Spreading and Wetting Behaviors of Sn2.5Ag0.7Cu0.1RE0.05Ni Solder on the Surface of Cu Substrate under Ultrasonic Vibration

Chenxiang Yin¹, Keke Zhang¹,²,³,*, Shijie Li¹, Junheng Li¹
¹School of Materials Science & Engineering, Henan University of Science and Technology, Luoyang, China
²Henan Province Key Laboratory of Nonferrous Metal Material Science and Processing Technology, Luoyang, China
³Collaborative Innovation Center of Non-ferrous Metals, Luoyang, China
*E-mail:zhkekekd@163.com

Abstract. The spreading and wetting behaviors of Sn2.5Ag0.7Cu0.1RE0.05Ni lead-free solder on the surface of Cu substrate under ultrasonic vibration were studied by SEM, EDS and other methods. The ultrasonic time was 1, 2, 3, 4, 5 s, respectively and was compared with the spreading of solder in the condition of soldering flux. The results showed that the Sn2.5Ag0.7Cu0.1RE0.05Ni solder was forced to spread instantly on the base metal surface under the action of ultrasonic vibration, and the ultrasonic cavitation can crush the oxide film on the surface of solder and base metal, resulting in the wetting of liquid solder and base metal. When the ultrasonic time was 3 s, the spreading area and spreading ratio of the solder achieved the maximum, and the ultrasonic cavitation could break the β-Sn and eutectic structure of the solder during solidification, refining the microstructure and improving the hardness of the solder matrix.

1. Introduction
With the development of electronic products in the direction of miniaturization, high reliability and green environmental protection, people demanding for the higher quality and reliability of micro-joint lead-free solder joints have been put forward. It has been a hot spot to develop environment-friendly lead-free solder with high reliability [1]. Sn-Ag-Cu solder alloy has become one of the most promising alternatives of Sn-Pb solders with its excellent performance [2, 3]. By means of solder alloying method, trace alloying elements (such as RE, Ni) are added to the lead-free solder alloy to improve the properties of the solder [2-4]. For example, the low-silver Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy developed in China, with high strength and toughness, providing significant technical and economic benefits. In order to obtain high-reliability lead-free solder joints to satisfy the increasingly harsh and demanding service environment, external energy assistance (such as ultrasonic vibration) is introduced during soldering, which can effectively remove the oxide film [5, 6] and promote solder wetting, achieving halogen-free high quality soldering of micro-joining lead-free solders [7-9]. At present, however, the research on the spreading and wetting behaviors of lead-free solder under ultrasonic vibration is not well understood. In the present study, we investigated the wetting interface microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder alloy by ultrasonic vibration during the spreading process. Our research provides theoretical and experimental basis for the development of environment-friendly and highly reliable soldering technology.
2. Materials and Methods

A copper plate with a purity of 99.9% and the size of 60 mm×30 mm×2 mm was used. The Sn2.5Ag0.7Cu0.1RE0.05Ni lead-free solder alloy was fabricated by a mixture of Sn, Ag, Cu, Ni (99.9% purity) and mixed rare earth (RE) containing Ce and La. A non-consumable electric furnace with a vacuum of 5×10^-3 Pa was used. The copper plate and the solder sample were cleaned with sand paper, and washed with acetone and preserved in an anhydrous ethanol solution for further use.

A 0.2 g of prepared solder was placed in the center of the polished copper plate, and completely covered with 1-2 drops of no-clean flux. Then the ultrasonic assisted soldering device (Figure 1), which was designed and manufactured by ourselves, was used for soldering. According to the previous study, the soldering temperature was set at 270°C and the soldering time was 240 s. Ultrasonic vibration was applied to the specimen during the soldering process. The ultrasonic power was 88 W and the ultrasonic time was 1 s, 2 s, 3 s, 4 s and 5 s, respectively.

The ultrasonic soldering samples were cut longitudinally and inlaid within resin. After that, the resin-inlaid samples were polished completely and etched with 4% hydrochloric acid ethanol solution. The microstructure of the wetting interface was observed by JSM-5610LV scanning electron microscope and composition analysis was carried out by EDS.

According to previously reported measurement method of the thickness and roughness of the micro-joint solder joint interface (Figure 2) [10], five random areas of the joint interface IMC were measured with AutoCAD software and the average thickness was obtained. The average thickness was used as a reference line (see the dotted line in Figure 2), and the distance between the peak of the selected area interface IMC and the reference line is measured, then the interface IMC roughness $R_{rms}$ (the average of the five random areas) was calculated according to the formula (1).

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

where: $R_{rms}$ means roughness, μm; $N$ means the number of measurement points in the selected area ($N \geq 15$); $Z_i$ means the distance between the IMC peak curve of the selected area to the measurement reference line, μm.

3. Results and Discussion

3.1. The Spreading Behavior of Sn2.5Ag0.7Cu0.1RE0.05Ni Solder/Cu under Ultrasonic Vibration Action

Figure 3 shows the spreading macrostructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder on the base metal surface in the condition of flux and under different ultrasonic vibration time, respectively. The spreading macrostructure of the solder under the action of ultrasonic was irregularly round (Figure 3(b)-(f)). This was because that, as the ultrasound spread in the liquid solder, the ultrasonic amplitude attenuated and the acoustic wave interacted with liquid viscous force, resulting in an acoustic pressure gradient along the direction of ultrasonic wave transferring, forcing the liquid solder to spread [11]. In
the condition of soldering flux, the spreading rate of solder was almost the same along all directions, so the macrostructure of solder after spreading was more regular (Figure 3(a)).

Figure 3. The spreading macrostructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder (a) in the condition of flux and different ultrasonic time (b) 1 s, (c) 2 s, (d) 3 s, (e) 4 s, (f) 5 s

Figure 4 shows the effect of ultrasonic time on the spreading area and spreading ratio of Sn2.5Ag0.7Cu0.1RE0.05Ni solder. When the ultrasonic power was constant, the spreading area and the spreading ratio of the solder increased with ultrasonic time and reached the maximum value at 3 s. That was because ultrasonic cavitation could break the oxide film on the surface of solder and base metal, promoting the spreading and wetting of solder. When the ultrasonic time exceeded 3 s, the spreading area and the spreading ratio decreased slightly with ultrasonic time. This may because that the ultrasonic wave acted on the liquid solder in a form of energy, and the solder absorbed this energy increasingly over time, resulting in an increasingly high temperature of the solder. This high temperature led to the solder oxidized. The formed oxide film was pushed by ultrasonic wave to the front of the spreading area, hindering the spreading of the liquid solder [12]. On the other hand, because of the attenuation of ultrasonic amplitude, the sound pressure at the spreading front of liquid solder was relatively small, generating a driving force not enough to continue to promote the spreading of solder. With the effect of these two factors, the spreading area of solder decreased accordingly.

Figure 4. The spreading area and spreading ratio of Sn2.5Ag0.7Cu0.1RE0.05Ni solder under the ultrasonic vibration
3.2. Microstructure of Wetting Interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu under Ultrasonic Vibration

Figure 5 shows the microstructure and EDS analysis result of the wetting interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu under ultrasonic vibration. The wetting interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu included Cu substrate, interface region and solder region (Figure 5a). The interface region was a “scalloped” IMC layer, which grew from the interface to the solder region. In the soldering of Sn-Ag-Cu solder and Cu, the wetting interface IMC usually consists of two layers, including Cu3Sn (near the base metal) and Cu6Sn5 (near the soldering seam). However, no Cu3Sn was observed in the interface area IMC, probably because the Cu3Sn layer was too thin to be detected (Figure 5b).

Figure 5. Microstructure of the wetting interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu under ultrasonic vibration (a) microstructure of wetting interface (b) EDS results of point A

Figure 6 shows the microstructure of the solder of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu wetting interface under ultrasonic vibration. The microstructure of the wetting interface under the action of ultrasonic vibration was just the same as that of conventional soldering, which was composed of primary β-Sn and reticulated eutectic structure. For conventional soldering, the size of primary β-Sn of the solder was large and irregular in shape (Figure 6(a)). Compared to that, the primary β-Sn of the solder under the ultrasonic vibration showed a smaller size, more regular shape (approximately equiaxed) and a larger proportion of eutectic structures (Figure 6(b)-6(f)). As is mentioned above, the ultrasonic vibration caused ultrasonic cavitation inside the liquid solder. Once the cavitation bubbles in the cavitation region collapsed, a strong shock wave was generated, which broke the β-Sn and eutectic structure generated by the liquid solder during solidification, increasing the number of crystal nuclei and rate of nucleation [13]; on the other hand, since the solder was forced to spread under the ultrasonic vibration, the liquid solder was uniformly heated, so that the solder could be simultaneously solidified. Consequently, the microstructure of the solder under the effect of ultrasonic vibration was refined and relatively uniform.
Figure 6. Microstructure of Sn2.5Ag0.7Cu0.1RE0.05Ni solder (a) in the condition of flux and different ultrasonic vibration time (b) 1 s, (c) 2 s, (d) 3 s, (e) 4 s, (f) 5 s

3.3. IMC of Wetting Interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu under Ultrasonic Vibration
IMC of the wetting interface of lead-free soldering is an important part of the soldering joint. Its shape and size are closely related to the reliability of the solder joint [10]. The morphology of the wetting interface IMC of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu under ultrasonic vibration are shown in Figure 7. The wetting interface IMC under different soldering conditions all showed "scalloped" shape. In conventional soldering (Figure 7(a)), the average thickness and roughness of IMC layer were 4.6 μm and 2.9 μm respectively, and local microvoids were observed. In comparison, the average interfacial IMC layer thickness and roughness of the wetting interface under ultrasonic vibration were (3.1 μm) and (2.0 μm), respectively (Figure 7(b)-7(f)). In addition, it can be seen that the interfacial IMC layer was thinner and uniform, and no local microvoids in the IMC layer. Specifically, the average thickness reduced by 32.6% and roughness reduced by 31.0%.

Figure 7. SEM images of IMC of the wetting interface of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu (a) in the condition of flux and different ultrasonic vibration time (b) 1 s, (c) 2 s, (d) 3 s, (e) 4 s, (f) 5 s
3.4. Hardness of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu Solder Matrix under the Effect of Ultrasonic Vibration

Figure 9 shows the Vickers hardness of Sn2.5Ag0.7Cu0.1RE0.05Ni/Cu solder matrix after ultrasonic action. The hardness of solder matrix after ultrasonic action was obviously higher than that without ultrasonic action, and increased with ultrasonic time, which was consistent with the microstructure refinement of solder matrix (Figure 6). When the ultrasonic time exceeded 3 s, the hardness of solder matrix tended to stabilize. According to Mahmudi et al. [14], eutectic phase affected the hardness of solder matrix by dispersion strengthening. After ultrasonic action, the Ag3Sn and Cu6Sn5 phases embedded in the eutectic phase were refined, and the eutectic phase obtained higher resistance against indentation force, hindering the dislocation along the eutectic phase region.

Additionally, the variation of solder matrix hardness with time after ultrasonic action may be related to the size variation of β-Sn. It has been reported that β-Sn is the softest component in SAC305 solder [15]. In the present research, a larger size of β-Sn was observed in the samples without ultrasonic action (Figure 6(a)), which may result in the lower hardness of solder matrix.

4. Conclusions

Under the ultrasonic vibration, the ultrasonic cavitation can break the oxide film on the surface of the solder and the base metal, so that the liquid solder was forced to spread and wetted with the base metal. When the ultrasonic time was no more than 3 s, the spreading area and spreading ratio of Sn2.5Ag0.7Cu0.1RE0.05Ni solder increased with ultrasonic time and reached their maximum at 3 s. When the ultrasonic time was over 3 s, the spreading area and spreading ratio decreased with time. Under the effect of ultrasonic vibration, primary β-Sn and eutectic microstructure of the solder matrix were refined and the proportion of eutectic structure increased, and average thickness and roughness of the wetting interface IMC reduced, and the hardness of solder matrix increased significantly.

5. Acknowledgments

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