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Active brazing of pure alumina to Kovar alloy based on the partial transient liquid phase (PTLP) technique with Ni–Ti interlayer

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Abstract

Pure alumina (99.9% grade compositions) was brazed to 4J33-Kovar alloy based on PTLP technique with nickel and titanium foils interlayer. The solder formed a sandwich microstructure: an α-Ti solid solution belt at mid part and Ti_2Ni intermetallics belts at two sides. This structure accounts for the good property of the joint. Microanalysis identified a reaction product at the alumina-braze interface as Ni_2Ti_4O phase. The special properties and structural compatibility of Ni_2Ti_4O contributed to the firm joint. The effects of brazing conditions on the joint properties were investigated. The joint shear strength showed the highest value of about 65MPa and did not monotonously increase with the brazing temperature ascending. It was shown that extending of brazing time gave thicker reaction layer and higher joint strength.

Keywords: Alloy; Al_2O_3; Brazing; Joining; Kovar; Microstructure; Ni_2Ti_4O

1. Introduction

Alumina is a kind of widely used ceramic material. It is applied in many areas such as vacuum tubes, insulation layers and so on. As techniques developing, more and more practical applications require highly pure alumina ceramics. In many cases, alumina needs to be bonded to metal to serve for certain functions. Among these metals, superalloy 4J33-Kova is most often introduced to bonding with pure alumina for it has a relatively close thermal expansion coefficient.[1]

Active brazing is an effective method for bonding pure alumina because the addition of active element in filler metals can effectively improve the wettability of ceramics.[2] Commercial brazing materials are generally systems as AgCu, AgCuTi, AgCuSnTi, AgCuInTi, Ti, etc. The eutectic composition of the system AgCu (mp 780 °C) is often preferred because it is relatively ductile and therefore able to limit the stresses arising between two materials with different thermal expansion coefficients.[3] Whereas, because of the noble metal component, these materials' operating temperatures are comparatively low.

Ni–Ti alloy solder can be used at higher temperature (lowest mp 955 °C) than those cited above. However, it has not been widely applied nowadays due to its bad ductility, which is important to release stress in brazing joint. It is also difficult for machining or band rolling, especially for Ni–Ti alloy with high titanium content.

In recent years a new technique, (partial transient liquid phase, PTLP), has been developed to join ceramics. In this technique original solder is composed of metal foils that stack together to form an A/B/A structure.[4] At brazing temperature the contact faces of two different metal foils melt into liquid phase alloy because of diffusion. As layer A is usually much thinner than layer B, in the span of short time layer A will melt completely. Afterwards, dissolution of layer B causes the isothermal solidification of liquid phase until the layer B is exhausted because component B in the liquid exceeds the solubility.

Based on PTLP technique, taking a proper Ni/Ti/Ni foil layer as brazing materials for bonding pure alumina with 4J33-Kovar can produce a firm and airtight joint, and make the solder machining easy because pure metals are relatively ductile. The technical processes and the joining mechanism were discussed in this paper.

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2. Experimental procedure

The sizes of alumina pieces used for brazing were $\phi15\times4$ mm, purity of which was 99.9%. The metal section was 4J33-Kovar alloy, melting point 1450 °C, and its dimension was $\phi6\times6$ mm. Table 1 lists the properties of the pure alumina ceramic. Table 2 shows the composition of 4J33-Kovar alloy.[5] Nickel foil and titanium foil, which were cut into round slices of the same diameter as Kovar section, were used as the brazing interlayer. The thickness of nickel foil was 15 μm and that of titanium 0.3 mm. The three brazing parts, pure alumina piece, 4J33-Kovar and Ni, Ti foils were assembled as shown in Fig. 1. Before assembling, the materials of the three parts should be taken through grinding and cleaning steps carefully.

The specimens were brazed at temperature ranging from 965 to 1025 °C and holding time ranging from 20 to 100 min in a vacuum furnace with 300–400 g/cm^2 pressure added to their tops to enhance interfacial reactions. After brazing, the shear strength of the specimens' joints was measured in the testing clamp by the method shown in Fig. 2. In order to observe solder microstructure by optical microscope and SEM, some brazed joints were cut vertically to the welding interface. X-ray diffraction method was used to identify interfacial reaction products by cutting the joints alone solder/alumina interface.

Table 1
Properties of pure alumina

Thermal expansion coefficient (K^{-1})	Melting point (°C)	Density (g/cm^{-3})	Porosity (%)	Young's modulus (GPa)	Bend strength (MPa)
8.0×10^{-6}	2050	3.97	<0.01	380	490

Table 2
Composition of 4J33-Kovar alloy (wt.%)

C	Mn	Si	Ni	Co	Fe
⩽0.05	⩽0.50	⩽0.30	32.1–33.6	14.0–15.2	Remnant percentage

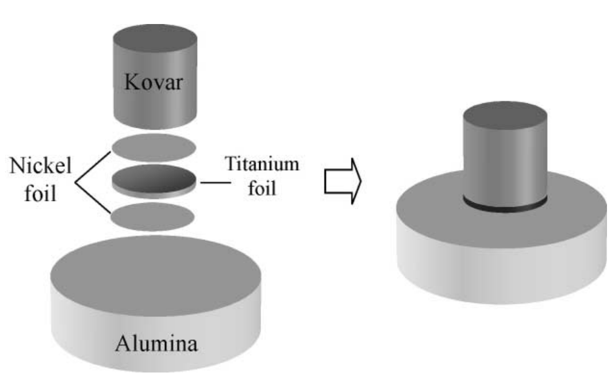

Fig. 1. Chart of assembling the brazing parts.

3. Results and discussion

3.1. Interlayer's melting process and microstructure

Fig. 3 shows the SEM micrograph of the solder by using 5%HF to slightly erode the joint vertical cutting/polishing plane. The dark color phase is α-Ti solid solution and the light color phase is Ti_2Ni intermetallics because the latter is much more resistant to erosion than the former. A sandwich structure is shown in the solder image, an α-Ti solid solution belt (actually mixed with tiny flakes of Ti_2Ni) at mid part and two Ti_2Ni intermetallics belts at sides.

The interlayer's melting was due to the diffusion between the contact faces of nickel foil and titanium foil. At brazing temperature, the diffusion formed Ni–Ti

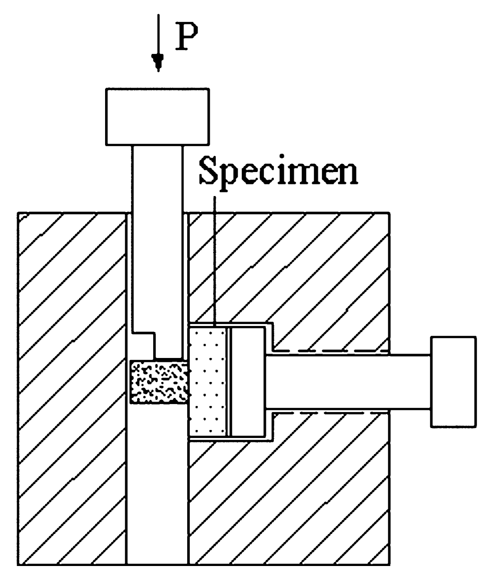

Fig. 2. Chart of the joints shear strength testing method.

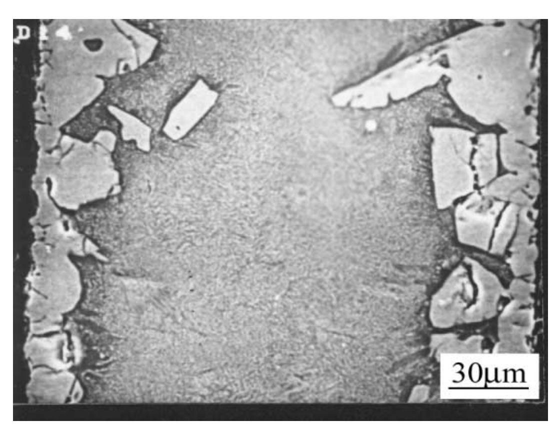

Fig. 3. SEM metallograph of the solder.

low melting point alloy that couldn't keep solid state in this condition. With holding time extending, very soon were the nickel foils exhausted so that the continuous dissolving of the remaining titanium foil resulted in the liquid alloy's isothermal solidification. This process did not end until the remaining titanium foil completely transformed into β-Ti solid solution that transformed into α-Ti solid solution mixed with tiny flakes of Ti_2Ni when temperature descending. Fig. 4 shows the sketch of the whole process.

When cooling, the remnant liquid alloy transformed into mainly Ti_2Ni intermetallics (about 70 wt.%), and few part α-Ti solid solution. So at room temperature, the solder's microstructure exhibits a sandwich structure as the image shown in Fig. 3. Ti_2Ni intermetallic compound is rigid while α-Ti solid solution is relatively ductile, so the α-Ti solid solution belt at mid part can function as a buffer layer. This fabric contributes to the brazing interlayer's better ability than Ni–Ti homogeneous alloy to release stress in the joint.

3.2. Interface microstructure and reaction products

3.2.1. Kovar/solder interface

The solder and 4J33-Kovar all belong to metal and consist of metal bonds. Because of the structural similarity, at brazing temperature the solder of liquid phase easily spreads on the surface of the Kovar section. After diffusion and dissolving, there developed firm linkage on the solder/Kovar interface. An interfacial reaction belt, which is about 3–4 μm thick, is shown in Fig. 5. As

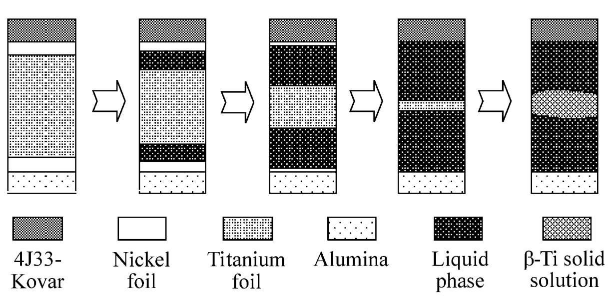

Fig. 4. Melting process of the interlayer in holding time (not for proportional scale).

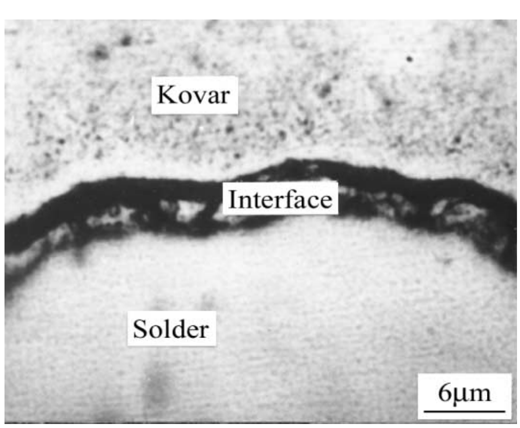

Fig. 5. Kovar/solder interface.

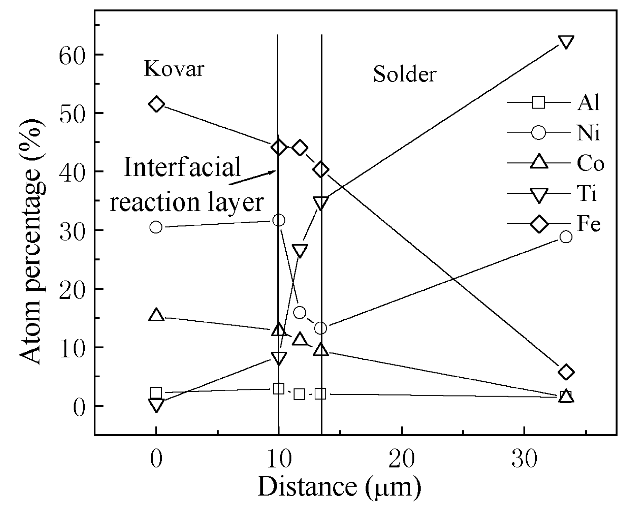

Fig. 6. EDS data of the Kovar/solder interface zone.

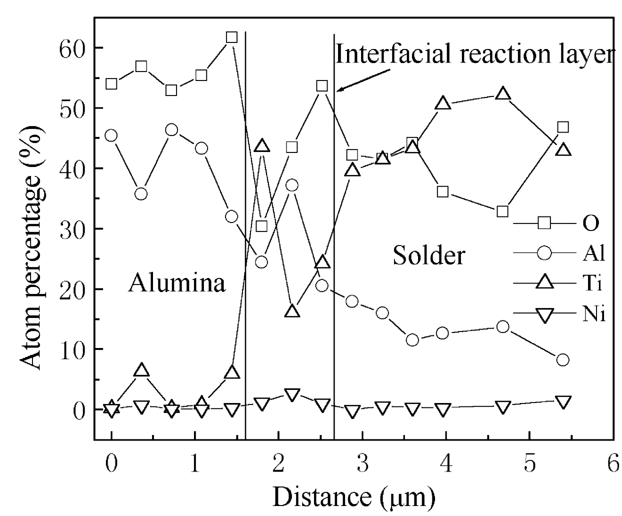

Fig. 7. EDS data of the alumina/solder interface zone.

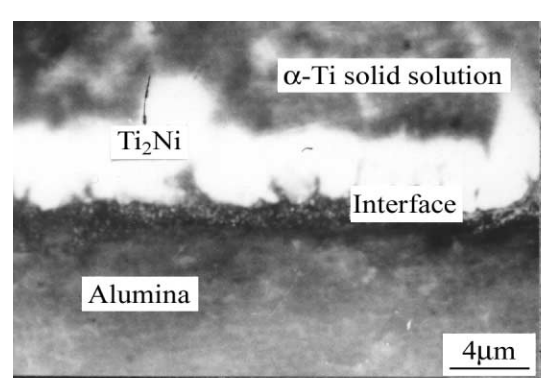

Fig. 8. Products layer on the alumina/solder interface.

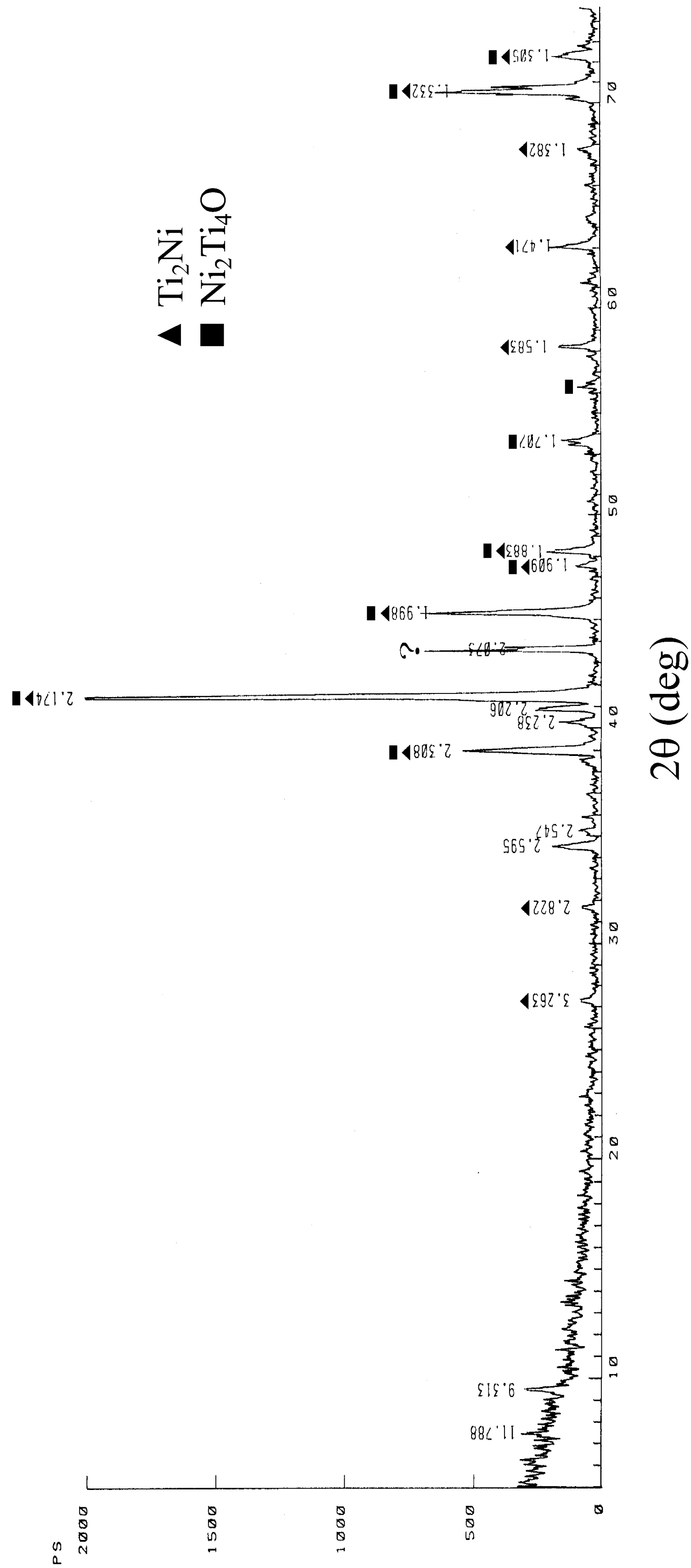

Fig. 9. Results of the interface products XRD analysis.

shown in Fig. 6 of EDS data, elements of Kovar and solder diffused through the Kovar/solder interface into each other matrix. It should be noticed that long holding time might cause severe erosion of the Kovar section when it is comparatively thin because of strong reaction on the Kovar/solder interface.

3.2.2. Alumina/solder interface

As mentioned above, the solder's two sides are both composed of Ti_2Ni intermetallics. So what is on the alumina section welding surface is mostly Ti_2Ni. Therefore, this zone should be corresponding to high concentration of Nickel (about 33 atm.%). But seen from EDS data shown in Fig. 7, actually the nickel concentration in the zone is very low while the titanium concentration is relative high as well as oxygen. Because oxygen has strong attraction to titanium, titanium atoms actually aggregated on the alumina/solder interface. By this mechanism, reactions between oxygen atoms of alumina and titanium atoms of solder occurred on the alumina/solder interface. Fig. 8 shows a reaction products layer about 1–2 μm thick on the alumina/solder interface. In different condition, the reaction products could vary.[6] According to XRD result shown in Fig. 9, in this experiment the reaction product is complex oxide, Ni_2Ti_4O. Oxides of Me_3Ti_3O or Me_2Ti_4O type with structures like Ti_2Ni were discovered in other experiments of bonding alumina by titanium active brazing as well as in this study.[7,8] These oxides are all metallic.[9] Here, Me represents Mn, Fe, Co, Ni or Cu.

Ni_2Ti_4O and Ti_2Ni both belong to space group Fd3m,[9,10] cubic system, so they are similar in structures. Furthermore, Ti_2Ni is somewhat soluble in Ni_2Ti_4O; therefore the creation of Ni_2Ti_4O favored the solder's wetting on alumina surface. Being metallic oxide as stated earlier, the Ni_2Ti_4O layer between alumina surface and Ti_2Ni belt of the solder functioned as the transition layer keeping some extent of structure consistency. In conclusion, oxide Ni_2Ti_4O was the linkage agent on the alumina/solder interface. Successfully brazing alumina by Cu_3Ti_3O and Cu_2Ti_4O interlayers in an experiment reported[11] also proved that oxides Me_3Ti_3O and Me_2Ti_4O could link with alumina firmly.

3.3. Joint shear strength

On the joint strength testing, all fractures happened in the alumina/solder interface or alumina section matrix. This indicates that the linkage between Kovar section and the solder are much firmer than that between alumina section and the solder. Thereby, the joint strength is determined mostly by the alumina/solder interface.

The brazing temperature had strong impacts on the melting of the interlayer and reactions on the interfaces. Variation of the brazing temperature influenced the joint strength in two aspects:

- Higher brazing temperature can enhance the interfacial reactions. This helps develop more strong joints. But if the temperature were too high such as 1025 °C, there would form many shrinkage cavities in the solder on the cooling process after brazing, which would weaken the joint. So too high brazing temperature is not good to the joint strength.[5]
- The liquid Ni–Ti alloy can dissolve more titanium in higher temperature, which will lead to a thinner α-Ti solid solution belt and thicker Ti_2Ni belts as cited above. Not like the rigid Ti_2Ni intermetallics belts, the α-Ti solid solution belt can act as the buffer layer, being relatively ductile; hence its impairment will reduce the interlayer's ability to decrease the stress in the joint. That is to say, the higher the temperature is, the thinner the buffer layer and the greater the stress in the joint.

Influenced by the two aspects, the joint shear strength exhibited severe fluctuation in the experiment temperature

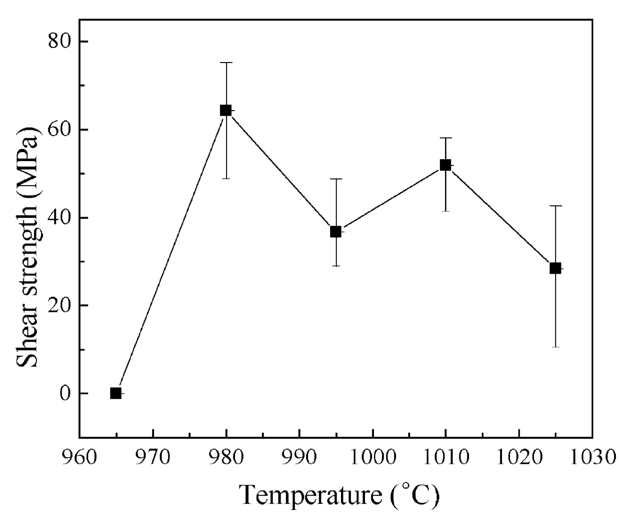

Fig. 10. Joint shear strength of different brazing temperature.

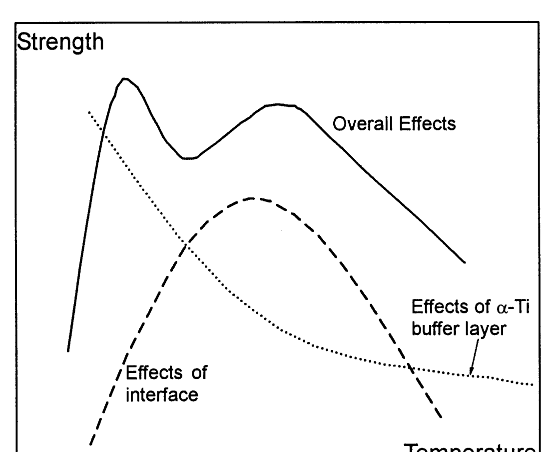

Fig. 11. Sketch map of the effects of α-Ti buffer layer and reaction interface.

range shown in Fig. 10, the holding time of which was 30 min. The two strength peaks in Fig. 10 can be described by different factors of interface and buffer layer, as schematically shown in Fig. 11. Because of this, the practical brazing temperature range is comparatively narrow and carefully temperature controlling should be taken when brazing.

Fig. 12 shows that the joint shear strength, which was brazed at 995 °C, increased rapidly with the holding time extending. While after 80 min, the increment reduced. The key fact of high joint strength is the forming of a continuous and integrated reaction layer on the alumina/solder interface. Long holding time promoted the growth of the reaction layer between alumina and the solder, as shown in Fig. 13. The rule of the growth is basically according to the equation $d=k\cdot t^{1/2}$ (d: the reaction layer depth; k: constant; t: the holding time). When the reaction layer was thick enough, more thickness did not help increase the joint strength any longer. Rather, because the reaction products were new phases to the matrix and had different thermal coefficient, a too thick reaction layer could cause big stress in the joint and therefore, lower the strength.[12] As this reason, the holding time should be selected properly and too long holding time may cause damage to the joint.

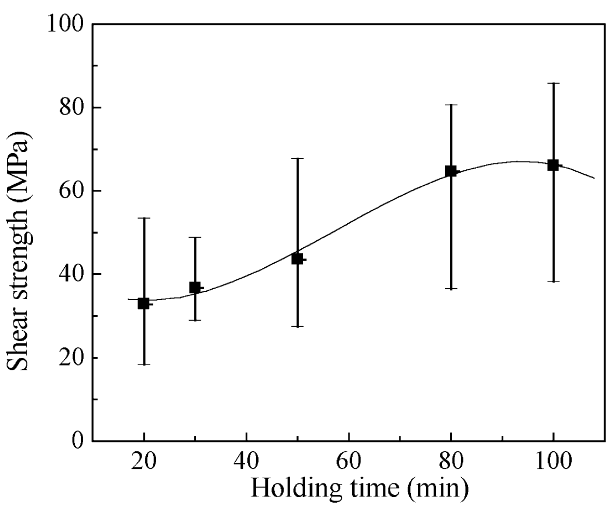

Fig. 12. Joint shear strength of different holding time.

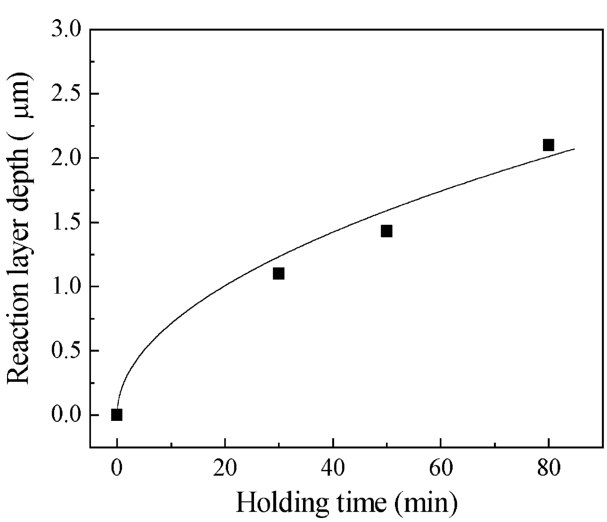

Fig. 13. Reaction layer depth of different holding time.

4. Conclusions

In this technique based on PTLP, the microstructure of the solder, formed by the interlayer's melting, is a sandwich-like structure, α-Ti solid solution at mid part and Ti_2Ni intermetallics at both sides. The α-Ti solid solution belt functioned as the buffer layer.

Titanium atoms of the solder gathered on the surface of the alumina section and reacted with oxygen atoms of that. The main reaction product is Ni_2Ti_4O that is the linkage agent and transition from the solder's metallic crystal lattice to alumina crystal lattice.

The joint strength did not monotonously increase with the brazing temperature ascending but fluctuated and the brazing temperature range is narrow for practical application; rather, it continuously rose when the holding time extending until 80 minutes, then the increment ceased nearly.

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