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Influence of melt overheating on microstructure and soldering properties of SnBiCu solder alloy

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Abstract

The melt structure transition behaviors of $SnBi_{17}Cu_{0.5}$ solder alloy were investigated in detail. By Differential Scanning Calorimetry (DSC) and electrical resistivity method, an anomalous change has been found in 835–875 °C during heating process on the ρ-T and DSC curves. It reveals that a liquid-liquid structure change (LLSC) occurs in the melt. Through melt overheating treatment, the influence of LLSC on solidification process and material properties has been further studied: bigger solidification undercooling degree in the solidification process, finer and more dispersing solidification structure, and more importantly, the mechanical and welding properties of the solder alloy have also been obviously improved.

K e y w o r d s: melt structure, liquid structure change, $SnBi_{17}Cu_{0.5}$ solder, soldering property, solidification

1. Introduction

As we know, Pb-free is the primary trend of development for solder alloys, and the existing Pb-free solder alloys are still difficult to replace the traditional tin-lead solder alloys [1, 2]. How to further improve the soldering properties of Pb-free solder alloys, is the issue we currently faced. Up to now, except for alloying method usually used, few works have been focused on the melt structure state of solder alloys, and it is interesting to explore the influence of melt structure on the solidified microstructure and properties (especially for soldering properties) of solder alloys.

Recently, temperature-induced LLSC has been found in many binary alloys, e.g. PbSn, InSn, CuSn and SnBi [3–7]. Further works also reveal that the LLSC has significant impact on the solidification process and properties of alloys [8–12]. All of these studies promoted our knowledge about the nature of liquid structure and the correlation of liquid-solid. However, the research area of LLSC is mainly limited to some binary alloys, there are more works needed to be done extensively.

In this paper, by DSC and electrical resistivity method, the existence of LLSC has been investigated in $SnBi_{17}Cu_{0.5}$ ternary alloy (SBC1705), which is a kind of representative lead-free solder alloy [13]. Through melt overheating treatment, the correlation between melt structure and solidification has also been studied. Experimental results show that the LLSC has significant effect on the solidification process and solidified microstructure of $SnBi_{17}Cu_{0.5}$ alloy, and can obviously improve the mechanical and soldering properties. It will be a benefit to find a new way for further improving the mechanical and soldering properties of solder alloys.

2. Experimental procedures

The $SnBi_{17}Cu_{0.5}$ alloy samples were prepared with pure Sn (99.99 %), Bi (99.99 %) and Cu (99.99 %) granules. After being melted and held at 500 °C protected with N_2 for 30 min, the melts were poured into quartz crucibles for the following experiments.

As a structure sensitive physical quantity, the electrical resistivity (ρ) is sensitive to the liquid structural change. In order to explore the existence of LLSC in the $SnBi_{17}Cu_{0.5}$ solder alloy melt, the resistivity experiments have been carried out by DC four-probe

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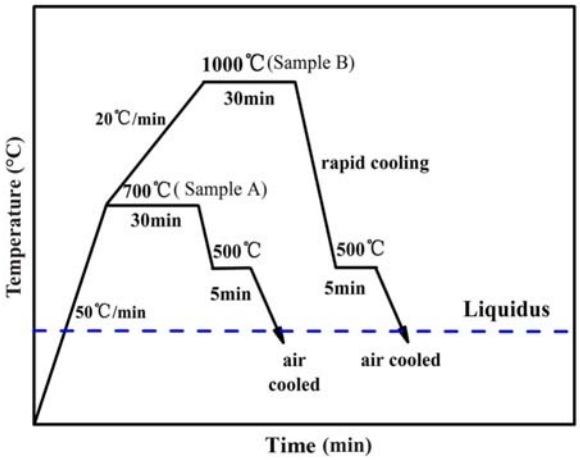

Fig. 1. Sketch of melt overheating treatment procedure of liquid $SnBi_{17}Cu_{0.5}$ alloys.

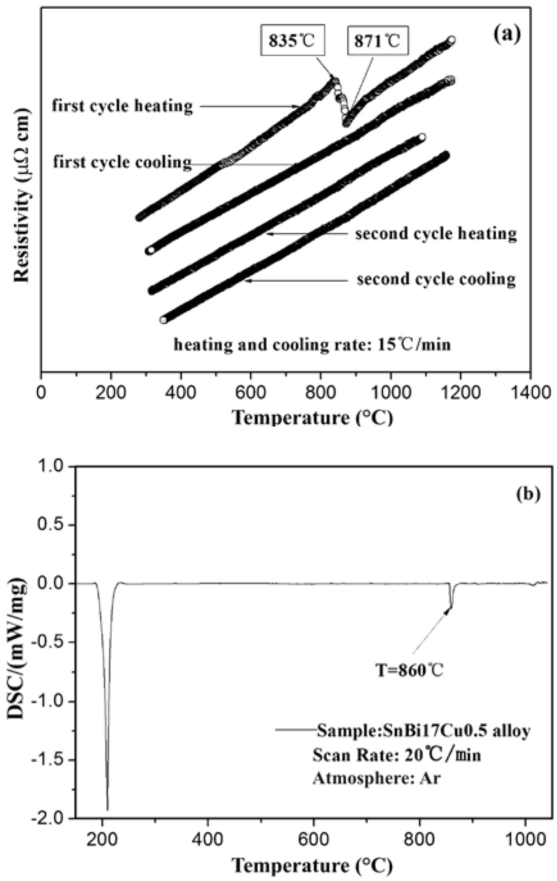

Fig. 2. The resistivity and DSC curves of $SnBi_{17}Cu_{0.5}$ alloy in heating and cooling process: (a) two cycles of heating and cooling resistivity curves, (b) DSC heating curve.

method during two cycles of heating and cooling process ranged from 0 to 1100 ℃, where the voltage is measured by KEITHLEY-2182 nanovoltmeter, and constant current of 500 mA is supplied by the PF66M sourcemeter. The details of the measuring method are the same as what we have described earlier [14]. In order to confirm the accuracy of the results obtained by the resistivity method, the DSC thermal analysis has also been adopted to study the LLSC in heating process by NETZSCH DSC 404 (the $SnBi_{17}Cu_{0.5}$ sample (50 mg) was held in Al_2O_3 ceramic crucibles, heating rate was 20 ℃ min^{-1}), because DSC is particularly suited to study discontinuous structure transitions [15].

The melt overheating treatment and solidification experiments have been done, the treatment procedure is as following Fig. 1. According to the anomalous change on the ρ-T and DSC curves in Fig. 2, the melt overheating temperatures are chosen as $T_1 \sim 700$ ℃ (before the starting temperature of LLSC) and $T_2 \sim 1000$ ℃ (after the final temperature of LLSC). Two completely identical samples were rapidly heated to T_1 and T_2 respectively, and held for 30 min. Prior to the pouring, the two melts were cooled down to the same temperature 500 ℃, and held for 5 min to eliminate the effect of sensible heat, and then casted into quartz crucibles or iron molds. During the air cooling procedure in quartz crucibles, the cooling curve of temperature versus time (T-t) was automatically recorded by a computer from a nanovoltmeter Keithley-2182 with a NiCr-NiSi thermocouple immersed in the specimen. The obtained treated and untreated samples have different melt thermal history and the same solidification thermal history for following comparative analysis. All the above experiments were carried out in purified argon media and under the shielding slag (B_2O_3, with thickness of 8–10 mm to avoid the evaporation and oxidation of metals).

Next, a series of experiments have been done to detect the influence of LLSC on microstructure and properties of $SnBi_{17}Cu_{0.5}$ solder alloy, such as the microscopic test of solidified samples and soldered joint (copper substrate), tensile test, wetting test by measuring the spreading area and wetting angle of samples (0.2 mg) on copper substrate.

3. Results and discussion

Figure 2a shows the ρ-T curves of $SnBi_{17}Cu_{0.5}$ alloy during two cycles of heating and cooling process. During first cycle heating process, the ρ-T curve increases linearly with temperature elevated just above the liquidus, while it changes abruptly from 835 to 871 ℃, and then increases linearly again after 871 ℃. Similar to the anomalous change on ρ-T curve, there exists an obvious endothermic peak between 850 and 875 ℃ on DSC curve (Fig. 2b). The difference between the two temperature ranges may be related to the different heating rates, or different measurements show the characters of different diffusion behaviors.

Many experimental and theoretical studies proved that the temperature and/or pressure induced LLSC might happen in some one-component and multiple--component liquids [16–19]. In our former works, by means of X-ray diffraction, we observed the occurrence of discontinuous structure changes in In-Sn melts directly [7]. In some other binary alloys, such as SnBi, SnCu alloys [20, 12], such a change has also been found by the electrical resistivity method and DSC experiments. So we have reason to believe that the abrupt change in Fig. 2 reveals a liquid structure change, which is an anomalous reconstruction process in the melt structure. But in the following cooling process of first cycle and heating or cooling process of second cycle, the anomalous change disappeared, which suggested that the LLSC was irreversible.

Now let us take a brief account of what is taking place during the LLSC reconstruction. It is known, for binary and multi-component molten alloys, the atomic bonds of crystals are only partly broken, and the melt structure is mainly composed by short range orders (SROs) inherited from solid structure and a few free atoms less than 10 % [21]. So the melt structure is microheterogeneous at the temperature not too far above the liquidus [22, 23]. Investigations of the high-temperature properties and SROs of the melts showed that their microheterogeneous states were metastable or non-equilibrium rather than thermodynamically stable [24]. With temperature increasing, the kinetic energy of the atoms increased correspondingly, and the energy barrier ΔE (mainly composed by atomic bonding forces) decreased with the increasing distance among atoms. When the temperature is heated up to a critical temperature of LLSC, the melt structure will gain enough energy to overcome the energy barrier ΔE, and the SROs either break up or disintegrate into smaller ones. The disordered melt becomes more homogeneous.

With the change of melt structure, the solidification process will also be affected, which can be seen clearly from the temperature-time (T-t) curves of treated and untreated samples both cooled from 500 ℃ in Fig. 3. Compared with untreated sample, treated sample has more apparent recalescence phenomenon and more latent heat of crystallization. The related solidification characteristic points are listed in Table 1, in which T_{L} and T_{e} denote the temperature of primary phase reaction and eutectic reaction, respectively, ΔT_{L} and ΔT_{e} are the undercooling degree of primary phase reaction and eutectic reaction, respectively. In addition, it is clear that ΔT_{L} and ΔT_{e} of treated sample are larger than those of untreated sample, which means that the melt structure transition increases the solidification undercooling degree and affects the solidification behavior remarkably.

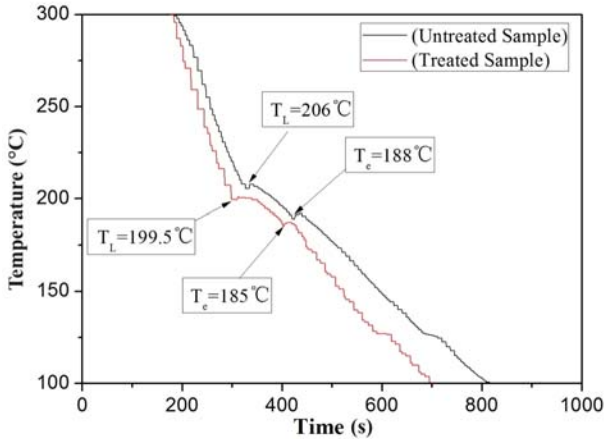

Fig. 3. The cooling curves of solidification process of $SnBi_{17}Cu_{0.5}$ alloys.

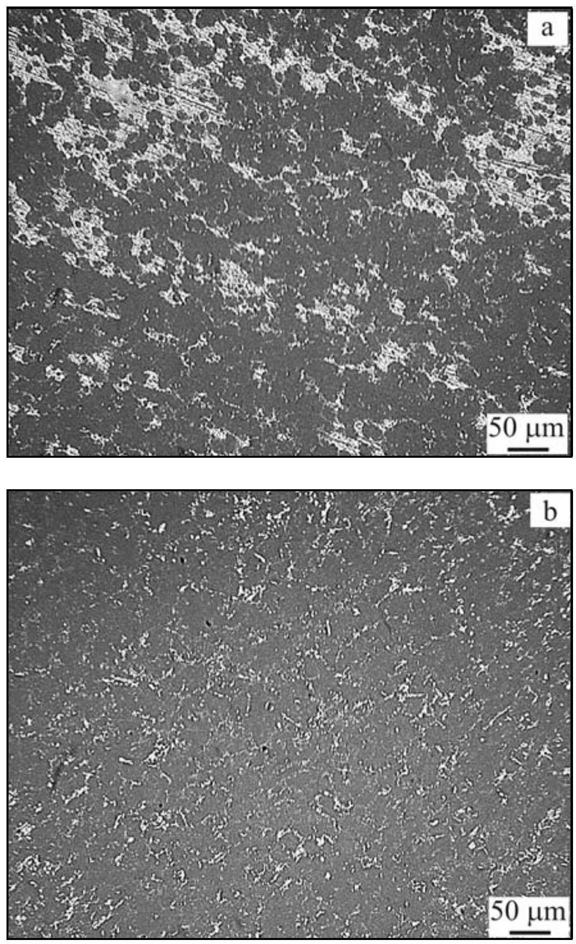

Fig. 4. Solidified microstructure of $SnBi_{17}Cu_{0.5}$ alloys: (a) untreated sample, (b) treated sample.

Figures 4a,b show solidified microstructure of untreated and treated samples, respectively. It can be observed that either the primary phase (mainly composed by white β-Sn phase and a few Cu_5Sn phase)

Table 1. Characteristic temperatures in cooling curves of $SnBi_{17}Cu_{0.5}$ alloys

Characteristic temperature (℃)	Temperature of equilibrium reaction (℃)	Untreated sample	Treated sample
T_L	209	206	199.5
ΔT_L		3	9.5
T_e	190	188	185
ΔT_e		2	5

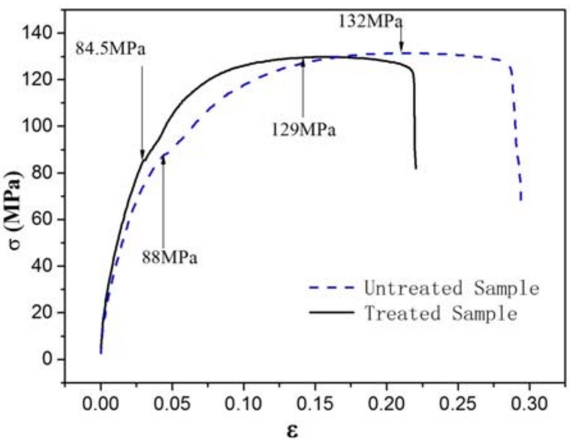

Fig. 5. Stress curves of $SnBi_{17}Cu_{0.5}$ alloys.

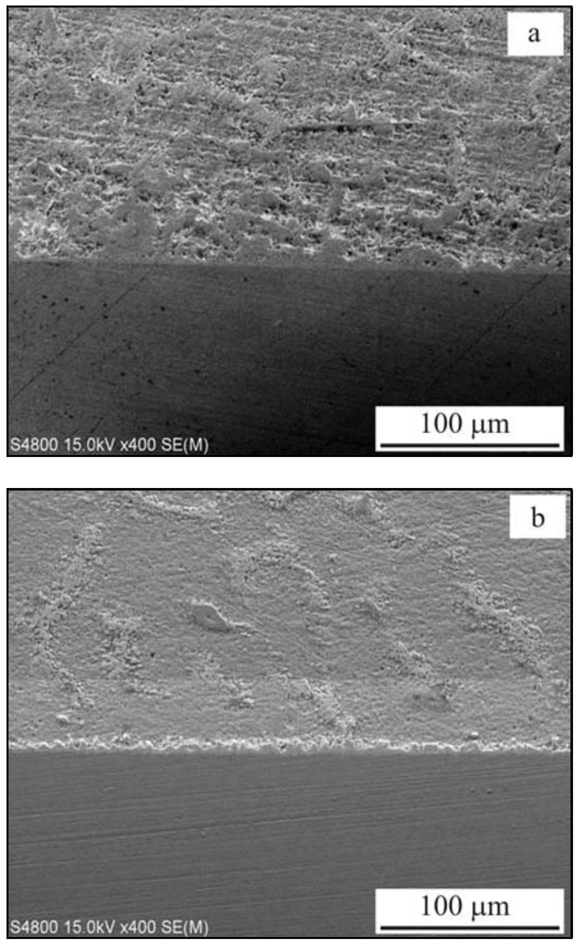

Fig. 6. The microscope of soldered joint (copper substrate): (a) untreated sample, (b) treated sample.

or the black eutectic phase of treated sample are evidently finer than those of untreated sample. Moreover, the shape of the primary phase changes from coarse flocculent structure into fine and dispersing fibrous structure.

Compared with treated sample, the melt of untreated sample has relatively big size SROs and the structure similarity between SROs and solid phase. So in solidification process, SROs of untreated melt can extend to the critical size of crystal nucleus under a low undercooling, and deposit on the sites of the corresponding solid crystal lattice more easily. However, when the melt underwent the irreversible LLSC, it is harder to nucleate because the smaller and more homogeneous SROs are distinct from solid phase, so it needs a larger undercooling to nucleate, and a higher nucleation rate I is obtained. According to the classical nucleation theory [25], with the increasing of undercooling, the critical crystal nucleus radius will also decrease, which means more SROs can reach or exceed the critical radius and become the stable nucleus. Either the increasing of the nucleation rate or the decreasing of the critical radius will lead to the finer solidification structure.

Tensile tests of treated and untreated samples under the same testing conditions were carried out and Fig. 5 shows different stress-strain curves. Compared with untreated sample, the strength parameters of treated sample (such as yield strength and tensile strength) have slightly increased, and the yield strain and tensile strain are improved about 53 and 50 %, respectively. Obviously, LLSC can effectively improve the mechanical properties of $SnBi_{17}Cu_{0.5}$ solder alloy, especially for the plastic property. It may be attributed to the refinement of the solidification structure.

In order to study the influence of LLSC on the soldering properties of $SnBi_{17}Cu_{0.5}$ alloy, the soldered joint was made according to the following steps. The treated and untreated samples (both 0.2 mg) were placed on copper substrate, covered with the same amount of rosin flux, then were rapidly heated to 240 ℃ and held for 60 s, finally cooled down to room temperature in air.

By the electron microscopy, the microstructures of

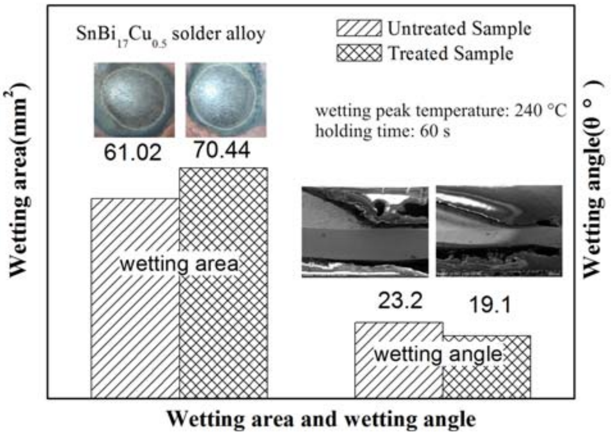

Fig. 7. The spreading area and wetting angle of $SnBi_{17}Cu_{0.5}$ solder alloys on copper substrate.

soldered joint are shown in Figs. 6a,b. Compared with untreated sample, the structure of treated sample is finer and more dispersing on the solder alloy side. It is consistent with the above description in Fig. 4. In addition, the weld seam in the soldered joint of treated sample is also thinner and smoother.

As an important soldering property, wettability has been studied by measuring the spreading area and wetting angle, shown in Fig. 7. Compared with untreated sample, treated sample shows better wettability with copper substrate: 15 % larger spreading area and 22 % smaller wetting angle. After preliminary analysis, we draw the following reasons.

During the molten process from crystal grain collapse to completely melt, the melting temperature range is closely related to the size and morphology of crystal grain. The refined crystal structure of treated sample means an increase of grain boundaries and surface area, which also means higher system free energy and lesser energy needed for crystal grain collapse and melt. So the treated solder alloy could melt at lower temperature range and with faster melting rate. In addition, because the size of SROs became smaller permanently after irreversible LLSC, and as all know that the smaller clusters size of melt, the smaller viscosity of melt, so the viscosity of treated melt is smaller than that of untreated melt, and it is more wetting and easier flow in the copper substrate under the same interface conditions. All these facts explain why and how LLSC can effectively improve the wettability of $SnBi_{17}Cu_{0.5}$ solder alloy.

5. Conclusions

Based on the results and discussions, the following conclusions were drawn:

1. The anomalous change on the ρ-T and DSC curves suggests that an irreversible temperature-induced LLSC occurs within temperature range of 835–875 ℃. The LLSC has significant effects on the solidification process and solidified microstructure of SnBi17Cu0.5 alloy: bigger solidification undercooling degree in the solidification process, finer and more dispersing solidification structure.

2. The melt overheating treatment obviously improved the mechanical properties of $SnBi_{17}Cu_{0.5}$ solder alloy, the yield strain and tensile strain are both improved about 53 % and 50 %, respectively. In addition, the welding properties also improved: 15 % larger spreading area and 22 % smaller wetting angle in wetting test, the more closely combined weld seam of the soldered joint. Using the theory of LLSC, the reasons of those phenomena have been explained.

Acknowledgements

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