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Influence of Ultrasonic Vibration Power on the Wettability and Interfacial Microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni Solder Alloy on Cu Substrate

Di Zhao[1], Keke Zhang[1,2,3,*], Jianguo Cui[1] and Chenxiang Yin[1]

[1]School of Materials Science & Engineering, Henan University of Science and Technology, Louyang, China
[2]Henan Province Key Laboratory of Nonferrous Metal Material Science and Processing Technology, Luoyang, China
[3]Collaborative Innovation Center of Non-ferrous Metals, Luoyang, China
*Corresponding author: Tel.: 86-0379-64276880; E-mail: zhkekekd@163.com

Abstract. The effect of ultrasonic vibration (USV) power on the wettability and interfacial microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy on Cu substrate were investigated during the fluxless wetting process. Results showed that the wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy improved with USV assisted. With the increasing of USV power, the wetting angle decreased and corresponding the spreading area and spreading ratio increased. A wetting angle minimum of 24.5°, the spreading area and spreading ratio maximum of 51.3 mm^2, 62.1%, respectively, were obtained from the solder sample treated with 100 W. The wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy on Cu substrate was better with the USV assisted compared to the commercial Sn3.0Ag0.5Cu solder alloy (SAC305). Additionally, with the increasing of USV power, the microstructure of wetting interfacial intermetallic compounds (IMCs) was refined, and the average thickness, roughness and grain size of the interfacial IMC decreased. When the USV power increased to 130 W, the thickness, roughness and $(Cu,Ni)_6Sn_5$ grain size of the wetting interfacial IMC decreased by 58.7%, 51.6%, and 35.1%, respectively.

1. Introduction

SnPb solder alloys were primarily used for the microelectronic manufacturing and board level packaging for a long time due to their excellent wettability properties on most of the substrate materials and good mechanical properties [1]. However, because of the inherent toxicity of Pb, the element Pb commonly used in the electronic packages has been restricted in many countries [2]. Thus, more and more attention has been focused on lead-free solder alloys. Among the various lead-free solder alloys, Sn-Ag-Cu system solder alloys, especially Sn-Ag-Cu-RE lead-free solder alloys, have a widely application, which has been regarded as one of the most substitutes of SnPb solder alloys owing to the good mechanical properties [3], while the wettability of Sn-Ag-Cu system solder alloys was inadequate comparing to SnPb solder alloys. In addition, with the high density and power of the electronic packages, especially the solder joints are subjected to severe application conditions, the wettability of Sn-Ag-Cu system solder alloys is still required for further improvement. Fluxs have been used to improve the wettability of lead-free solder alloys. However, some fluxs contains corrosive substances, and residual flux can corrode circuit boards. Therefore, seeking new methods to improve the wettability of lead-free solder alloys is still in progress.

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Nowadays, some researchers have found that the ultrasonic vibration assisted soldering process can be realized. Yan and his co-workers [4, 5] have investigated the spreading behavior of Zn-Al solder alloys on the surface of aluminum matrix composites. It was found that the ultrasonic cavitation can remove the interfacial oxide film, which was facilitated to the spreading of solder. Li and his team [6] adopted *in-situ* investigation of mechanism of ultrasonic in liquid metal medium by high-speed photograph. They found that the ultrasonic vibration promoted the interfacial wetting in the soldering process. Zhao et al [7] have studied the combine effect of ultrasonic vibration and electric field on the wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloys on Cu substrate. Results showed that the wetting angle decreased 18% and the spreading area increased 20.4% under the ultrasonic vibration and electric assisted. However, there were fewer reports related to the wettability of the lead-free solder alloys with USV assisted. Therefore, in the present work, we adopted the USV during the wetting process and investigated the influence of USV power on the wettability and interfacial microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloys on Cu substrate. This will promote a new approach for lead-free soldering under the condition of halogen-free flux.

2. Materials and methods

2.1 Preparation of the materials

The pure Sn, Ag, Cu, Ni (purity 99.9 %) and mixture RE (with 40% Ce and 60% La) were used as the raw materials. Firstly, the Cu-RE inter-alloy was fabricated in non-consumable melting furnace (type ZHW-600A) at the vacuum 5×10^{-3} Pa. Then the Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy was prepared under the same conditions with the suitable quantity Sn, Ag, Cu and Ni. The wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy experiment on Cu substrate was processed according to the requirement of Chinese National Standard GB 11364-2008 (solder spread-ability and caulking test method). Place 0.20 ±0.01 g weight solder alloy in the center of Cu substrate with the dimension $40\times40\times2$ mm, and then covered with a commercial no-clean flux. The samples were placed in the electric chamber furnace and heated at ambient atmosphere. Figure 1 shows the scheme of the USV assisted wetting process. When the electric chamber furnace temperature reached 270 ℃, the ultrasonic horn was loaded on the Cu substrate and applied 60 s vertical vibration with the different USV power of 0 W, 40 W, 70 W and 100 W. Then the wetting sample was cooled down to room temperature.

2.2 Characterization methods

The Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy spreads on the Cu substrate, forming a dome-shape spreading after solidification as indicated in the wetting schematic figure 2. The wetting angle, spreading area, diameter of the spreading area (*D*) and the height of solder after spreading(*H*) on the substrate surface measured by Auto CAD software. The spreading ratio (*K*) was calculated by the equation (1). To determine the roughness of the IMC, the deviation of the peaks and troughs of the interface from the mean surface level (MSL) were measured as shown in figure 3. The total area of the interfacial IMC layers (*A*) and the length of the coverage (*L*) were measured by image analysis software. The average IMC thickness (*d*) was calculated using equation (2). The roughness (R_{rms}) of the wetting interfacial IMC was determined by the equation (3) [8]. In order to reduce measurement error, five random measurement places were selected and the final result was expressed as the average of these measurements.

$$K = \frac{D - h}{D} \times 100\% \tag{1}$$

$$d = \frac{A}{L} \tag{2}$$

The root mean square roughness (R_{rms}) was calculated by the equation (3), in which the Z_i was the deviation of the peaks and troughs of the interface from the average thickness of the IMC and *N* was the data number of Z_i.

$$R_{\mathrm{rms}} = \sqrt{\frac{\sum_{i=1}^{N} Z_i^{\,2}}{N}} \tag{3}$$

The wetting samples were cross-sectioned and grinded, polished. All the samples were etched with 4% HCl-96% ethanol solution. The microstructures and phases compositions of the wetting samples were analyzed by JMS-5610LV scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) and D8-ADVANCE X-ray diffractometer (XRD) with an accelerating voltage of 40 kV, a current of 40 mA and a scanning range of 25 °-80 °, respectively. In order to observe the top view of the interfacial IMC, the deep etching with 20% HCl-80% ethanol solution removed β-Sn from solder sample surfaces to expose the interface.

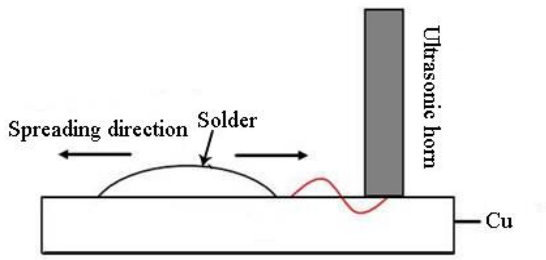


Figure 1. Schematic of USV assisted wetting process

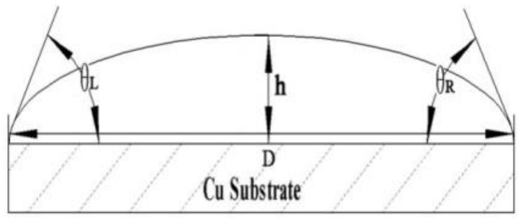


Figure 2. Schematic of wetting on the Cu substrate

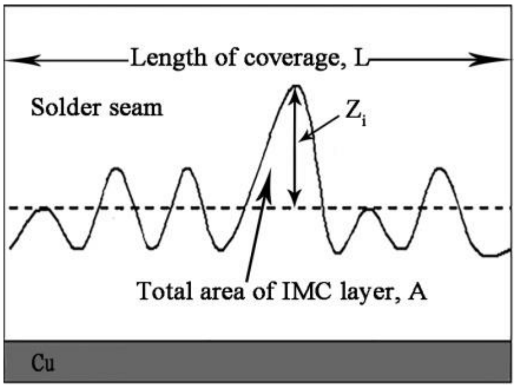


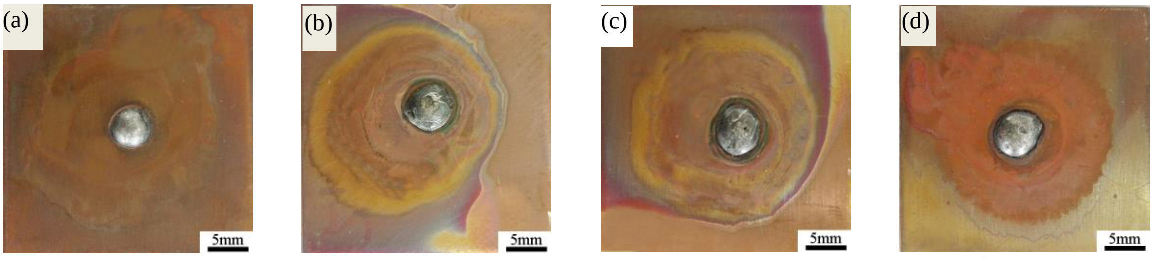
Figure 3. Schematic diagram of interfacial IMC Thickness and R_{rms}

3. Results and discussion

3.1. Wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy on Cu substrate with various USV power

A good wettability of Sn2.50.7Cu0.1RE0.05Ni on Cu substrate is very vital to obtain the high reliability interconnection. Figure 4 displays the typical appearances of spreading samples under different USV powers. It can be seen that the spreading samples shown circular shape. In comparison to the control sample without treated USV, we can see that the spreading area of the samples with the USV assisted were larger than that the control sample. Additionally, the sample treated with 100 W displayed the largest spreading area among the four samples. At the same time, it can be found that the surface of the control sample appeared uneven shape, while the surface of the samples shows brightness and smoothness with the USV assisted.

Figure 5 shows the wetting angle, spreading area and spreading ratio as a function of USV power. It was obvious that the spreading area and spreading ratio increased, while the wetting angle decreased with the increasing of USV power. The wetting angle decreased by 14.7 °, correspondingly, the spreading area and spreading ratio increased by 15.9 mm2, 14.6%, respectively. A wetting angle minimum of 24.5°, the spreading area and spreading ratio maximum of 51.3 mm2, 62.1%, respectively, were obtained from the solder sample treated with 100 W. This was ascribed to the acoustic cavitation effect induced by application USV assisted during the wetting process. When the USV was applied in the wetting process, the acoustic cavitation may occur and induce many tiny bubbles in the melted solder alloys. These collapsed bubbles may reduce the surface interface energy and remove the oxidation film of the molten solder alloys [9]. Additionally, the spreading area and spreading ratio of Sn2.5Ag0.7Cu0.1RE0.05Ni with the USV assisted was higher than that of the commercial Sn3.0Ag0.5Cu (SAC305) solder alloys. The wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni with the USV assisted satisfied the requirements of microelectronic connection for lead-free solder spreading characteristic.



(a) 0 W (b) 40 W (c) 70 W (d) 100 W

Figure 4. Wetting samples of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloys on Cu sbustrate

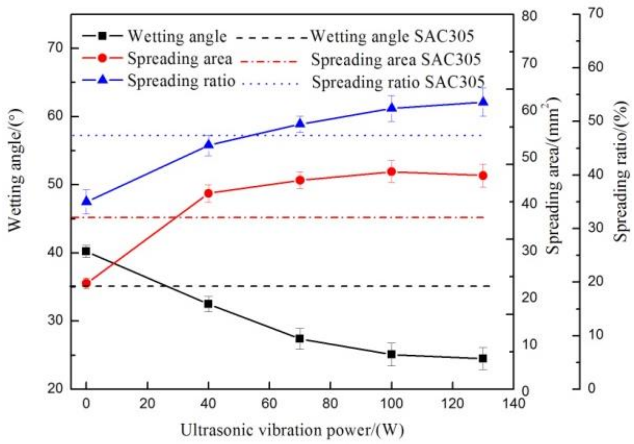


Figure 5. Wettability of solder alloys spreads on the Cu substrate

3.2. Interfacial microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy wetting on Cu substrate with various USV power

Figure 6 shows the microstructures of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu wetting interface under different USV power. It can be seen that the wetting interface was mainly composed of scallop shape IMC, which confirmed to be $(Cu, Ni)_6Sn_5$ by EDS analysis results (table 1). This was due to the fact that Ni and Cu atoms possessed the same crystal structure (with face-centered cubic structure), and the atomic radius of Cu (0.128 nm) was very close to that of Ni (0.125 nm). Thus, partial Ni atoms in the solder melting process substituted Cu atoms in Cu_6Sn_5 and occupy Cu sites in the IMC lattice [10]. It can be seen that the wetting interface IMC was uneven without ultrasonic vibration assisted. In addition, some micro-holes appeared in the local scallop type IMC. With the increasing USV power, the wetting interface IMC became flatter. This may be ascribed to the ultrasonic cavitation increasing the nucleation rate and certainly decreasing the grain size [11-13].

Figure 6(a_1-d_1) displays the top view of the wetting interfacial IMC layer. Cobblestone-type grains with the size of 3-5 μm can be seen in figure 6(a_1-d_1), which was in accordance with the scallop shape

IMC in figure 6(a-d). To determine what these cobblestone-type grains, the XRD analysis was conducted on the sample under the 100 W USV assisted (figure 7). In addition to Cu peaks which clearly belong to Cu substrate below those cobblestone-type grains, the $(Cu,Ni)_6Sn_5$, Cu_3Sn, and Ag_3Sn peaks were found according to the XRD analysis results. Both $(Cu,Ni)_6Sn_5$ and Cu_3Sn were products of reactions between solder and Cu. Because of the peak intensities of $(Cu,Ni)_6Sn_5$ was much higher than that Cu_3Sn, most of cobblestones grains were $(Cu,Ni)_6Sn_5$. This was consistent with the EDS analysis result of the point "A" in figure 6(a). The average size of $(Cu,Ni)_6Sn_5$ grains decreased from 3.7 μm to 2.4 μm with the increase of ultrasonic power. Additionally, it was observed that some nanoscal particles was absorbed in the $(Cu,Ni)_6Sn_5$ grains, which was confirmed to be Ag_3Sn particles by EDS analysis result of the point "B" in table 1.

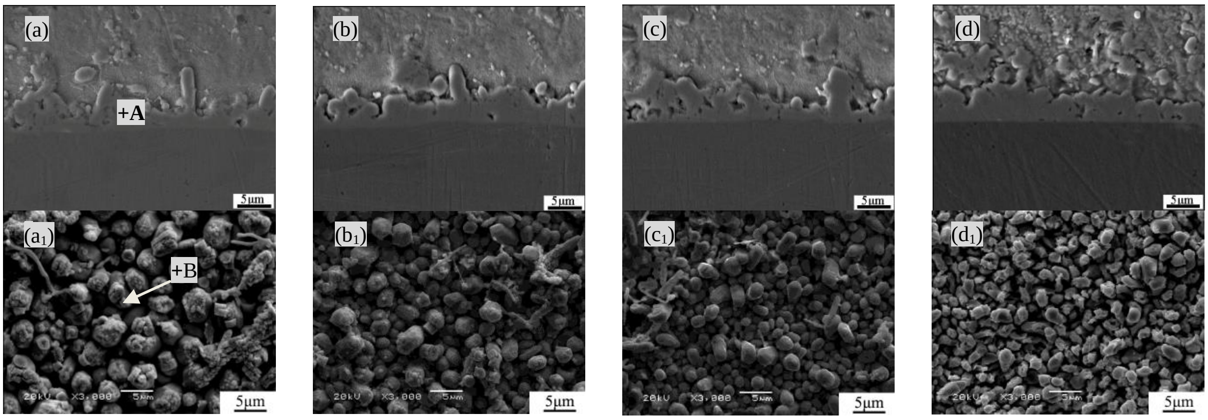


Figure 6. Cross section micrographs of wetting interface (a-d) and top surface morphology (a_1-d_1) of interfacial IMC treated with USV powers of (a) 0 W, (b) 40 W, (c) 70 W, (d) 100 W

Table 1. EDS analysis results of the wetting interface point "A" and "B" shown in figure 6(a) and figure 6(a_1)

Point	Mole fraction/ %			
	Sn	Cu	Ni	Ag
A	43.34	54.21	2.45	-
B	24.71	3.94	-	72.35

The thickness and morphology of wetting interfacial IMC have significantly effect on the mechanical properties of solder joints. Figure 8 shows the roughness and thickness of wetting interfacial IMC at varied USV powers. It was obvious that the roughness and thickness of wetting interfacial IMC decreased with the increased of USV powers. When the USV power increased to 100 W, the roughness and thickness decreased by 4.49 μm and 1.7 μm, respectively.

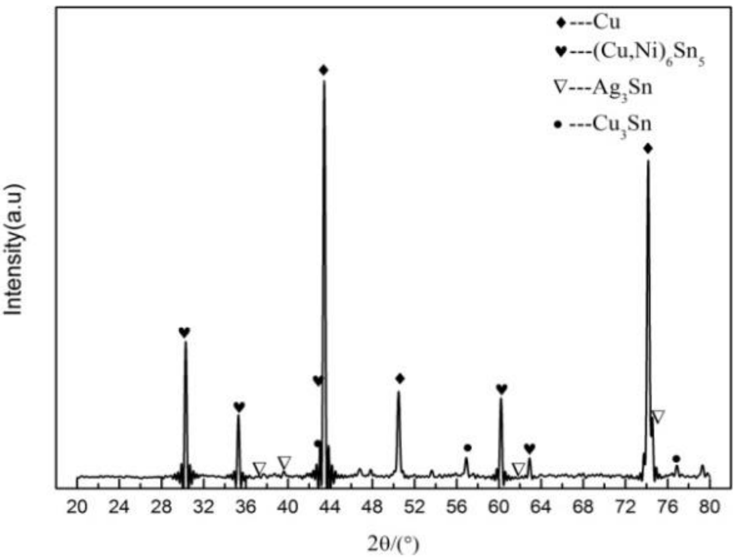


Figure 7. XRD analysis of the top view interfacial IMC

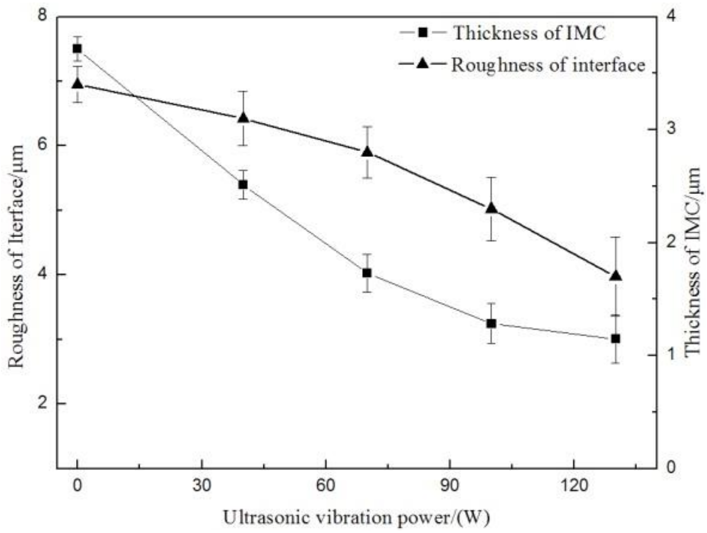


Figure 8. Roughness, Thickness of the wetting interfacial IMC

4. Conclusion

The wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy improved with the USV assisted. With the increasing of USV power the wetting angle decreased and the spreading area and spreading ratio increased. The wettability of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy on Cu substrate was better with the USV assisted compared to the commercial Sn3.0Ag0.5Cu solder alloy (SAC305). A wetting angle minimum of 24.5 °, the spreading area and spreading ratio maximum of 51.3 mm2, 62.1%, respectively, were obtained from the solder sample treated with 130 W Additionally, With the increasing of USV power, the microstructure of wetting interfacial IMC was refined, and the average thickness, roughness and grain size of the interface intermetallic compound (IMC) decreased. When the USV power increased to 100 W, the thickness, roughness and (Cu,Ni)6Sn5 grain size of the wetting interfacial IMC decreased by 58.7%, 51.6% and 35.1%, respectively.

5. Acknowledgments

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Center of Non-ferrous Metals, Henan Province, China, and Henan Province Key Laboratory of Nonferrous Metal Material Science and Processing Technology, Luoyang, China.

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