strength when the pressure is below 7 MPa, but coarser intermetallic compounds would embrittle the bonding zone metal and decrease the joint's strength. In a word, the optimal pressure is 7 MPa when the constraining strengthening and the intermetallic compounds strengthening reach the best match.

Fig. 4 shows the strength changes of joints,

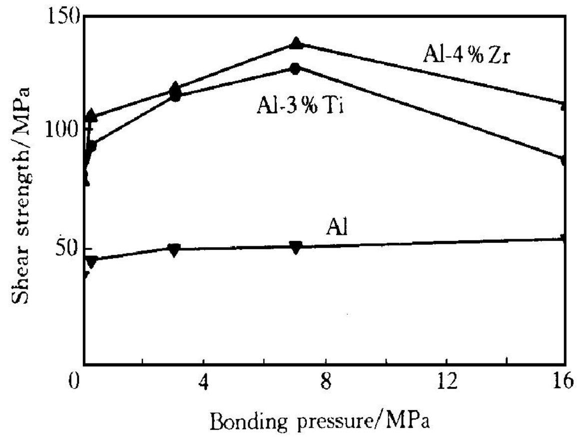

Fig. 3 Effects of bonding pressure on room temperature shear strength of joints

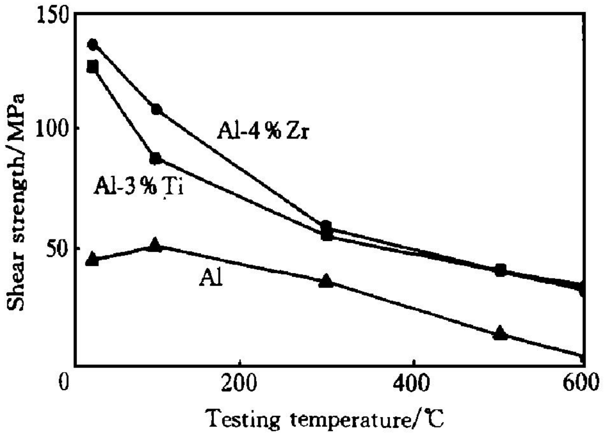

Fig. 4 High temperature strength of joints

which individually have the highest room strength. The strengths of the joints bonded with Al-3%Ti and Al-4% Zr alloys are considerably higher than that with aluminum. The former joints shear strength remains at 32~ 34MPa at 600 ℃, while the latter joint's shear strength is only 4.5MPa. As a result, the efficiency of improving the joint's strength by using SLSPB is quite obvious.

The fracture usually occurs in the bonding zone metal adjacent to Si_3N_4 ceramics/metal interfaces in both room temperature and high temperature shear fracture test, but when the strength reaches the maximum, the fracture appears both in ceramics and bonding zone metal which are all near the interfaces. Thus, the relatively low bonding temperature used in this study is high enough for the formation of the strong interfaces when aluminum and Al-Ti, Al-Zr alloys are used as bonding materials. In this case, the bonding zone metal near the ceramics/metal interfaces is still the weakest position of the joint.

For Al/Al_3Ti alloy, the dispersed Al_3Ti phases can harden the matrix through baffling the movements of dislocations, restraining the recrystallization and counteracting the grain coarsening at high temperature. The prime factors determining the properties of the heat resistant of the Al_3Ti-dispersion strengthened Al/Al_3Ti alloy include the content, the grain size and the distribution of Al_3Ti phases. Several technologies, such as casting, rapid solidification and mechanical alloying were developed. The mechanical technique is the best one, by which Al_3Ti grains measuring 20~ 250 nm can be obtained. For example, the tensile strength of Al-12% Ti (mass fraction) alloy manufactured by mechanical alloying technique with suitable parameters can retain 120 MPa at 500 ℃[8,9]. In the present study, Al_3Ti grains of 15~ 25 μm obtained by SLSPB, being approximated to that obtained with casting technique, are obviously larger than those obtained with mechanical alloying. This is the essential reason why the joint's strength with SLSPB is lower than that of the mechanical alloyed Al/Al_3Ti alloy. Although the Al_3Zr grains in the bonding zone metal are relatively small, they are still much larger than that obtained by mechanical alloying. Joints with better high temperature properties may be obtained by developing new methods through controlling the size and the distribution of the intermetallic compounds grains in the bonding zone metal.

3.3 Bonding mechanism of Si_3N_4 ceramics/bonding zone metal interfaces

The XRD patterns of the fracture appearances of the joints are shown in Fig. 5. Fig. 5(a) indicates that a small amount of TiN and Ti_5Si_3 are produced by the reactions between Al-Ti alloy and Si_3N_4 ceramics, while Fig. 5(b) indicates that a small amount of AlN phase is produced by the reaction between the Al-Zr alloy and Si_3N_4 ceramics. Moreover, the results of the EPMA of the ground appearance and joints' cross-sections demonstrate that the reaction layer between Si_3N_4 ceramics and the bonding zone metal contained Al, Si, N, O, Ti and Al, Si, N, O, Zr, respectively. In summary, the reactions with Al-Si-N-O type of compounds as products between aluminum and the Si_3N_4 ceramics are the dominant reactions, and there exist some reactions between Ti, Zr and Si_3N_4 ceramics as well.

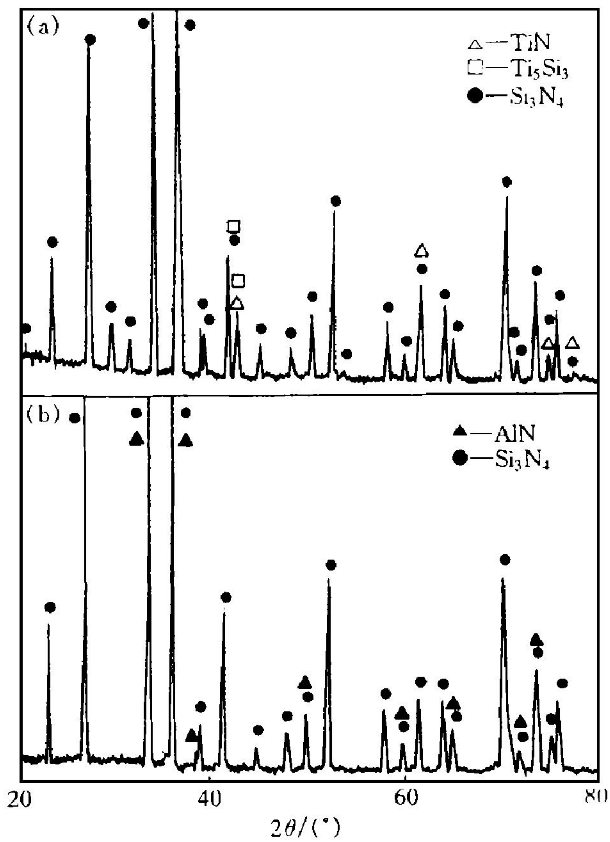

Fig. 5 XRD patterns of joints' shear fracture appearances

(a) —Al-3%Ti as bonding material, p_B= 7MPa, θ_B= 800 ℃, t_B= 20min; (b) —Al-3%Ti as bonding material, p_B= 7MPa, θ_B= 800 ℃, t_B= 20min

According to the previous investigations[3, 4, 8, 9], a reaction layer, which is amorphous or crystalline, $mAl_2O_3 \cdot nSiO_2$, near the bonding zone metal, another reaction layer, which is β′-Sialon, near Si_3N_4 ceramics, and a small amount of AlN phase are usually formed when the bonding of Si_3N_4 ceramics is performed by using aluminum as filler metal at relatively low temperature such as about 800 ℃, and the thickness of the entire reaction layer usually ranges 0.4~1.0 μm. It is interesting to find that the microstructures of the joints bonded with SLSPB at low temperature are quite similar to those of the previous investigations. In the present investigation, however, the complex Al-Si-N-O type compounds, are not detected by XRD. It is considered that the result is induced by a variety of factors, for instance, the whole reaction layer is too thin, reaction products $mAl_2O_3 \cdot nSiO_2$ are amorphous and the crystal lattice structure of the dominant reaction product β′-Sialon is similar to that of Si_3N_4 ceramics. At the same time, the second active element Ti or Zr may also react with Si_3N_4 ceramics to some extent to promote the formation of the bonding interfaces, when Al-Ti or Al-Zr alloy is utilized as bonding material with SLSPB. Since the very active aluminum solution in the solid-liquid state alloy during the holding time contained 0.6% ~ 0.7% (mole fraction) Ti or Zr, however, the reaction products containing Zr are not enough to be detected by XRD . The above reactions may be expressed by the reaction Eqns. (1) ~ (4)[7, 10], which are thermodynamically feasible because their Gibbs free energy is negative:

$$4Al + Si_3N_4 = 4AlN + 3Si \quad (1)$$

$$\Delta G_1^{\ominus}/(kJ \cdot mol^{-1}) = -126.88 + 0.01649\,T$$

$$9Ti + Si_3N_4 = 4TiN + Ti_5Si_3 \quad (2)$$

$$\Delta G_2^{\ominus}/(kJ \cdot mol^{-1}) = -1370 + 0.1637\,T$$

$$4Zr + Si_3N_4 = 4ZrN + 3Si \quad (3)$$

$$\Delta G_3^{\ominus}/(kJ \cdot mol^{-1}) = (-690 \sim -655) \quad (498 \sim 1298\,K)$$

$$\{Al\} + (O_2) + Si_3N \rightarrow \langle Al\text{-}Si\text{-}N\text{-}O \rangle \quad (4)$$

4 CONCLUSIONS

1) When aluminum based alloys containing a small amount of intermetallic compounds Al_3Ti or Al_3Zr are used as bonding materials and of solid-liquid state during bonding, the content of the intermetallic compounds in the bonding zone metal can be increased by exerting enough pressure on the bonding couples, which leads to strengthening the bonding zone metal and improving heat resistant properties of joints. There, however, exists an optimum bonding pressure, and excessive pressure can embrittle the bonding zone metal and degrade the properties of the joints.

2) In the formation of the interfacial bond, the reaction between aluminum and Si_3N_4 ceramics, which produces Al-Si-N-O type compounds and another compound AlN, is the dominant one when the bonding alloy is Al-Zr alloy, while the reaction between the second active element Ti or Zr also occurs to some extent.

3) Solid-liquid state pressure bonding developed in this investigation is a novel bonding method. With this method, bonding temperature may be decreased by the low melting point of the matrix of the bonding alloy, and heat resistant ceramic joints may be obtained by exerting appropriate bonding pressure.

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