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

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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 mm², 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)₆Sn₅ 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. Fluxes have been used to improve the wettability of lead-free solder alloys. However, some fluxes 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.
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 40×40×2 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°C, 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_m) 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.

\[ K = \frac{D - h}{D} \times 100\% \]  \hspace{1cm} (1)

\[ d = \frac{A}{L} \]  \hspace{1cm} (2)

The root mean square roughness (R_m) 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.
The wetting samples were cross-sectioned and ground, 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](image1)

![Figure 2. Schematic of wetting on the Cu substrate](image2)

![Figure 3. Schematic diagram of interfacial IMC Thickness and $R_{rms}$](image3)

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 Sn2.5Ag0.7Cu0.1RE0.05Ni 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 showed 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 of 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.

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

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)₅Sn₅ 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 Cu₆Sn₅ 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(a₁-d₁) 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(a₁-d₁), 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)$_6$Sn$_5$, Cu$_3$Sn, and Ag$_3$Sn peaks were found according to the XRD analysis results. Both (Cu,Ni)$_6$Sn$_5$ and Cu$_3$Sn were products of reactions between solder and Cu. Because of the peak intensities of (Cu,Ni)$_6$Sn$_5$ was much higher than that Cu$_3$Sn, most of cobblestones grains were (Cu,Ni)$_6$Sn$_5$. This was consistent with the EDS analysis result of the point “A” in figure 6(a). The average size of (Cu,Ni)$_6$Sn$_5$ grains decreased from 3.7 μm to 2.4 μm with the increase of ultrasonic power. Additionally, it was observed that some nanoscale particles were absorbed in the (Cu,Ni)$_6$Sn$_5$ grains, which was confirmed to be Ag$_3$Sn particles by EDS analysis result of the point “B” in table 1.

![Image](image.png)

**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

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

**Table 1.** EDS analysis results of the wetting interface point “A” and “B” shown in figure 6(a) and figure 6(a$_1$)

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.
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.

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6. References
[1] K Zeng, and K N Tu Six cases of reliability study of Pb - free solder joints in electronic packaging technology 2002 Mater. Sci. Eng. R Reports 38 55-105
[2] K N Tu and K Zeng Tin-lead (Sn Pb) solder reaction in flip chip technology 2001 Mater. Sci. Eng. R Reports 34 1-58
[3] H R Kotadia, P D Howes and S H Mannan A review: On the development of low melting temperature Pb-free solders 2014 Microelectron. Reliab 54 1253-73
[4] Z Xu, J Yan, B Zhang, X Kong and S. Yang Behaviors of oxide film at the ultrasonic aided interaction interface of Zn-Al alloy and Al2O3p/6061Al composites in air 2006 Mater. Sci. Eng. A 415 80-6
[5] Z Xu, J Yan, G Wu, X Kong and S Yang Interface structure of ultrasonic vibration aided interaction between Zn–Al alloy and Al 2O3p/ 6061Al composite 2005 Compos. Sci. Technol. 65 1959-63
[6] H Li, C Li and Z Li. Progress in power ultrasound effect on molten metal shaping and its visualization 2017 Journal of materials engineering. 45 (5) 118-126
[7] K Zhao, K Zhang, X zhang, Y Liu, Z Zhang, H Shi, and R Qiu. Effect of electric field on wettability of Sn2.5Ag0.7Cu0.1RE/Cu assisted by ultrasonic vibration 2013 Welding technology 42(10) 7-9
[8] D Q. Yu and L Wang. The growth and roughness evolution of intermetallic compounds of Sn-Ag-Cu/Cu interfacial behavior during solidification 2008 J. Alloys Compd 458 542-7
[9] R K Chinnam, C Fauteux, J Neuenschwander and J Janczak-Rusch Evolution of the microstructure of Sn-Ag-Cu solder joints exposed to ultrasonic waves during solidification 2011 Acta Mater. 59 1474-81
[10] P Liu, P Yao, and J Liu. Evolutions of the interface and shear strength between SnAgCu-xNi solder and Cu substrate during isothermal aging at 150 ℃ 2009 J. Alloys Compd. 486 474-9
[11] A T Tan, A W Tan, and F. Yusof Effect of ultrasonic vibration time on the Cu/Sn-Ag-Cu/Cu joint soldered by low-power-high-frequency ultrasonic-assisted reflow soldering 2017 Ultrason. Sonochem. 34 616-25
[12] H Ji, Q Wang, M Li and C Wang Ultrafine-grain and isotropic Cu/SAC305/Cu solder interconnects fabricated by high-intensity ultrasound-assisted solidification 2014 J. Electron. Mater. 43 2467-78
[13] A T Tan, A W Tan and F Yus of Evolution of microstructure and mechanical properties of Cu/SAC305/Cu solder joints under the influence of low ultrasonic power 2017 J. Alloys Compd. 705 188-97.