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Bonding of Al_2O_3 ceramic and Nb using transient liquid phase brazing①

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Abstract: The brazing of Al_2O_3 to Nb was achieved by the method of transient liquid phase (TLP) bonding. Ti foil and Ni-5V alloy foil were used as interlayers for the bonding. The base materials were brazed at 1 423-1 573 K for 1-120 min. The results show that the shear strength of the joint first increases and then decreases with increasing holding time and brazing temperature. The joint interface microstructure and elements distribution were investigated. It can be concluded that a composite structure, in which the base metals are solid solution Nb(V) and Nb(Ti) reinforced by Ni_2Ti, is formed when the brazing temperature is 1 473 K and holding time 15 min, and a satisfactory joint strength can be achieved. The interaction of Ti foil and Ni-5V foil leads to the formation of liquid eutectic phase with low melting point, at the same time the combination of Ti come from the interlayer with O atoms from Al_2O_3 results in the bonding of Al_2O_3 and Nb.

Key words: Al_2O_3 ceramic; Nb; transient liquid phase bonding
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1 INTRODUCTION

Al_2O_3 ceramic has excellent heat-resistance, corrosion-resistance and wear-resistance, insulation and other properties. It has been widely used in engineering fields. Niobium (Nb) has the features of high melting point, relatively lower density and high resistance to corrosion of some liquid alkali metals (K, Na), and the price of Nb is also relatively cheap, so its application is promoted further. For these reasons, the bonding of Al_2O_3 ceramic and Nb is very important for certain engineering applications.

There are many methods to achieve the bonding of ceramic and ceramic, such as active metal brazing, solid-state diffusion bonding, TLP bonding. The interface reaction mechanism was also explored[1-4]. However, researches on the TLP bonding of Al_2O_3 with Nb can hardly be found.

In this study, Al_2O_3 and Nb were bonded by TLP bonding with Ti foil and Ni-5V alloy foil. The interface morphologies, diffusion behavior of elements, formed phases and joint strengths were investigated. Finally, the interfacial reaction mechanism and the effect of brazing parameters on the morphologies were discussed.

2 EXPERIMENTAL

Al_2O_3(purity 99.6%, 30 mm × 10 mm × 3 mm) and Nb (20 mm × 10 mm × 3 mm) were bonded with pure Ti foil(50 μm thick) and Ni-5V alloy foil (50 μm thick). The base materials and interlayers were assembled as Fig. 1(a). During brazing a small pressure was loaded to provide close contact between base materials and interlayers[5]. The brazing parameters are as follows: vacuum is 3×10^{-3} Pa; brazing temperatures are 1 423, 1 473, 1 523 and 1573 K, respectively; and the holding times are 1, 5, 15 and 120 min, respectively. During the temperature-rising stage, the furnace temperature was raised at a rate of 10 K/min when below 1 073 K, then the temperature was kept for 60 min at 1 073 K for achieving excellent vacuum degree, then the temperature was raised to brazing temperature. During the cooling stage, the temperature was decreased at a rate of 25 K/min to 1 373 K, at which the temperature was kept for 30 min. At last, the furnace was cooled to room temperature with furnace power off.

The surfaces of bonded specimens were polished by serial diamond rubbing powder: W40, W28, W14 and W1.5 in turn, and then were etched with hydrofluoric acid. At last, they were eroded with iron chloride and cleaned by water and alcohol. Finally, the surfaces to be analyzed were sprayed with carbon. The morphologies and element distributions were investigated with scanning electronic microscope (SEM, JSM-6300) equipped with energy disperse spectrum (EDS, JXA-840A) and the interface product phases were determined by X-ray diffraction

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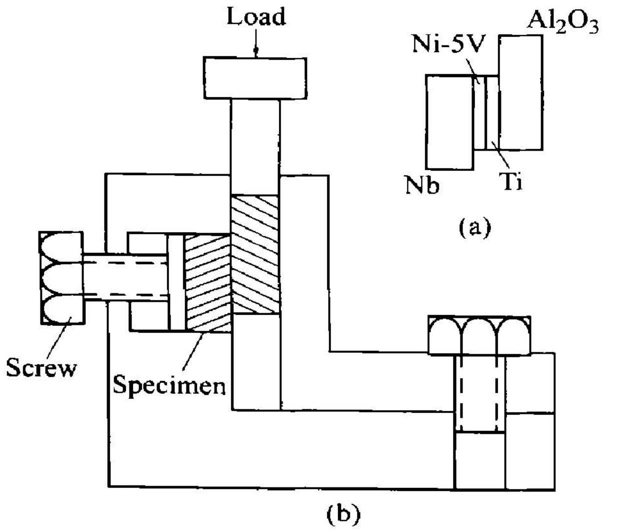

Fig. 1 Schematic of bond joint assembly(a) and shear testing apparatus(b)

(XRD, DMAX-RB). The strength of the joints was measured by shear tests using compressive loading at room temperature at a crosshead speed of 0.5 mm/min, with the apparatus assembled as shown in Fig. 1(b). The shear strength of the lap joints was determined by dividing the fracture load by the cross-sectional area of the joints[6].

3 RESULTS

3.1 Effect of brazing parameters on morphology

The interface morphologies of Al_2O_3/Ti/Ni-5V/Nb joints brazed with different parameters were investigated by SEM. Fig. 2 shows the SEM backscatter images of joints brazed at 1 473 K for 1 min, 15 min and 120 min, respectively. It can be seen from Fig. 2(a) that a very thin deep gray reaction layer with uneven edge has been formed. In the center region, the phases are relatively uniform and the white phases are produced with black phases alternately. The corresponding linear scanning image shows clearly a very high concentration gradient of Ti exists in the interface region, indicating a great deal of Ti has diffused from the interlayer into the interface between Ti foil and base materials. At the same time, some relatively fewer Ti atoms have also diffused into the Ni-5V layer. And Ni, V have been distributed across the whole brazing zone to some extent. V is added into the interlayer to promote the activity of interlayer and joint properties at high temperature because of its strong affinity with Ni and Ti. So this method can be effectively used to diminish the brittle Ni-Ti intermetallic compounds at the interface. It can be concluded that the existence of V restrains the detrimental effect of Ni to produce intermetallic compound effectively. And Nb has diffused into the reaction interface of Al_2O_3 and interlayer too.

From Fig. 2(b), it can be seen that the reaction layer becomes thicker than that in Fig. 2(a); and the black phases segregate further. Fig. 2(c) shows that more reaction has occurred and more product phases come forth. Moreover, the dissolution of Nb in the brazing zone has made the interface of the Nb move towards the center region gradually. EDS results show that the distribution of Ti tends to be more uniform, illustrating the diffusion of Ti in the interlayer reaches equilibrium.

In order to explore the effect of brazing temperature on morphologies, Al_2O_3 ceramic and Nb were brazed at 1 523 K and 1 573 K for 5 min, respectively. It can be seen from Figs. 3(a) and (b) that the reaction layer grows more remarkably and the black phase in the brazing zone segregates rapidly with temperature increasing. Compared with the effect of brazing time as shown in Fig. 2, Fig. 3 illustrates that the effect of temperature on elements diffusion speed is more effective than that of time.

3.2 Determination of product phases

The reaction product phases at 1473 K for 15 min were analyzed carefully. From Fig. 2, there are mainly two regions in the joints: interface reaction layer and brazing seam. XRD analysis(Fig. 4) shows that Ni_2Ti_4O and Ti_2O form at the interface region. EDS results of some critical points along the reaction layer indicate that a lot of Ni have diffused through Ti layer into reaction interface and participated in the interface reaction. As for the phases in the central region, the EDS data show that the black phases are mainly composed of element Ni and Ti, and the white phases are composed of Nb, Ni and a little V. In this work, though the effect of temperature and brazing time cause the diversity in interface morphologies, the EDS analysis reveals that the chemical composition does not change distinctly.

3.3 Effect of brazing parameters on joint strength

It is known that the filler metal or interlayer affects the properties of joints directly. However, the brazing parameters also play a very important role in brazing process. In this experiment, the parameters mainly include vacuum, holding time and brazing temperature. Obviously, vacuum must be controlled to the best. While the relationship between the latter two factors should be determined carefully. Fig. 5 shows the effect of brazing temperature and holding time on joint strength. At 1 423 K, the shear strength increases with time increasing. This is mainly because the brazing temperature is low, the diffusion and the reaction is not sufficient, so the bonding can't be obtained well. But with the holding time in-

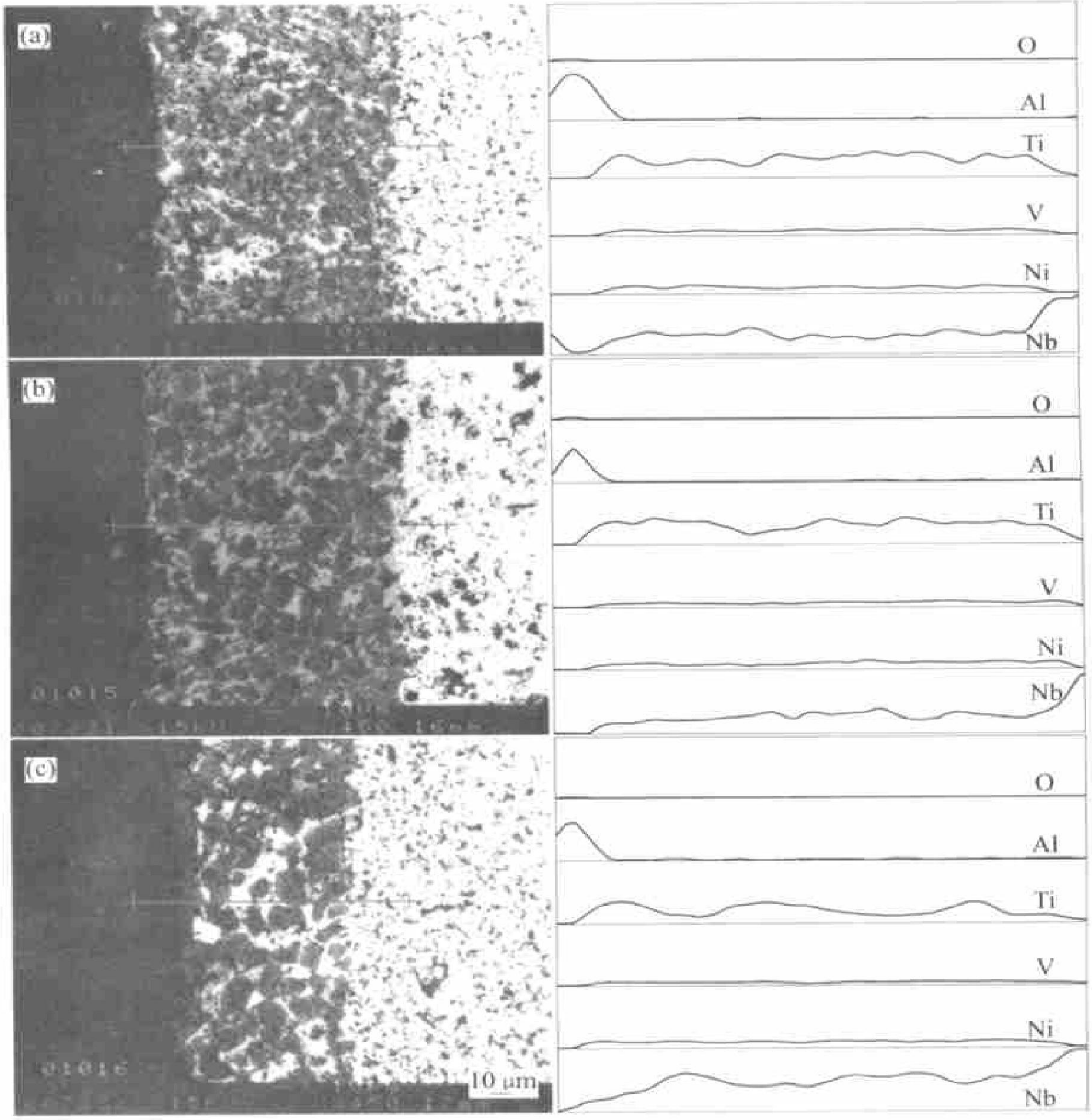

Fig. 2 SEM backscattered images and corresponding elemental distribution of Al_2O_3/Ti/Ni-5V/Nb joint brazed at 1 473 K for 1 min(a), 5 min(b) and 120 min(c) respectively

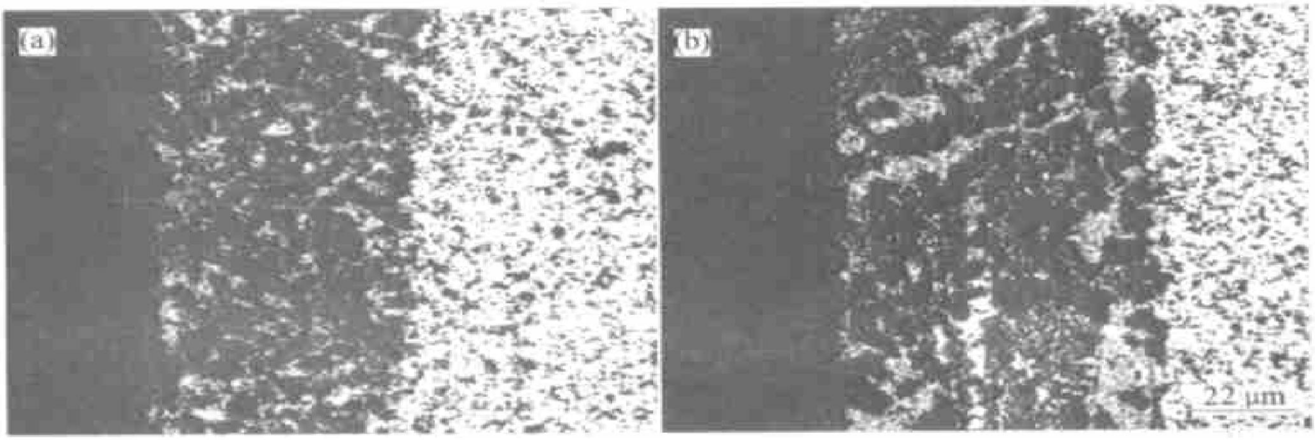

Fig. 3 SEM backscattered images of Al_2O_3/Ti/Ni-5V/Nb joint brazed for 5 min at 1 523 K(a) and 1 573 K(b)

creasing, the diffusion and the reaction become much more evident relatively, so the joint strength increases. At 1 473 K, the joint strength can reach 162 MPa at 15 min; even at 120 min, the value just decreases by 13%. When the temperature rises up to 1 523 K and 1 573 K, the joint strength reaches the peak point after holding for 3 min and then decreases sharply. From the view of stability of technique,

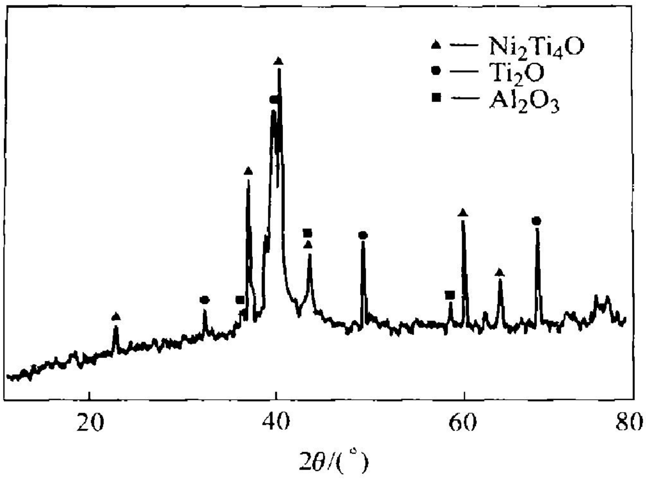

Fig. 4 XRD analysis results for interfacial structure of Al_2O_3/Ti/Ni-5V/Nb joint brazed for 15 min at 1 473 K

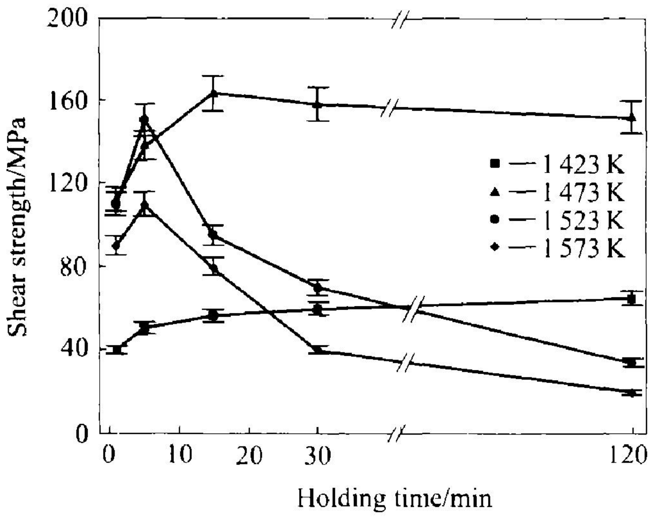

Fig. 5 Relationship between joint shear strength and holding time for Al_2O_3/Ti/Ni-5V/Nb joint at different brazing temperatures

though a higher joint strength can be got at 1 523 K and 1 573 K, it can not be considered as an optimal brazing temperature for its sharply decreasing strength with time increasing. When the brazing temperature is too high, the effect of thermal expansion mismatch between the elements of the joints on joint strength is remarkable. So the excessively long holding time and too high temperature lead to the increasing of residual stresses in the joint. Fig. 6 shows more clearly the relationship between brazing temperature and strength. Comparing it with the influence of holding time(Fig. 5), it can be concluded that these two parameters affect the strength with similar principle. There exists an optimal value of parameters, when they are below the value, the strength increases gradually and then decreases at different velocities.

It is known that the brazing parameters affect the strength through influencing the growth process of interface reaction layer and phases at brazing zone.

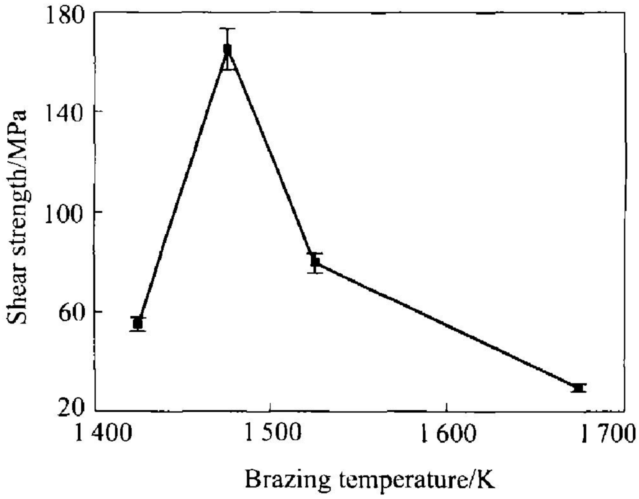

Fig. 6 Relationship between brazing temperature and joint strength of Al_2O_3/Ti/Ni-5V/Nb joint brazed for 15 min

The thickness of reaction layer and the distribution of product phases at brazing zone are the most important factors. With relative low temperature or short holding time, the reaction layer does not grow fully, thus causes a very thin brittle reaction layer and incompact contact between the base material and interlayer. In this case, the interface may be the weakest position. While at optimal temperature and holding time, the reaction layer becomes thicker and the brittle oxide of Ti combines with Ni_xTi_y into complex compound with better plasticity. At the same time, the brittle Ni_xTi_y (black phase in Fig. 1) with very high strength dispersed in the solid solution can be used as a reinforcement phase in the base of Nb(Ti) and Nb(V) solid solution, so a satisfactory joint strength is obtained. However, as the temperature or holding time exceeds the optimal value, the strength will decrease because of the excessively segregating of Ni_2Ti, which causes the whole brazing zone to be brittle. For these reasons, it is of great importance to control brazing parameters precisely.

4 DISCUSSION

In this work, during the brazing process, the atoms in Ti foil and Ni-5V alloy foil diffuse into each other. As furnace temperature reaches the eutectic point of Ni-Ti binary alloy[7], only a little Ti diffuses into Ni-5V foil, resulting in the formation of liquid phase of low melting point between the two interlayers. With increasing time and temperature, the diffusion behavior induces the dissolution of interlayers entirely. The Ti atoms in liquid phase will segregate to the surface of Al_2O_3 and react with the Al and O discomposed by diffusion deoxidization reaction[8]. Here the interface reaction can be concluded as:

$$Al_2O_3 + 2Ti = Ti_2O + Al_2O_2 \quad (1)$$

$$(Ti) + (O) \rightarrow Ti_2O \quad (2)$$

However, the formation of Ti_2O or TiO is considered to be very important by many material researchers for these two kinds of oxide will lead to the difference of joint strength. In order to declare the reaction mechanism, thermodynamic calculation of Gibbs free energy of formation can be used as an effective approach to estimate the product phases. As shown in Table 1, the formation Gibbs free energy of Ti_2O is less than that of TiO, thus Ti_2O may be the possible product phase. Although the reaction kinetic conditions of TiO can be fulfilled more easily, the EDS results in this work show a concentration gradient of Ti caused by thermodynamic driving force at interface is high enough to reach the kinetic condition. In fact, the kinetic condition is influenced mostly by brazing parameters and assemble mode of specimen.

Table 1 Gibbs free energy of compounds

Compound	$\Delta G/(kJ\cdot mol^{-1})$	Ref.
1/3 Al_2O_3	-410.26	[9]
Ti_2O(αTi(O))	-456.10	[10]
TiO	-412.22	[11]
Ti_2O_3	-384.87	[11]
Ti_3Al	-18.38	[11]
TiAl	-26.67	[11]
NiTi	-171.88	[10]
$NiTi_2$	-245.92	[11]
Ni_2Ti	-349.40	[11]

For the whole reaction system, reactions will not stop until the Gibbs free energy of every element reaches equilibrium. For this reason, it can be concluded that the reactions at interface and brazing zone will go further before equilibrium. The XRD results of Ni_2Ti_4O just illuminates the combination of Ti_2O and Ni_2Ti intermetallic compound. As for Ni_2Ti compound, the product can be concluded approximately. As shown in Table 1, the ΔG of Ni_2Ti is less than those of the other two Ni-Ti compounds, thus Ni_2Ti may be the most possible phase. Therefore, the further reaction happened at interface can be expressed as:

$$2Ni + Ti \rightarrow Ni_2Ti \quad (3)$$

$$Ti_2O + Ni_2Ti \rightarrow Ni_2Ti_4O \quad (4)$$

At the beginning, the Ti and Ni atoms in Ni-5V interlayer and Ti interlayer diffuse through some contact region. And with the holding time and temperature increasing, the diffusion speed of atoms increases remarkably. When the temperature reaches the eutectic point of Ni-Ti binary alloy and the amount of atoms diffused each other are enough, Ni-Ti binary eutectic with relatively low melting point comes into forth between the two interlayers. With time prolonging, the vis-à-vis diffusion will lead to the transformation of interlayers into liquid brazing alloy. During the diffusing process, driven by thermodynamic gradient, Ti atoms diffuse to the surface of Al_2O_3 ceramic and combine with O to form Ti_2O. And then Ti_2O will react with Ni_2Ti come from liquid brazing alloy and form the complex compound of Ni, Ti and O, named Ni_2Ti_4O.

In general the thermodynamic gradient of elements plays a key role during brazing process. However, brazing parameters such as holding time and brazing temperature also remarkably affect the properties of joints from the viewpoint of kinetics. By comparing the effect of holding time and brazing temperature on joint morphologies, it can be seen clearly that there are distinct differences between them. As shown in Fig. 2 and Fig. 3, the rising of temperature causes the segregating of black phases much more remarkably than the effect of time. In fact, the difference of these parameters on morphologies is caused by their effect on diffusion speed of atoms. According to Arrhenius equation,

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

where D is diffusivity coefficient, D_0 is the frequency factor which is taken as independent of temperature, and Q is the Arrhenius activation energy, it can be found that temperature affects elements diffusion in a high speed, which is in agreement with the experimental results. On the other hand, the atoms in the brazing zone always tend to congregate together and form a single-phase from the viewpoint of thermodynamics. Thus it can be concluded that, during the practical brazing process, the brazing temperature should be controlled accurately, and then proper holding time should be chosen based on the determined temperature[12].

5 CONCLUSIONS

In this work, Al_2O_3 ceramic and Nb metal were brazed with Ti and Ni-5V foils by TLP brazing at 1 423 - 1 573 K for 1 - 120 min. Both the reaction mechanism and the effect of brazing parameters on joint strength were discussed.

1) When brazing at 1 473 K for 15 min, the joint strength reaches the maximum value (162 MPa). With the holding time increasing, the strength only decreases by 13%. While at 1 523 K and 1 573 K, after reaching the peak point, the strength decreases sharply with the holding time prolonging.

2) When brazed at low temperature and held for a short time, the incompact contact between the reac-

tion layer and the base material and the brittle Ti_2O cause relative low strength. While brazed at the optimal parameters, the high strength is attributed to the reaction layer with proper thickness and Nb-base solid with dispersive distribution of Ni_2Ti solution. However, at too high temperature or for too long holding time, a low strength is obtained because of the increasing of brittleness in joint and the high residual stress.

3) During the bonding process, the diffusing of atoms of Ti and Ni-5V interlayer and the formation of eutectic phase with low melting point cause the dissolution of the two interlayers. And the combination of Ti with O to form Ti_2O achieves the bonding of Al_2O_3 ceramic and Nb.

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