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Microstructure and properties of Sn-3.8Ag-0.7Cu-xCe lead-free solders with liquid-liquid structure transition and Ce addition

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Abstract

Our previous work suggested that the Sn-3.8Ag-0.7Cu-xCe (x takes 0%, 0.2%, 0.5% and 1.0wt%) solder melt experienced a temperature-induced liquid-liquid structure transition (L-LST) which was reversible during two heating and cooling cycles far above the liquidus. In this work, the effects of liquid state manipulations and rare earth element Ce addition on solidified Sn-3.8Ag-0.7Cu-xCe structures and properties were investigated. The results revealed that the microstructure was remarkably refined, the spread ability and the shear strength were enhanced when the melt experienced L-LST and Ce addition. Meanwhile, 0.2 wt% Ce addition showed the most homogenous microstructure, leading to better properties. This work elicited that melt manipulations and Ce addition could be an effective way to optimize microstructure and properties of Sn-3.8Ag-0.7Cu-xCe soldered joints.

1. Introduction

Ideal solidified structures lead to a better performance for materials. Many researches have pursued this goal for decades. In order to get refined solidified crystals, various liquid manipulations like melt overheating [1, 2], melt thermal treatment [3, 4] have been applied and sometimes it appears effective. In the past, a lot of researchers explored the thermal history which had an important influence on the microstructure and properties of alloys. It has been found that the liquid-liquid structure transition (L-LST) existed in some liquids [5–7]. It has been demonstrated that temperature or pressure induced liquid structure transitions can occur in some melts of pure elements and alloys by means of *in situ* synchrotron radiation [8], neutron diffraction [9], viscosity [10], x-ray diffraction and internal friction [11], resistivity [12] and computer simulations [13] etc. The experiments proved that the microstructure of amorphous alloys was much more homogeneous if the alloy melts were much overheated. It was accepted that the structure transition was related to the metastable local short range orders (SROs) or covalent clusters remained in melts at temperature above the liquidus slightly [14].

Considering the inherent toxicity of lead and lead containing alloys to environment and human healthy, lead-free solders have been developed to respond the trend of lead-free electronic packing [15, 16]. SnAgCu lead-free solder with good thermal mechanical properties was regarded as one of the most promising candidates for the traditional Sn-Pb solder in electronic assembly. As rare elements (RE) have been called the vitamin of metals, some researchers studied the addition of pure RE like Eu [17], Sm [18], Yb [19], Pr [20], La [21], Nd [22], Ce [23] and mixed-RE [24, 25] to enhance the properties of SnAgCu lead-free solders and great achievements have been obtained.

In this article, the overheat temperature for melts was based on the result of our previous work [26], solidification experiment, spread ability test and shear strength test were conducted to investigate the effects of Ce and L-LST on microstructure and properties of Sn-3.8Ag-0.7Cu-xCe lead-free solder.

Table 1. Starting temperature and ending temperature of L-LST for Sn	ı-
3.8Ag-0.7Cu-xCe alloys.	

	Transition temperature(°C)		
Composition	Starting temperature	Ending temperature	
Sn-3.8Ag-0.7Cu	770 ± 2	960 ± 2	
Sn-3.8Ag- 0.7Cu-0.2Ce	762 ± 2	831 ± 2	
Sn-3.8Ag- 0.7Cu-0.5Ce	771 ± 2	988 ± 2	
Sn-3.8Ag- 0.7Cu-1.0Ce	601 ± 2	626 ± 2	

Table 2. Treatment temperature and time of solidification experiment.

Composition	Holding temperature and time		
	Group A	Group B	
Sn-3.8Ag-0.7Cu	$500 \ ^{\circ}\text{C} \times 40 \ \text{min}$	$1000 \ ^{\circ}\text{C} \times 30 \ \text{min} \rightarrow 500 \ ^{\circ}\text{C} \times 10 \ \text{min}$	
Sn-3.8Ag-0.7Cu-0.2Ce	500 $^{\circ}$ C \times 40 min	1000 °C \times 30 min \rightarrow 500 °C \times 10 min	
Sn-3.8Ag-0.7Cu-0.5Ce	500 $^{\circ}$ C \times 40 min	1000 °C \times 30 min \rightarrow 500 °C \times 10 min	
Sn-3.8Ag-0.7Cu-1.0Ce	500 °C \times 40 min	1000 °C \times 30 min \rightarrow 500 °C \times 10 min	

2. Experimental procedure

2.1. Solidification experiment

The Sn-3.8Ag-0.7Cu-xCe alloys were prepared by melting high purity granular Sn, Ag, Cu and Ce in a resistivity furnace. During melting, the melts were covered with shielding flux B₂O₃ to prevent the evaporation and oxidation of metals. The Sn-3.8Ag-0.7Cu-xCe melts experienced a temperature-induced L-LST which was reversible during two heating and cooling cycles far above the liquidus while the heating temperature was above the ending temperature [26]. The transition temperature was shown in table 1.

In this experiment, the holding temperature was shown in table 2 which was chosen according to table 1. Taking Sn-3.8Ag-0.7Cu as an example, the group A was heated to 500 °C with a dwelling time of 40 min. Group B was firstly heated to 1000 °C with a dwelling time of 30 min. Then, the melt was shifted expeditiously to a 500 °C furnace for 10 min to unify the purring condition. After heat treatment, the melts were poured into an iron mold. The specimens for microstructures were prepared by standard metallographic procedures with the etchant of FeCl₃ + HCl + H₂O solution and observed under optical microscope.

2.2. Spread ability test

Copper with a purity of 99.97 wt% was used as substrate, which was cut into the size of 40 mm \times 40 mm \times 2 mm. The Cu substrate was polished before cleaning with ethanol. The solder was cut into 0.2 \pm 0.0002 gram with the same diameter. Spread ability tests were conducted at 260 °C with a dwelling time of 120 s after melting in a resistance furnace. The activated rosin was used as flux. The same measurement conditions were applied to all samples for a reliable comparison of their wettability. Spreading area was measured to judge the wettability by Image Pro Plus assisted by Photoshop. Six specimens were made for each condition.

2.3. Tensile test

Several soldered joints were prepared by using the solidified solders as specimens for tensile test, the Cu plate as substrate. Dimensions of specimen for tensile testis were shown in figure 1. The average values of every tensile strength were estimated from 5 measurements.





3. Results and discussion

3.1. Solidification microstructure

The microstructures of Sn-3.8Ag-0.7Cu-xCe are represented in figure 2. It is worth pointing out that no obvious porosity/hole was observed in all the solidified samples. The microstructure of Sn-3.8Ag-0.7Cu-xCe consists of the light colored β -Sn phase surrounded by dark eutectic networks of β -Sn and inter metallics phase (Cu₆Sn₅ and Ag₃Sn) [27]. It can be clearly seen that, after the melts experienced L-LST, the microstructure of β -Sn is dramatically refined. It is generally accepted that lots of residual micro-clusters or shortrange orders (SROs) or covalent clusters still remain in the melt near liquidus [5–7]. These SROs are disrupted and dispersed into smaller clusters which could offer more nuclear sites, leading to a much homogenous microstructure. It can be





observed in figures 2(a), (c), (e) and (g), with 0.2 wt% Ce addition, coarse β -Sn grains are remarkably refined. It is known that the standard Gibbs free energy of formation of Sn-RE IMCs is lower than those for Ag-RE and Cu-RE [28]. Accordingly, in this work, Ce has a higher affinity for Sn, Ce atoms are more easily attach the growing interface of Sn, therefore, the growth steps were blocked and this explains the refinement of β -Sn. However, dendrites appear again as Ce addition reaches to 0.5 and 1%. It can be concluded that manipulating parent liquid state and Ce addition can be effective for optimizing materials solidified structures.

3.2. Wettability

The result of the spread ability testing of the solders is shown in figure 3. It can be seen from figure 3 that the wettability of solders is increased with Ce addition and after solder melts experienced liquid structure transition. After the melts experienced L-LST, the wetting area of Sn-3.8Ag-0.7Cu was increased by 5.78% and Sn-3.8Ag-0.7Cu-0.5Ce was increased by 1.32% compared with that no Ce addition. With 0.5 wt% Ce addition, the wetting area of Sn-3.8Ag-0.7Cu.

As shown in Figure 4, wettability can be represented by contact angle θ which is defined by the Young-Dupre equation [12],

$$\cos\theta = \frac{\gamma_{SF} - \gamma_{SL}}{\gamma_{LF}}$$

where γ_{SF} is the surface tensions of the substrate/flux; γ_{SL} is the surface tensions of the substrate/liquid solder interfacial area and γ_{LF} is the surface tensions of the liquid solder/flux. γ_{SF} can be regarded as a constant which is determined by same substrate and flux. According to the Ce–Cu binary alloy phase diagram, the interaction between Ce and Cu is very low when the temperature is below 300 °C [28]. Therefore, γ_{SL} , the surface tension of Cu substrate and solder, is impossible to reduce. That is to say, in such a situation, γ_{SF} and γ_{SL} are constants. γ_{LF} is determined by the property of the molten alloy. The melts which experienced L-LST are more disordered and



homogeneous than that not, which resulted in a more active state of atoms and smaller SROs, so the free energy is increased, which means that the solders would melt with less energy absorbed. For these two reasons, the wettability of solders is increased after melts experienced L-LST. Ce is a surface active element, so the surface tension of Sn-3.8Ag-0.7Cu-xCe melts is decreased with addition of Ce. However, more Ce-based intermetallic and dioxide is generated with increasing Ce addition, which would prevent molten alloy from spreading on the Cu substrate, and the wettability is decreased at last. The L-LST and Ce doping decreased γ_{LF} , and the contact angle θ is decreased, so the wettability is increased.

3.3. Shear strength

Figure 5 shows the shear strength of soldered joints fabricated by Sn-3.8Ag-0.7Cu-xCe solders before and after L-LST. It can be seen from figure 5, shear strength is enhanced by L-LST and Ce addition. Shear strength of Sn-3.8Ag-0.7Cu is 33.0 MPa. With 0.2 wt% Ce addition, the shear strength of Sn-3.8Ag-0.7Cu-0.2Ce reached 36.3 MPa, increased by 10%. When Ce content increased to 0.5 and 1.0 wt%, the shear strength decreased. Nevertheless, it is still better than that of no Ce addition. After the melts experienced L-LST, shear strength is increased about 3.0%-4.7%. One reason of this enhancement is the refinement of β -Sn. On the other hand, CeSn₃ tends to be absorbed at grain boundary and decrease boundary movement [29]. In addition, the strain field of large RE atoms and dislocations interact and restrain the movement of dislocations, thus increasing the tensile strength of a solder joint [28]. Excessive intermetallic compound growth in solder joints will significantly decrease the reliability of the joints [30], so when Ce addition Reached 0.5 and 1.0 wt%, shear strength was decreased.

4. Conclusions

Microstructure and properties of Sn-3.8Ag-0.7Cu-xCe lead-free solders with L-LST and Ce addition are investigated in this work. In the summary, the microstructure was refined by L-LST and Ce addition, leading to the enhancement of spread ability and shear strength of Sn-3.8Ag-0.7Cu-xCe lead-free solders. Consequently, this work confirmed that melts manipulations and Ce addition could be an effective way to optimize Sn-3.8Ag-0.7Cu-xCe lead-free solders microstructures and properties.

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