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Effect of Mixed Rare Earths on the Wetting Behavior and Interfacial Reaction between Sn-0.70Cu-0.05Ni Solder and Amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ Alloy

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Abstract. In order to explore the effect of addition of mixed rare earths (MRE) on the wetting behavior and interfacial reaction between Sn-0.70Cu-0.05Ni solder and amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ alloy, 0.25 wt.% percentage of the MRE, which are mainly elements La and Ce, were added into the solder. Results show it can refine the microstructure of the solder alloy, and there is limited change of melting temperature with the addition of MRE in the solder. The wettability of the solder on amorphous substrate is improved by adding 0.25 wt.% percentage of the MRE into Sn-0.70Cu-0.05Ni solder. Moreover, research results indicate that, with the increase of wetting temperature, the final equilibrium wetting angles of Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-0.25MRE on amorphous substrate decrease gradually, indicating the better wettability at the higher wetting temperature. In addition, with the increase of temperature, the distribution of intermetallic compound (IMC) $FeSn_2$ formed at the interface between the two solders and amorphous substrate is changed from discontinuous state to continuous state. The thickness of the interfacial IMC layer between solder and amorphous substrates reduced with the addition of MRE, indicating that the presence of 0.25 wt.% percentage of the MRE is effective in suppressing the growth of IMC layer.

1 Introduction

Due to excellent mechanical, physical and chemical properties, amorphous alloys are ideal materials for aviation and spacecraft structures owing to the high specific strength, which is vital in the field of aerospace[1]. However, at present, the critical sizes of amorphous alloys with excellent deformability prepared by fast cooling method are limited within millimeters, constraining their wide applications as engineering materials[2]. In order to overcome the size limitation and spread their applications, it is necessary to explore appropriate joining techniques to obtain larger size amorphous alloys. As a low temperature joining process, soldering is an effective and reliable technique because of the advantage of little influence on the structure of amorphous alloys. In addition, the good wettability and interfacial reaction of solders on the amorphous alloys are prerequisites for the high soldering reliability. Therefore, the research on the wetting behavior and the interfacial reaction between solders and amorphous alloys are of great significance.

Owing to environmental and legal issues of using Pb in electronic packaging, large quantities of investigations have been carried out on lead-free solders for the substitutes of Sn-Pb solder[3]. Among the lead-free solders, SnCuNi solder is widely used in wave soldering process because of its cheapness. However, the physical properties and wetting ability of SnCuNi are lower than those of the traditional Sn-Pb solder[4]. Moreover, rare earth (RE) elements, which are called the “vitamin”of metals, can greatly enhance the mechanical and physical properties of metals. In addition, several researchers have reported that the addition of rare earth Ce or La+Ce into lead-free solders can obviously refine microstructures and improve mechanical properties[5,6]. Further, the wettability and interfacial reaction of solders with rare earth addition on the copper substrate have been widely studied[4,5]. However, thus far, the effects of the addition of RE elements on the wettability and interfacial reaction between the lead-free solders and the Fe-based amorphous alloy substrates are seldom discussed.

In this study, the mixed rare earth (MRE) elements La and Ce were selected as additives added into Sn-0.70Cu-0.05Ni lead-free solder. The purpose of the current research is to investigate the effects of trace amounts of MRE on microstructure evolution, melting property, wetting behavior and interfacial microstructure of Sn-0.7Cu-0.05Ni solder on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate.

2 Experimental procedure

In this study, the raw materials used for this study are Sn, Cu, Ni (purity 99.9%) and MRE (with about 60% Ce and about 40% La). First, Cu-RE master alloy was melted in an electronic resistance furnace at 500 ℃ for two hours. Second, the master alloy and suitable weights of other metals (Sn, Cu and Ni) were mixed together and melted under the same conditions to prepare Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-0.25MRE solders. A stainless steel rod was used to stir the liquid solder every 10 min to ensure the uniformity of solder. In order to prevent oxidation during the melting, KCl + LiCl molten salt with the mass ratio of 1:1.3 was used to cover the surface of the liquid solder. In order to measure and analyze thermodynamic parameters of the amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ alloy and the two solders, DSC (NETZSCH STA 449C) measurements were carried out at the heating rate of 20 K min^{-1} in the Ar atmosphere. The structures of the amorphous samples were examined by X-ray diffraction (D8 ADVANCE, Germany) with Cu Kα radiation. The XRD patterns and DSC curves of amorphous substrate are shown in Fig. 1. Fig. 1(a) presents that no crystalline peak is visible, which indicates that the substrate was in the amorphous state. There are two successive exothermic events in the crystallization process with peak temperatures about 515 ℃ (T_{p1}) and 555 ℃ (T_{p2}). Meanwhile, the glass transition temperature is about 488 ℃ (T_g), and the starting temperature of the crystallization is about 511 ℃ (T_x), as shown in Figure 1(b).

The wetting experiments of solders on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrates were carried out by the sessile drop method using Dataphysics OCA-20 in the N_2 atmosphere. The solder samples were made into small balls and cleaned ultrasonically together with amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrates in the acetone. The solders with an activated flux were placed on the center of the amorphous substrates placed into stainless-steel chamber. Then, the chamber was heated to 250 ℃, 300 ℃, 350 ℃ and 400 ℃, respectively, to investigate the wetting behavior between the solders and amorphous substrates. The drop profiles were recorded by a high resolution charge-coupled- device camera and analyzed by a drop-analysis program to record the variation of contact angles with time and calculate the final equilibrium contact angle. The wetting process was held for 30 min and then the samples were air-cooled by taking them out from chamber. The solidified samples were sectioned to examine the interfaces between solders and amorphous substrates. The interfacial microstructure and the chemical composition of interface compounds were identified using the scanning electron microscope (SEM, SUPRA 55V) equipped with energy diffraction spectrum (EDS).

3 Results and Discussion

3.1. Melting Temperature of Solders.

The initial point of the DSC heating curve is recognized as the solidus temperature while the peak point is considered to be the liquidus temperature of solders[7]. Fig.2 shows the solidus temperature and liquidus temperature of Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-MRE solders. Clearly, the solidus temperature and liquidus temperature decrease slightly with the addition of 0.25 wt.% MRE. The liquidus temperature ranges from 230.66 to 231.29 ℃, while the solidus temperature is between 228.85 and 227.56 ℃. It can be concluded that the addition of MRE has a slight influence on the melting temperature of Sn-0.70Cu-0.05Ni solder.

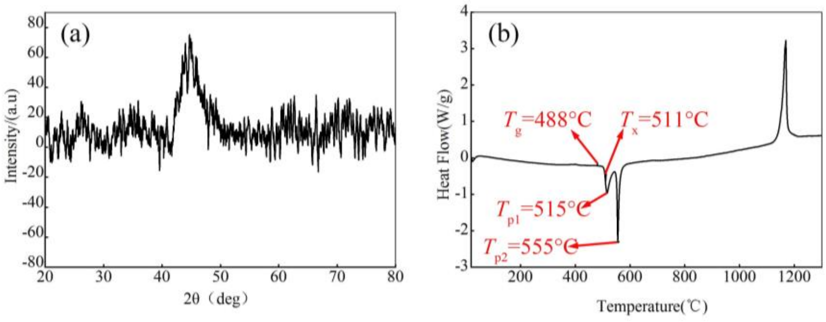

Figure 1. XRD patterns (a) and DSC curve (b) of amorphous substrate.

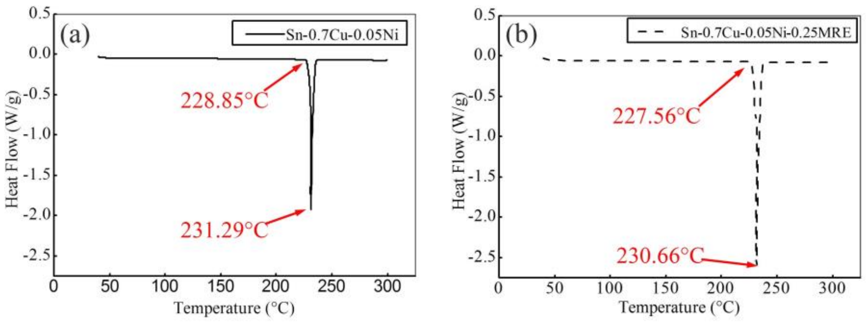

Figure 2. DSC curves of Sn-0.70Cu-0.05Ni (a) and Sn-0.70Cu-0.05Ni-MRE (b).

3.2 Microstructure of the Solders

Figure 3 is the typical optical microscope (OM) photograph of the as-solidified Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-MRE solders, and there are three regions: the light-colored regions, which are pure β-Sn grains; the gray regions, which is eutectic network band containing both β-Sn and $(Cu,Ni)_6Sn_5$ phases and surround the light-colored regions, and the dark-colored regions, which is mainly $(Cu,Ni)_6Sn_5$. With the addition of 0.25 % MRE elements, intermetallic compounds $(Cu,Ni)_6Sn_5$ grains have been transformed into smaller grains, and refine the microstructure of the solder alloy[8].

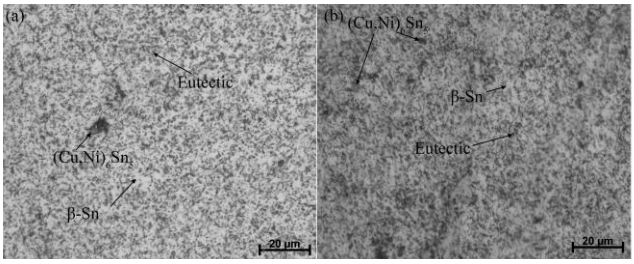

Figure 3. The typical OM photograph of the as-solidified Sn-0.70Cu-0.05Ni (a) and Sn-0.70Cu-0.05Ni-MRE(b) solders.

3.3 Wetting Behavior

Figure 4 shows the variations of contact angles with time and the final equilibrium contact angles for Sn-0.70Cu-0.05Ni solder on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate at 250 °C, 300 °C, 350 °C and 400 °C, respectively. Apparently, the initial contact angle is the largest when the solder is melted completely (i.e., 0 s), then it decreases gradually and finally keeps equilibrium state. The final equilibrium contact angle for Sn-0.70Cu-0.05Ni solder on substrate gradually decreases with the increase of wetting temperature, see Fig. 4(b). Similarly, the wettability of Sn-0.70Cu-0.05Ni-MRE solder on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate also follows the rules. The wettability can be measured by the contact angle determined by the Young equation as follows:

$$\cos\theta = \left(\sigma_{sg} - \sigma_{sl}\right) / \sigma_{lg} \qquad (1)$$

where σ_{sg}, σ_{lg} , and σ_{sl} refer to the surface tensions of the solid-gas, liquid-gas and solid-liquid interfaces, respectively. The smaller contact angle (i.e. smaller σ_{lg}, σ_{sl} and larger σ_{sg}), the better the wettability. On the one hand, with the increase of wetting temperature, the surface tension of solder (σ_{lg}) is gradually decreased, resulting in the decrease of contact angle (θ), and the wettability becomes better. On the other hand, the activity and diffusion capacity of Fe atoms in amorphous alloy substrate and Sn atoms in solder gradually increased, inducing the formation of interfacial intermetallic compound, thus further promoting wetting process and improving wettability.

Figure 5 shows the curves of variations of contact angles with different time at 250 °C and the final equilibrium contact angles at different temperatures for Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-MRE solders on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate. Clearly, the final equilibrium contact angle of Sn-0.70Cu-0.05Ni solder on amorphous substrate is larger than that of Sn-0.70Cu-0.05Ni-MRE solder at the same wetting temperature. Meanwhile, the final equilibrium contact angle can be reduced obviously with the addition of MRE. It can be concluded that the wettability of Sn-0.70Cu-0.05Ni are improved by adding 0.25 wt.% MRE elements.

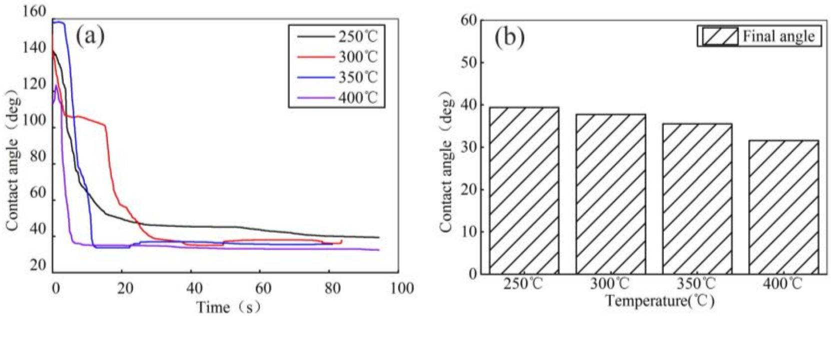

Figure 4. Wetting curves for Sn-0.70Cu-0.05Ni solder on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate at different temperatures: (a) variations of contact angles vs time; (b) final equilibrium contact angles vs temperatures.

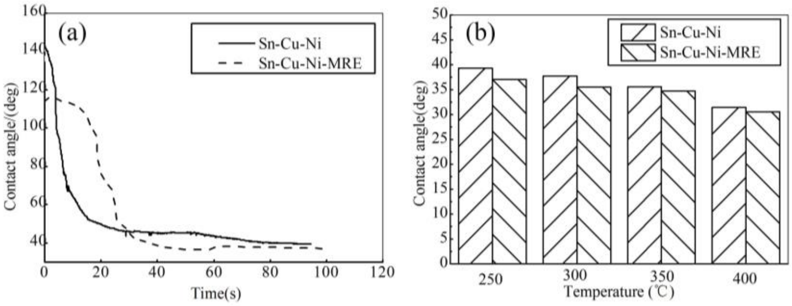

Figure 5. Wetting curves for Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-MRE solders on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate: (a) contact angles vs time at 250 ℃; (b) final equilibrium contact angles vs temperatures.

The improvement of wetting obtained by adding 0.25 wt.% MRE elements can be explained by the effects of MRE on the interfacial tensions. It is easier for MRE to accumulate at the solder interface in the molten state due to the high reactivity. Thus, MRE reduce the interfacial tension of molten solder effectively. According to Eq. (1), the decrease of σ_{lg} is beneficial for obtaining a smaller contact angle, resulting in improving wetting quality after the addition of MRE[9].

3.4 Interfacial Characteristics

Figure 6 presents SEM micrographs at the center of interface between Sn-0.7Cu-0.05Ni solder and amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate after wetting at different temperatures for 30 min. Clearly, thin-layer intermetallic compounds discontinuously distribute at the interface between Sn-0.7Cu-0.05Ni solder and amorphous substrate wetting at 250 °C and 300 °C. However, a continuous compound layer is formed at the interface when the wetting temperature rises to 350 °C and 400 °C, and there are intermetallic compounds in block state inside the solder close to the interface. Accordingly, with the temperature is increased from 250 °C to 450 °C, the intermetallic compound distributed at the interface between Sn-0.7Cu-0.05Ni solder and amorphous substrate is changed from discontinuous to continuous distribution. It can be concluded that the interfacial reaction between Sn-0.7Cu-0.05Ni solder and amorphous substrate becomes more and more intense with the increase of wetting temperature. EDS analysis shows that the big block of intermetallic compounds containing Sn and Fe formed at the interface and in the solder near the interface, and the ratio of atomic percentage of Sn and Fe is about 2:1, as shown in the Table 1. According to the Sn-Fe phase diagram[10], it is believed that $FeSn_2$ is formed at the interface for the wetting tests performed at 400 °C[11].

For Sn-0.7Cu-0.05Ni-MRE, a similar phenomenon can also be clearly observed that big block of intermetallic compounds $FeSn_2$ are formed forms at the interface and in the solder closing to the interface when wetting at 400 °C, both consist of Sn and Fe, and the atomic percentage is about 2:1, as shown in the Table 1, and intermetallic compounds $FeSn_2$ at the interface are changed from discontinuous to continuous state with the increase of wetting temperature, see Fig. 7.

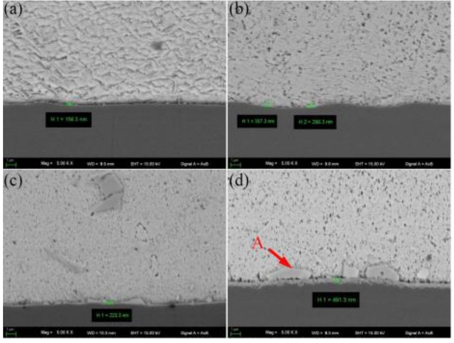

Figure 6. SEM micrographs at the center of interface between molten Sn-0.7Cu-0.05Ni and amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate after wetting at different temperatures for 30 min: (a) 250 ℃; (b) 300 ℃; (c) 350 ℃; and (d) 400 ℃.

It is found that the thickness of the interfacial intermetallic compounds is reduced by adding MRE. Especially when wetting at 350 °C, the intermetallic compounds are distributed continuously at the interface between Sn-0.7Cu-0.05Ni solder and amorphous substrate, while the interfacial intermetallic compounds are in discontinuous state with the addition of MRE. It is concluded that the growth of interfacial intermetallic compounds is inhibited with the presence of MRE.

The thickness of the interfacial intermetallic compounds $FeSn_2$ reduced by adding MRE elements is attributable to the fact that La and Ce have higher affinity for Sn[12]. It will lead to a reduction in the activity of Fe with Sn due to the formation of Sn-MRE compound, thus depressing the growth of the $FeSn_2$.

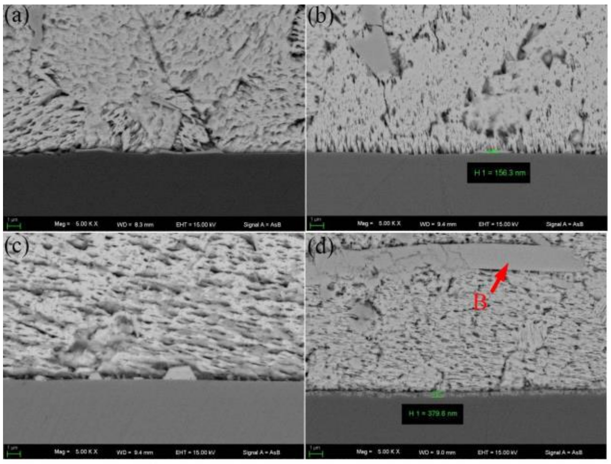

Figure 7. SEM micrographs at the center of interface between Sn-0.7Cu-0.05Ni-MRE solder and amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate after wetting at different temperatures for 30 min: (a) 250 ℃; (b) 300 ℃; (c) 350 ℃; (d) 400 ℃.

Table 1. EDS analysis of points marked in Fig.6 and Fig.7

	Sn (%)	Fe (%)	Si (%)
A	63.60	33.41	2.99
B	68.44	31.56	-

4 Summary

The solidus temperature and liquidus temperature decrease slightly with the addition of 0.25 wt.% MRE. The final equilibrium contact angle for both Sn-0.70Cu-0.05Ni and Sn-0.70Cu-0.05Ni-0.25MRE solder on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate gradually decreases with the increase of wetting temperature. With the increase of wetting temperature, the intermetallic compounds $FeSn_2$ distributed at the interface are changed from discontinuous to continuous state. The wettability of Sn-0.70Cu-0.05Ni on amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate is improved by adding 0.25 wt.% MRE elements. The presence of 0.25 wt.% percentage of the MRE is effective in preventing the growth of the intermetallic compounds $FeSn_2$ formed at the interface between solders and amorphous $Fe_{84.3}Si_{10.3}B_{5.4}$ substrate, results in a decrease in the thickness of the interfacial intermetallic compounds by adding MRE.

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