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Wetting Characteristics of Novel-type 63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi Solder Alloy

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6061 aluminum alloy has many advantages, and soldering is the most attractive joining method for 6061 aluminum alloy. In order to expand application of 6061 aluminum alloy, a novel 63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi solder alloy was prepared. The melting characteristic and microstructure of the solder were analyzed by differential scanning calorimetry and scanning electron microscope. Its spreading on the 6061 aluminum alloy was also studied. The results show that its melting temperature range is 456.34-463.68 K, and the temperature interval between the solidus and the liquidus is 6.34 K. The solder on 6061 aluminum alloy had better wetting characteristics. A precursor film appears ahead of the spreading droplet. The microstructure at the interface between the solder and the 6061 aluminum alloy was analyzed. It was clear that the intermetallic compound, Ag_2Al phase, was formed at the interface between the solder and the 6061 aluminum alloy.

Keywords interfacial reaction, precursor film, solder, wettability

1. Introduction

The 6000 series aluminum alloy are heat treatable and widely used in structural applications due to their specific mechanical properties, corrosion resistance and formability from simple to complex profiles by extrusion (Ref 1). Soldering can be a very attractive joining method for aluminum with much less heat distortion due to its lower process temperature than brazing and fusion welding. Soldering of these alloy is often required but, unfortunately, spreadability problems do exist, namely, aluminum oxide layer, the position of aluminum in the electromotive series, low heat capacity, annealed at temperatures as low as 598-623 K in a relatively short time (Ref 2-5). It is necessary that soldering process can be accomplished in a short time and relatively at a low temperature.

There are some conventional solder alloys for aluminum alloys, such as $Zn_{8-10}Cd_{8-10}Sn_{29-33}Pb_{49-53}$, $Zn_{56-60}Sn_{38-42}Cu_{1.5-2.5}$, and $Zn_{58-62}Cd_{30-42}$ (Ref 3). The temperature interval between the solidus and the liquidus of these solder alloy is large ($>$60 K). The tendency of the segregation increases with large temperature interval between the solidus and the liquidus (Ref 4). As such, Sn-Pb-Zn alloys are an excellent low temperature solders. Thus, it is of interest to investigate how they would interact with the 6XXX aluminum alloys when a solder interconnect is made at the terminal of a 6XXX aluminum alloys. In this study, we have carried out an experimental work on the wetting and spreading behavior of 6061 aluminum alloy with a new Sn-Pb-Zn solder at low temperature.

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Soldering can be done with either soft solders (Sn-based, lower temperature) or hard solders (Zn-based, higher temperature), with appropriate fluxes to fit processing temperature ranges. Zinc-based hard solders (below 673 K melting point and bulk shear strength approaching 175 MPa or 25,000 psi) use fluxes that require over-heating of the aluminum alloy. The soldering process with zinc-based hard solders can deteriorate the strength of the aluminum alloy. Although there have been a lot of works on the reactions between Al- and Sn-based solders, especially Sn-Pb-Zn solder, information about soldering reactions with 6061 aluminum alloy are not available in literature. Previously, it is recommended that 91Sn9Zn be the bonding alloys for soldering aluminum. Prasad et al. (Ref 5) had studied surface segregation and surface tension in Al-Sn-Zn liquid alloys. They found that the surface tension decreases when decreasing the constant Sn to Zn ratio, which makes the melting point of the solder increase. Also, in recent work, Weis and Hoyer (Ref 6) studied the microstructure of soldered joints with $SnAg_{3.5}$ + 5-35 vol.%$(Al_2O_3)_p$; Toru Nagaoka et al. (Ref 7) studied the joint strength of aluminum soldered under liquidus temperature of Sn-Zn hypereutectic solder. However, their work employed ultrasonic energy for soldering process.

2. Experimental Procedure

By analyzing the affect of Ag, Cu, and Bi, it can be seen that Ag can enhance the strength of the solder and Bi can decrease the melting point of the solder. The temperature will vary within a certain range when eutectic transformation occurs for the alloy, and the temperature gap between solidus and liquidus for the alloy is minimum at its eutectic point. According to the analysis above, the author researched and designed a solder alloy, namely, 63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi.

Table 1 Major alloying elements of 6061 aluminum alloy (mass%)

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
0.4-0.8	0.7	0.15-0.4	0.15	0.8-1.2	0.04-0.35	0.25	0.15	Bal.

The elements 99.9%Sn, 99.9%Pb, 99.9%Ag, 99.9%Cu, 99.9%Zn, and 99.9%Bi were melted in Ar under temperature of 1073 K and cast into a steel mold. The 5 mm diameter rod ingot then was left to cool in air. Chemical compositions of specimens are given in Table 1.

6061 Aluminum alloy sheets of 10 mm by 10 mm by 2 mm for wetting experiment were prepared. Rod solder of 2 mm by 5 mm diameter for wetting experiment was prepared. Thermal analysis of solders was performed by Perkin-Elmer Pyris 6 differential scanning calorimetry (DSC). Specimens for DSC were about 20 mg. Heating was carried out at rate of 5 K/min in Ar flow. Wetting experiment was conducted with flux in Ar. The experiment was carried out for varying time and temperature.

Specimens for observation were etched in a solution of 4 vol.% concentrated nitric acid and 96 vol.% C_2H_5OH after polished. Microstructure of the solders and the interfaces was observed by optical microscopy (OM) and scanning electron microscopy (SEM). The interface between the solder and the 6061 aluminum alloy was analyzed by x-ray diffraction (XRD).

3. Results and Discussion

3.1 Melting Characteristic of the Solder Alloy

DSC analysis was carried out in order to investigate the fundamental thermal reactions on heating of the solder alloy. Figure 1 shows the typical DSC curves obtained for the solder alloy on heating. The onset point of the DSC heating curve corresponds to the solidus temperature, and the peak point is recognized as the liquidus temperature of the alloy. As shown in Fig. 1, the melting temperature is in the range of 456.34-463.68 K, and the temperature interval between the solidus and the liquidus is 6.34 K. The endothermal peak on the curve has a sharp change of enthalpy in the course of melting. No lower temperature, endothermic peak was observed on DSC curve, which indicated that adding elements serving to change the spreadability would not induce the formation of lower melting-temperature, eutectic composition in the SnPb alloy. According to the Sn-Pb (Ref 8) binary phase diagrams, the Sn/Pb system exhibits an eutectic temperature of 453 K. There is an obvious endothermic peak similar to that of the eutectic reaction; it can decrease the tendency of the segregation. It is believed that this contributes to the formation of a good connection with high reliability in soldering and in service.

3.2 Microstructure of the Solder Alloy

Microstructures of the tested alloy are shown as Fig. 2. Clear $\alpha + \beta + \gamma$ eutectic structure is formed in the solder alloy, primary crystal phase α is brittle phase with high content of Pb element, and phase β is Sn-Pb solid solution, and phase γ is tough phase with high content of Sn element. Depending on the Sn-Pb phase diagram (Ref 8), upon cooling of the single-phase liquid solution to a temperature of approximately 463.68 K,

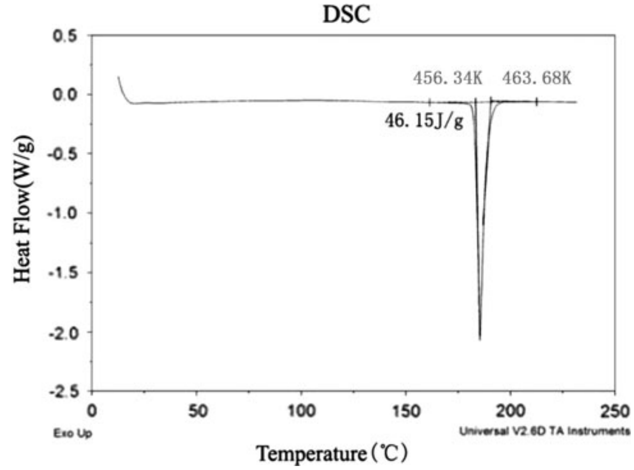

Fig. 1 The DSC curve of the tested alloy (63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi)

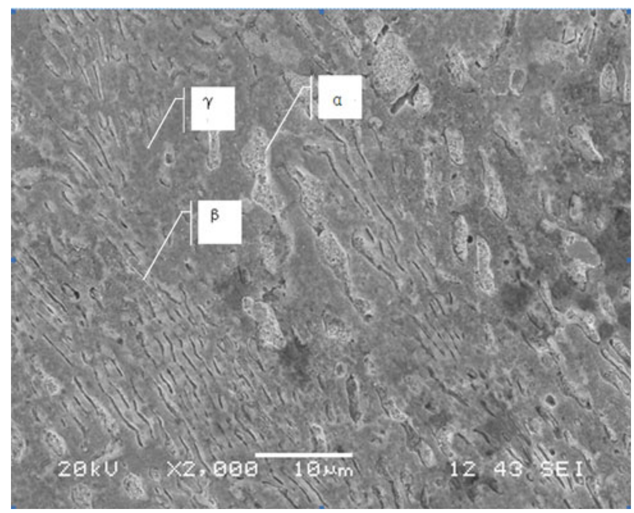

Fig. 2 Microstructures of the tested alloy (63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi)

a segregation of solid crystals of α (lead solid solution) occurs. This, in the overall diagram, leaves a more tin-rich liquid behind. Upon further cooling, additional α is segregated, and the liquid that is left tends to become more and more tin-rich until the composition is reached at a temperature of 456.34 K, a segregation of solid crystals of γ (Sn solid solution) occurs. Because the cool velocity is very quick, this eutectic composition is reached at a temperature of 456 K. This eutectic tin-lead liquid freezes completely with time.

To a solder alloy, besides the requirement of melting temperature range, it is expected to have good capacity of spreading. Eutectic alloy will have a good spreadability because of the narrow melting temperature range.

3.3 Spreadability of the Solder Alloy

The spread test was carried out to examine the wettability of the solders on 6061 Aluminum alloy and to clarify the interfacial reaction between the solder and 6061 Aluminum alloy. Solder wettability was experimentally assessed by measuring the spread area of solders on the 6061 Aluminum alloy.

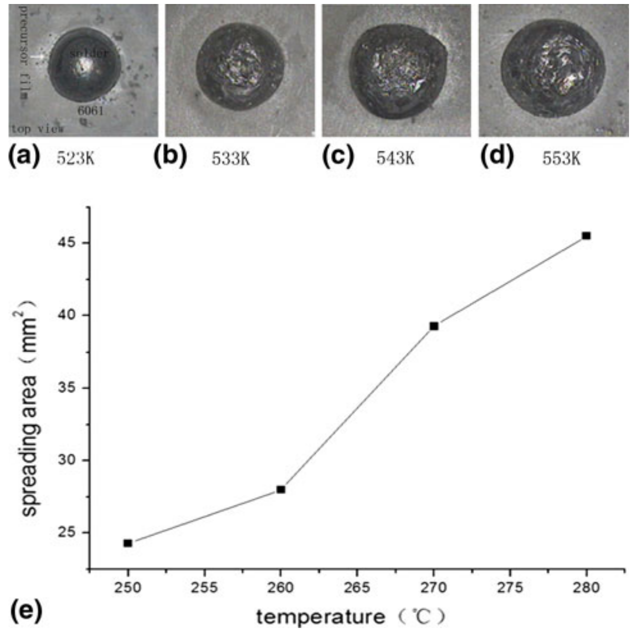

Fig. 3 The appearance of typical spread test specimens for the solder (a) 523 K; (b) 533 K; (c) 543 K; (d) 553 K; and (e) Spreading area as a function of brazing temperature

Figure 3 shows the appearance of typical spread test specimen for the solder after the spread test. The temperature of the spread test was, respectively, at 523-553 K. Figure 3 shows the results of spread area measurements for the solder at 523-553 K for 300 s. And the wetting area is increased from 523 to 553 K, which is in line with the general rules of wetting. In this figure, the differences in the wet area are clear. The wetting area at 553 K is the most.

Meanwhile, there is always a wetting ring in the front edge of the melting solder alloy (Ref 9). If a precursor film appears ahead of the spreading droplet, a better wettability of the liquid on the solid will be expected. Researchers have given some reasons as follows: the early explanation was the evaporation-condensation mechanism (Ref 9); another early explanation of the formation of a precursor film was the surface diffusion mechanism (Ref 9); the last explanation is a mechanism of rapid adsorption followed by film overflow (Ref 10).

The early school of thought was that the vapor pressure of some element is high. It is possible that these elements evaporated during the soldering and deposited on the base metal after volatilizing partially. When the temperature reaches melting point, the whole solder will begin to flow and overlay on the deposit. The uncovered section makes up the precursor film. However, the experiment was done with Ar as protective gas, the experimental temperature was about 573 K. The vapor pressure of Bi and Pb was low. So there was little possibility to volatilize, the reason is disagree with the evaporation-condensation mechanism.

And others think that some active atoms in the spreading droplet diffuse along the solid surface, particularly, along some surface defects. But the solder has no active atom, which is disagree with the surface diffusion mechanism.

The last school of thought was that the tin solubility is exceeded in the liquid film during cooling. The tin ring could appear. The solder temperature is low. So, this assumption of the formation of a precursor film cannot explain the wet ring in the low temperature solder-aluminum wetting system.

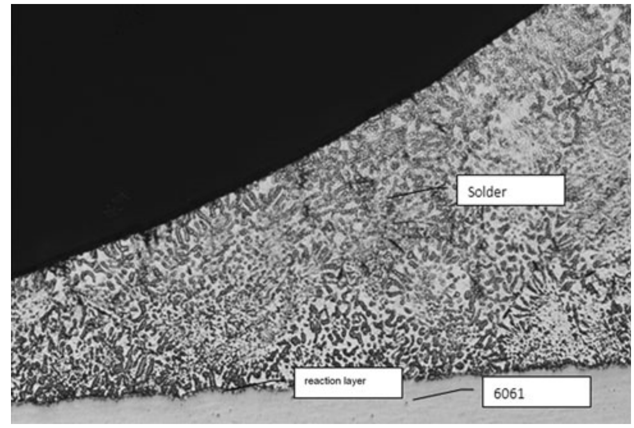

Fig. 4 The interface between the solder and the 6061 aluminum alloy

The authors think the reason for the wetting ring as following: when the temperature exceeds the solidus point, phase α can begin to extend all-around along base metal prior to the main solder part. Then the main solder part begins to flow along base metal and influx together with former. The un-merging zone can make up the precursor film, and because the phase α contains rich Pb, so the film is brittle (Ref 11). The wetting temperature is low, and the fluidity is almost the same, so the width of the ring is almost the same.

3.4 Microstructure of the Spread Specimen

Using the spread test specimen, the interface between the solder and the 6061 aluminum alloy was characterized. The OM image of the interface between the solder and the 6061 aluminum alloy at 553 K for 300 s was shown Fig. 4. The specimen was wet by the solder rightly. The interface between the solder and 6061 aluminum alloy was compact. It can be seen the reaction layer grew between the solder and the 6061 aluminum alloy. The primary crystal phase α was most near the interface. It was connected with the cooling velocity of the molten solder. The conductivity factor of the aluminum alloy is great. Heat transfer velocity of the solder was greater at the interface than that in other place of the solder. The primary crystal phase α can easily be found near the interface.

The solder at 553 K was invested by XRD layer-by-layer from the top of the solder to the 6061 aluminum alloy. Figure 5 shows the curve of the XRD. The curve 1 shows the phase near the 6061 aluminum alloy; the curve 2 shows the position slightly near the 6061 aluminum alloy; and the curve 3 shows the position near the solder. The result with three-layer structure of the XRD analysis is the same with the OM analysis. The Ag_2Al is formed at the surface of the 6061 aluminum alloy. Ag_2Al can improve the capacity of corrosion resistance.

4. Conclusions

A novel-type 63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi solder alloy was prepared. The spread test was performed to

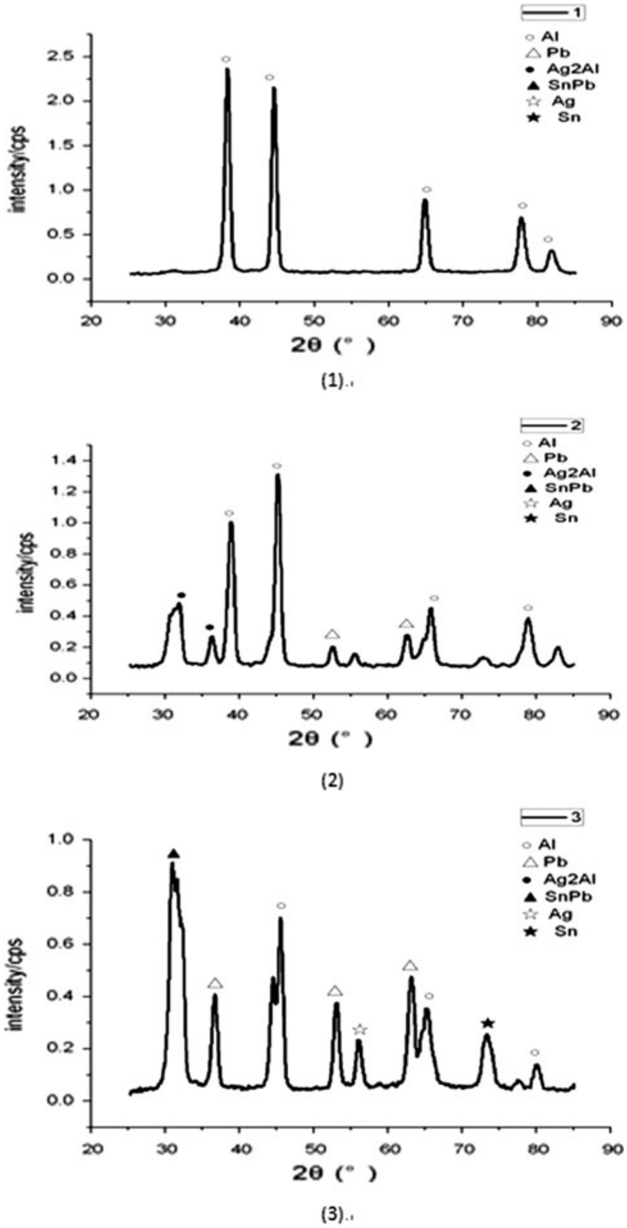

Fig. 5 XRD result of the wet specimen (a) XRD of the phase near the 6061 aluminum alloy; (b) XRD of the position slightly near the 6061 aluminum alloy; (c) XRD of the position near the solder

clarify the wetting behavior for 6061 aluminum alloy at low temperature and to characterize the interface between the solder and 6061 aluminum alloy. The main results were summarized as follows:

(1) Novel-type 63Sn-29.2Pb-6Zn-1Ag-0.38Cu-0.42Bi solder alloy could be prepared by a furnace with Ar. Its melting temperature range is 456.34-463.68 K, and the temperature interval between the solidus and the liquidus is 6.34 K. It is clear that the eutectic structure has formed.
(2) When the soldering temperature is in the range of 523-553 K, the solder alloy has a good wettability and wetting precursor appears, the main composition of the wetting ring is Pb.
(3) There is a diffusion layer between the solder alloy and the base metal. Thickness of the reaction layer was not related to the wet temperature. The layer was identified to be Ag_2Al by XRD.

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