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EFFECT OF A NANO-ZnO ADDITION ON THE WETTABILITY AND INTERFACIAL STRUCTURE OF Sn-BASED Pb-FREE SOLDERS ON ALUMINUM

VPLIV DODATKA NANO-ZnO NA OMOČLJIVOST IN STRUKTURO NA FAZNI MEJI PRI SPAJKANJU ALUMINIJA S SPAJKAMI NA OSNOVI Sn BREZ DODATKA ŠKODLJIVEGA SVINCA

Qingfeng Wang[1], Yu Ding[2], Fengjiang Wang[2*]

[1]School of Naval Architecture & Ocean Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China
[2]Provincial Key Laboratory of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, P. R. China

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Aluminum soldering with a low-temperature Pb-free solder is very important in electronics and radiator applications. In this paper, a nano-ZnO addition was introduced into the interfacial reaction between a Sn-3.5Ag or Sn-9Zn solder and aluminum to improve the wettability, interfacial structure and mechanical properties of joints. A spreading test showed that the Sn-3.5Ag solder had higher wettability than Sn-9Zn. With the nano-ZnO addition, the wettability of these two solders was obviously improved. An analysis of the interfacial structure showed that the bonding between Sn-Zn and Al was realized with a Zn-Al solid solution, while that between the Sn-3.5Ag solder and Al was realized with an Ag_2Al intermetallic layer. The introduction of nano-ZnO obviously accelerated the formation of Ag_2Al of Sn-3.5Ag on Al. Finally, a shear test showed that the nano-ZnO addition helped increase the shear strength of Al solder joints.

Keywords: aluminum soldering, wettability, interfacial reaction, shear strength, nano-ZnO

Za spajkanje aluminija, na primer radiatorjev in elektronskih sestavnih delov so zelo pomembne spajke brez dodatka škodljivega svinca. V članku avtorji opisujejo vpliv dodatka nano-ZnO na reakcijo, ki poteka na fazni meji med spajko Sn-3,5Ag oz. spajko Sn-9Zn in aluminijem. Ta je bil dodan za izboljšanje omočljivosti, medfazne strukture in mehanskih lastnosti spoja. Test porazdelitve spajk je pokazal, da ima spajka Sn-3,5Ag boljšo omočljivost kot spajka Sn-9Zn. Dodatek nano-ZnO je, dokazano v primeru obeh spajk, izboljšal njuno omočljivost. Analiza strukture na fazni meji je pokazala, da je prišlo v primeru spajkanja s spajko Sn-9Zn do nastanka močne vezi med Sn-Zn in Al z nastankom trdne raztopine Zn-Al, medtem ko je med spajko Sn-3,5Ag in Al nastala intermetalna plast Ag_2Al. Uvedba nano-ZnO je očitno pospešila tvorbo Ag_2Al iz Sn-3,5Ag na Al. Nazadnje je strižni preizkus pokazal še, da dodatek nano-ZnO pomaga izboljšati strižno trdnost spajkanega spoja Al.

Ključne besede: spajkanje, omočljivost, reakcije na fazni meji, strižna trdnost, nano-ZnO

1 INTRODUCTION

In the electronics industry, copper and aluminum are the most commonly used materials for heat sinks due to their excellent thermal conductivities. Aluminum, especially, exhibits a low density at a low cost and a high corrosion resistance, and it often replaces copper. To enhance the heat transfer across diverse media, the recent heat-sink-construction development has aimed to form true metallurgical bonds between aluminum-based products using the low-temperature soldering method with Sn-based solders because it causes less heat distortion.

Currently, the most recommended Sn-based solder is the Sn-Zn Pb-free series.[1–6] X. Chen et al.[7–8] observed the interfacial structure of Sn-9Zn/Al and found that the metallurgical bonding between them was carried out due to the dissolution of Al into the solder.To improve the Sn-9Zn/Al joint performance, M. L. Huang et al.[3–5,] incorporated small amounts of Ag, Al or Ni into a Sn-Zn solder to obtain higher shear strength and corrosion resistance of the joints. Besides the Sn-Zn solder, Y. Yao et al.[10] tried to use a Sn-3.5Ag solder, and found that the bonding between the solder and Al was realized due to the formation of Ag-Al intermetallic compounds (IMCs).On the other hand, due to the poor wettability of Sn-based solders on Al during soldering,[2,6] ultrasonic assisting has also been introduced into Al-soldering in recent years, which helps increase the joint strength and expand the soldered Al-alloys from the 1000 series to 5000–7000 series.[11–16]

Although Al-soldering was first illustrated by Spragen in 1940,[17] there are still some issues concerning the wettability arising from the existence of an alumina oxide film, deterioration of the joint strength arising from the formation of brittle intermetallic compounds (IMCs) at the interface and poor corrosion resistance arising from a large difference in the electrode potential between Al and solders.[18–20] In this paper, to improve the

*Corresponding author's e-mail:
fjwang@just.edu.cn (Fengjiang Wang)

performance of a solder on Al, nano-ZnO powders were introduced into the interfacial reaction between solders and Al, and the wettability and interfacial structures were investigated.

2 EXPERIMENTAL PART

The selected solders were Sn-9Zn and Sn-3.5Ag Pb-free solders. They were fabricated from pure Sn, Zn and Ag with a purity of 99.9 *w*/%. Appropriate amounts of the raw materials were encapsulated into a quartz tube with an evacuation system, melted at 600 °C for 6 h and then cast into a steel mold to obtain these two solders. The used substrate was 1060 pure Al. To effectively clean the oxide film on Al, an alkaline-paste flux was developed, based on references, into MSDS sheets of commercial-aluminum solder fluxes. The main components were N-(2-Hydroxyethyl) ethylenediamine (CAS: 111-41-1), triethanolamine (CAS: 102-71-6) and ammonium tetrafluoroborate (CAS: 13826-83-0) with PEG-6000 as the thickening agent. Then, about 5 *w*/% of nano-ZnO powders with sizes of 1–100 nm were fully mixed into the paste flux to complete the addition of nano-ZnO.

Wetting was finished with a spreading test following the standard of JIS Z 3198. The dimensions of Al-pads were (40 × 40 × 0.5) mm. Chemical cleaning was used for pad cleansing, which used NaOH solvents and acids to remove contaminant residues and oxide films, respectively. It was then followed by a DI-water rinse and drying. The mass of the solder used for the wetting test was 0.3 g. The weighted solder was melted and solidified into a solder ball in a molten rosin, followed by ultrasonic cleaning with acetone. The solder ball covered with the flux was then wetted on an Al-pad at a temperature of 250 °C for 30 s. The spreading area was measured to evaluate the wettability of the solder on Al.

After the wetting test, the wetted samples were cross-sectioned, mechanically grinded with waterproof abrasive paper, polished with a 0.05-μm colloidal-silica solution and then etched with a 3-% HNO_3 solution. Interfacial structures were observed with an optical microscope (OM) and a scanning electron microscope (SEM). Energy dispersive X-ray spectroscopy (EDS) was used for a compositional analysis.

To evaluate the effect of the nano-ZnO addition on the mechanical properties of the solder, lap-solder joints were prepared with two Al pieces with a size of (40 × 40 × 0.5) mm. The thickness of the solder was 0.5 mm. A shear test was then carried out on the joints with a speed of 0.3 mm/min.

3 RESULTS

Figure 1 presents the morphologies of the Sn-9Zn and Sn-3.5Ag solders on Al-pads after the wetting tests using the flux without or with the addition of nano-ZnO. The average spreading area of the solders on the Al-pads was then calculated and the results are shown in **Figure 2**. Without the addition of nano-ZnO, the wetting area of the Sn-9Zn and Sn-3.5Ag solders on 1060 Al was about 60 mm^2 and 80 mm^2, respectively. The wettability of the Sn-3.5Ag solder was a little higher than that of the Sn-9Zn solder during aluminum soldering. After the addition of nano-ZnO, the wetting areas for both the Sn-3.5Ag and Sn-9Zn solders increased to about 150 mm^2. Therefore, the nano-ZnO addition obviously promoted the wettability of the solder on aluminum. In **Figure 1**, we also clearly see a wetting ring of a bright color at the outer edge of the solder. M N. Popescu et al.[21] defined it as the precursor film, which emanated from the three-phase contact-line region. E. B. Webb et al.[22] suggested that the precursor film provided for a better wettability. From the morphology of the precursor film in **Figure 1**, it can be concluded that the addition of nano-ZnO results in a strong affinity of the solder with the aluminum substrate, promoting the wettability of the solder on an aluminum substrate.

From the binary-phase diagrams of Sn-Al, Zn-Al and Ag-Al, it is clear that the Al atoms mainly interact with the Ag or Zn atoms, but not with the Sn atoms. In the Zn-Al binary system, as shown in **Figure 3a**, mutual dissolubility between Al and Zn produces a solid solution with a wide range of the solution content of Zn in Al. In the Ag-Al binary system, as shown in **Figure 3b**, Al reacts with Ag to produce different kinds of intermetallic compounds (IMCs). They produce different types of metallurgical bonding at the interfaces of Sn-9Zn/Al and Sn-3.5Ag/Al. To investigate the interfacial structures, the wetted samples were cross-sectioned and polished. **Figure 4** shows interfacial microstructures obtained with optical observation, in which the upper and bottom areas

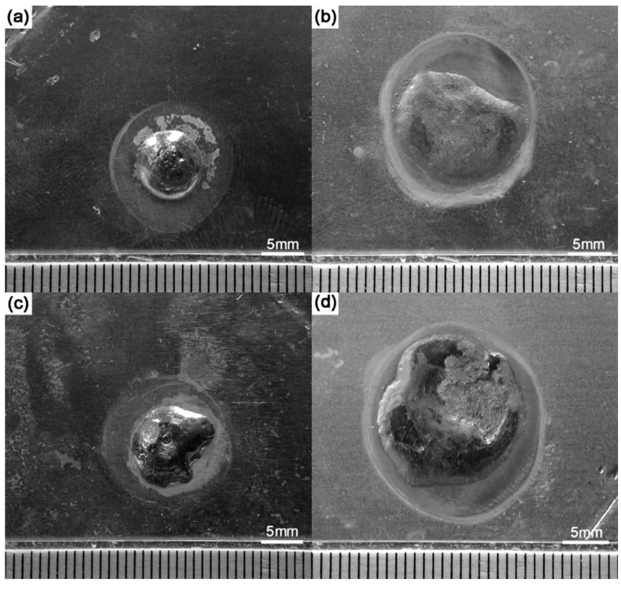

Figure 1: Photographs of wetted samples on Al: a) Sn-9Zn without ZnO, b) Sn-9Zn with ZnO, c) Sn-3.5Ag without ZnO and d) Sn-3.5Ag with ZnO

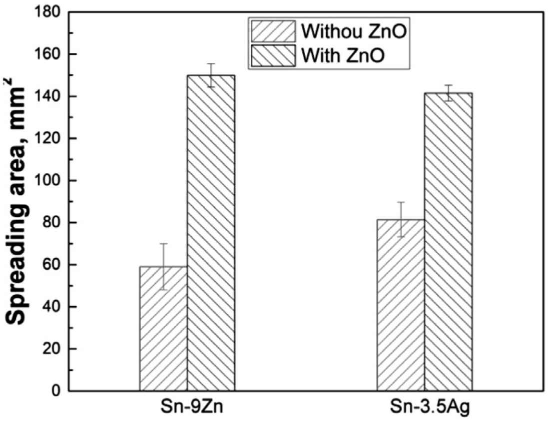

Figure 2: Spreading areas of solders on Al

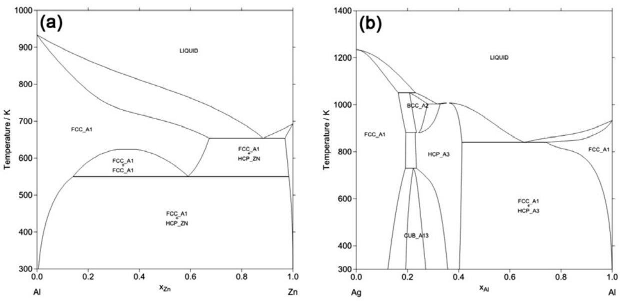

Figure 3: Phase diagrams of:a) the Zn-Al and b) Ag-Al binary system

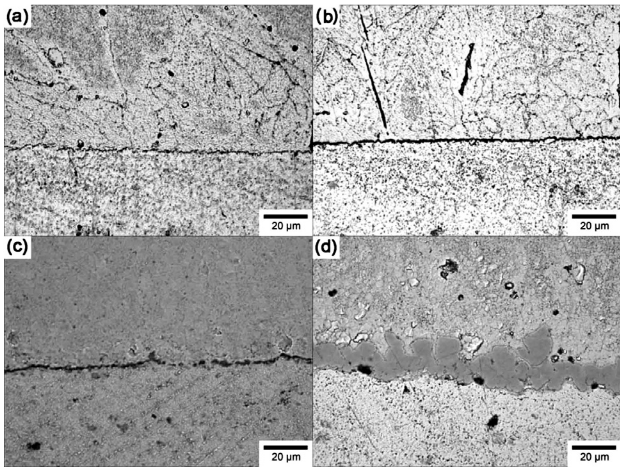

Figure 4: OM interfacial structures of wetted samples: a) Sn-9Zn without ZnO, b) Sn-9Zn with ZnO, c) Sn-3.5Ag without ZnO and d) Sn-3.5Ag with ZnO

are the solder and the aluminum substrate, respectively. As observed in **Figure 4a**, the bonding between the Sn-9Zn solder and aluminum was realized with a thin layer. With the nano-ZnO addition, the thickness of this interfacial bonding layer was thickened, as shown in **Figure 4b**. Meanwhile, many rod-like phases of a dark color are observed in the Sn-9Zn solder matrix. At the

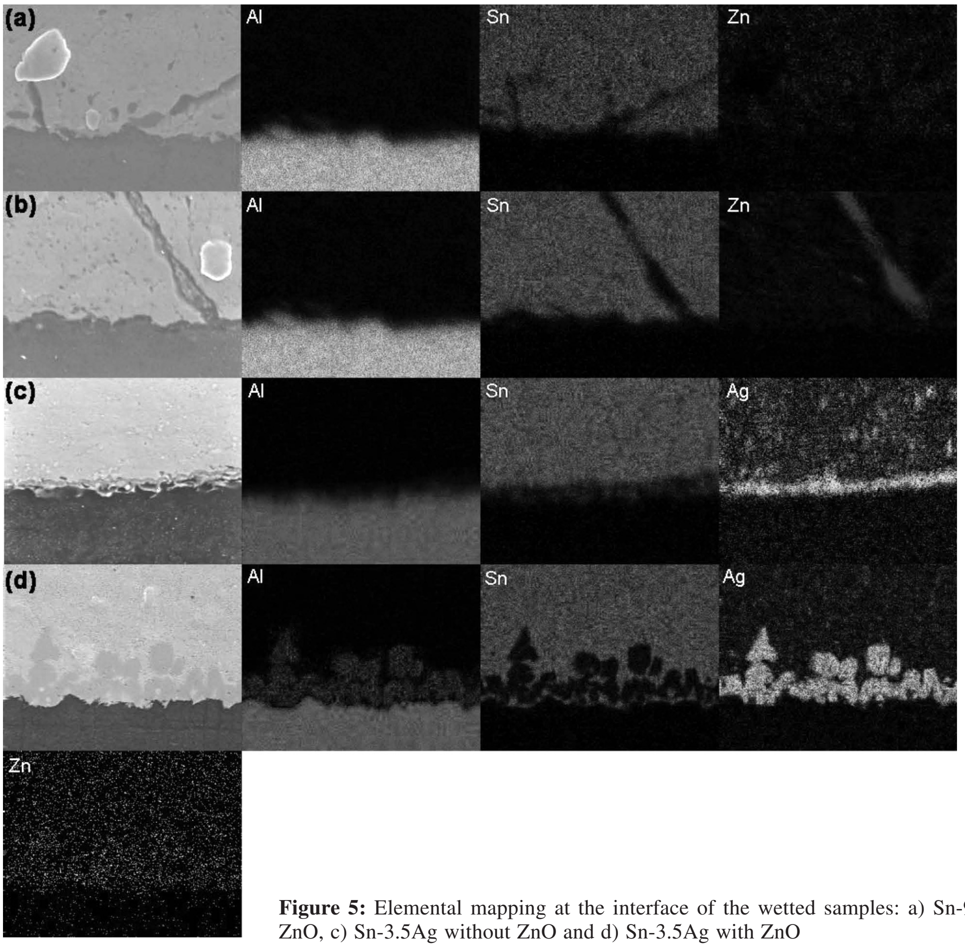

Figure 5: Elemental mapping at the interface of the wetted samples: a) Sn-9Zn without ZnO, b) Sn-9Zn with ZnO, c) Sn-3.5Ag without ZnO and d) Sn-3.5Ag with ZnO

interface of the Sn-3.5Ag/Al couple, an interfacial bonding area with a thinner thickness of about 2 μm was also produced, as shown in **Figure 4c**. With the nano-ZnO introduced into the reaction between the Sn-3.5Ag solder and Al (**Figure 4d**), the interfacial bonding phase between the solder and Al was obviously thickened to a thickness of about 20 μm.

To further confirm the compositions of these interfacial phases, SEM observation and EDS elemental mapping were used, and the results are shown in **Figure 5**. At the interface of the Sn-9Zn solder and Cu, the bonding between them was mainly realized with Al and Zn, and it was not influenced by the addition of nano-ZnO. It is clear from the EDS compositional analysis that it was composed of Zn, Al and a small amount of Sn, forming the Zn-Al solid solution from the Zn-Al phase diagram. At the interface of the Sn-3.5Ag solder and aluminum without the addition of nano-ZnO, the interfacial phase included Ag, Al and Sn, as shown in **Figure 5c**. With the nano-ZnO addition, it seems that the addition of ZnO obviously promoted the reaction between Sn-3.5Ag and Al, as shown in **Figure 5d**. The phase at the interface was mainly composed of Ag and Al. Moreover, Zn was also accumulated at the interface of Ag and Al. According to the Ag-Al phase diagram, it belonged to an IMC phase. As there were three IMC phases in the Ag-Al system, the μ, β and δ phases, we ultrasonically cleaned the solder residue on the Al substrate on the Sn-3.5Ag/Al wetted sample and then used X-ray diffraction (XRD) to detect the composition of this interfacial layer. The result is shown in **Figure 6** and it can be confirmed that the IMC layer between the Sn-Ag solder and Al was the Ag_2Al intermetallic compound. Therefore, as in the case of the addition of nanoparticles to another solder,[23] nano-ZnO was accumulated at the interface during the reaction between the solder and the Al substrate, altering the composition of the interfacial IMC.

Figure 7 shows the shear strength of Al/solder/Al lap joints with the effect of the nano-ZnO addition. The

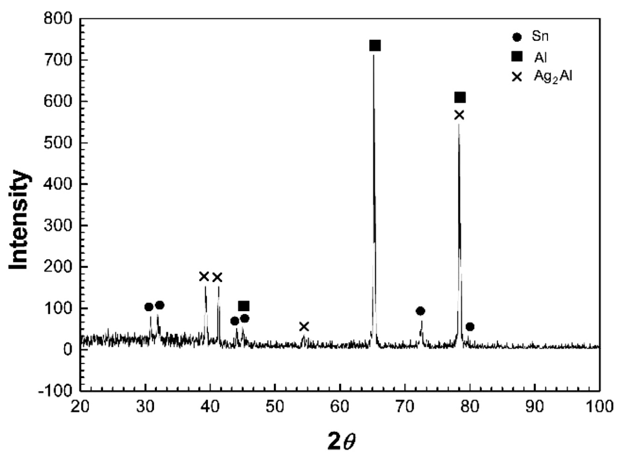

Figure 6: XRD result for the interface of Sn-3.5Ag/Al

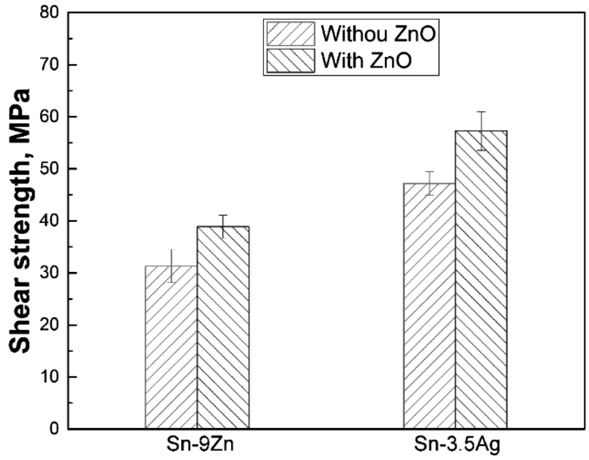

Figure 7: Shear strength of the solder joints

results show that the Sn-3.5Ag solder had a higher strength than the Sn-9Zn solder. Moreover, the addition of nano-ZnO allowed an increase in the strength of the solder joints on Al. This can be attributed to the formation of a thicker IMC at the interface and also the higher strength of the Sn-3.5Ag solder.

4 DISCUSSION

In the Sn-3.5Ag solder, Ag commonly reacted with Sn to produce the Ag_3Sn IMC phase, which was uniformly distributed in the solder matrix. However, during the Sn-Ag soldering on Al, Ag accumulated at the interface and reacted with Al to form the Ag_2Al IMC phase. This can be attributed to the fact that Ag-Al had a stronger chemical affinity than Ag-Sn. The chemical affinity between two elements can be calculated with the chemical bond parameter function. The function between atoms A and B can be described as follows in Equation (1):[24]

$$\phi=\phi\left[(Z/r)_{\mathrm{A}},X_{\mathrm{A}},(Z/r)_{\mathrm{B}},X_{\mathrm{B}}\right] \tag{1}$$

Where Φ is the chemical bond parameter function, *Z*/*r* is the ratio of electric charge to ionic radius and *X* is the negative electricity of an atom. Accordingly, the chemical affinity between two atoms (*f*) is:

$$f=\frac{(Z/r)_{\mathrm{A}}}{(Z/r)_{\mathrm{B}}}+\Delta X \tag{2}$$

The chemical affinities between atoms that occurred in the soldering with Al can be calculated, and the results are listed in **Table 1**. In the Sn-Zn/Al system, Al-Zn exhibited a higher bonding strength than Sn-Zn, and the interfacial phase was mainly composed of the Al-Zn solid solution. In the Sn-3.5Ag/Al system, Al-Ag had the maximum value of chemical affinity and was the principal product at the interface. With the ZnO introduced into the interfacial reaction, Zn/Ag also had a higher affinity and, therefore, Zn was accompanied by Ag to precipitate at the interface.

Table 1: Calculated values of chemical affinities between atoms

Metallic couple	Al/Ag	Al/Zn	Sn/Ag	Zn/Ag	Zn/Sn
$\frac{(Z/r)_A}{(Z/r)_B}$	6/0.79	6/2.70	1.82/0.79	2.7/0.79	2.7/1.82
ΔX	0.4	0.1	0.1	0.3	0.2
f	7.995	2.322	2.403	3.718	1.68

5 CONCLUSIONS

In this paper, the wettability and interfacial structures of the Sn-9Zn and Sn-3.5Ag Pb-free solders on aluminum were studied. To improve the performance of solder joints, a nano-ZnO addition was introduced into the interfacial reaction. The following results can be drawn:

The spreading test showed that the Sn-3.5Ag solder had a higher wettability than the Sn-9Zn solder on aluminum. The addition of nano-ZnO can obviously promote the wettability of both the Sn-9Zn and Sn-3.5Ag solders.

Reaction products between the solder and Al were determined by the solder-alloy composition and the chemical affinity between the atoms. The Zn-Al solid solution and Ag_2Al intermetallic phase were obtained with the Sn-9Zn solder and Sn-3.5Ag solder, respectively. The addition of nano-ZnO accelerated the growth of the Ag_2Al layer at the interface of Sn-3.5Ag/Al.

The shear test showed that the Sn-3.5Ag/Al solder joint had a higher shear strength than the Sn-9Zn/Al joint. The nano-ZnO addition also helped improve the shear strength of solder joints.

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