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Investigation of the Wetting Properties of Ternary Lead-Free Solder Alloys on Copper Substrate

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In the present study, wetting behaviors of Sn–9Zn–*x*Al ternary lead-free solder alloys produced by the addition of Al in various amounts binary Sn–9Zn eutectic lead-free solder alloy (wt%) were investigated. Contact angles of alloys were measured by using of the sessile drop method. Microstructures, inter-metallic phases, and melting temperatures of alloys were characterized by optic microscope and scanning electron microscope and energy dispersive X-ray spectroscopy, X-ray diffraction, and differential scanning calorimeter, and effects of the amount of Al on microstructure were investigated. As a result, the studies show that Al-rich areas were found on microstructure of Sn–9Zn–*x*Al alloys. The lowest melting temperature for Sn–9Zn–0.5Al and Sn–9Zn–0.7Al alloys was determined as 200.9 °C. It was determined that wetting capability of Sn–9Zn–*x*Al alloys failed because of oxidation.

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1. Introduction

Within the precautions taken by numbers of countries around the world to prevent environmental pollution, the European Union (EU) banned various pollutant materials after 2006 [1, 2]. Therefore, instead of Sn–Pb lead solder alloys utilized by the electronic industry as a solder material, necessary efforts are spent in development of alternative alloys. In available studies, since melting temperature was reported at a point close to the eutectic Sn–Pb alloy (198 °C) and they have low-cost, Sn–9Zn lead-free solder alloys were taken into consideration [3]. Sn–Zn alloys have now been comparable with Sn–Pb alloys in terms of melting temperature and mechanical properties. Nevertheless, resistances of Sn–Zn alloys against oxidation and corrosion were low [4, 5]. Owing to its diffusion and heating capabilities, tin constitutes basic component of majority of solder alloys used in electronic applications. When general properties of Sn–Zn alloys are taken into consideration, their superior solder capability and their harmless nature for human health increase attention toward usage these alloys in the industry. Soldering is the process of combination of two or more metal components by a filler metal with low melting temperature. Wetting or wettability is defined as diffusion tendency of the liquid phase on solid surface and this diffusion capability is determined by the contact angle between the two surfaces [6]. Therefore, in the present study, wetting performances of various alloys produced by addition of different amounts of aluminum into the Sn–9Zn eutectic alloys was investigated.

2. Materials and method

In this study, while different amounts (0.5–0.9%) aluminum into the eutectic Sn–9Zn alloy were added, new

lead-free solder alloys were produced. In determination of wetting behavior of these alloys, 99.85% pure electrolytic copper substrate were used. The sessile drop method was used in the wetting tests. By means of this method, the Sn–9Zn–*x*Al solder alloy was dropped on copper substrate at various temperatures of 215 °C, 230 °C, and 250 °C. Casio Made Pro EX-F1, 600 FPS Model camera employed to capture views of drops at the 5th, 10th, 15th, 30th, 60th, 90th, 120th, and 150th seconds and these images were transferred into Corel Draw X5 Software to measure contact angles of each drop from the right and left profiles. As a result of these processes repeated for each temperature, mean angle values were calculated and new diagrams were drawn through the Sigma Plot 11.0 Software. In order to determine melting temperatures of alloys, the DSC analysis were carried out on specimens in maximum 30 mg weight and at 40 °C–300 °C temperature range (5 min). Standard metallographic processes were carried out for microstructure examinations. Prepared specimens were etched with 100 ml H₂O, 2 ml HCl, 10 g FeCl₃ solution for 45 s. The etched specimens were characterized by the scanning electron microscope and energy dispersive X-ray spectroscopy (SEM+EDS) and X-ray diffraction (XRD).

3. Results and discussion

In Fig. 1 there are given microstructure SEM images of Sn–9Zn, Sn–9Zn–0.5/0.7/0.9 Al lead-free solder alloys.

From the microstructure SEM images in Fig. 1, it could be realized that Sn–9Zn alloy has an eutectic lamellar structure (Fig. 1a). Light colored regions in Sn–9Zn alloy were β -Sn phases. In some of previous studies, it was emphasized that the areas between the dark colored regions and the primary β -Sn phase were eutectic and that their structure were β -Sn rich [7]. Acicular and dark colored regions within the structure of the Sn–9Zn alloy were Zn-rich areas. It was determined that addition of Al into the Sn–9Zn alloy resulted in thinning in Zn phases and Al-rich regions were formed (Fig. 1b–d).

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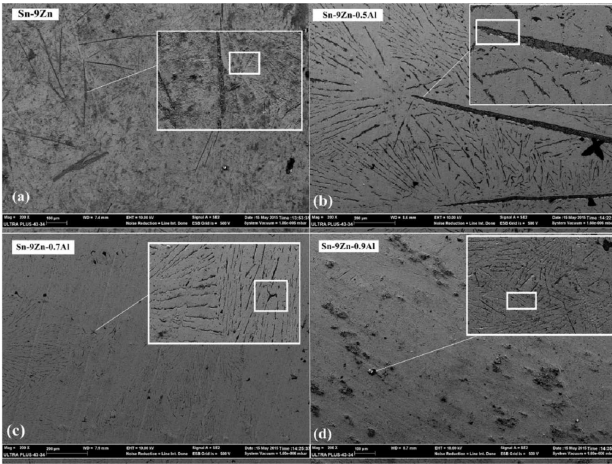


Fig. 1. SEM images of Sn-9Zn (a), Sn-9Zn-0.5Al (b), Sn-9Zn-0.7Al (c), Sn-9Zn-0.9Al (d) alloys.

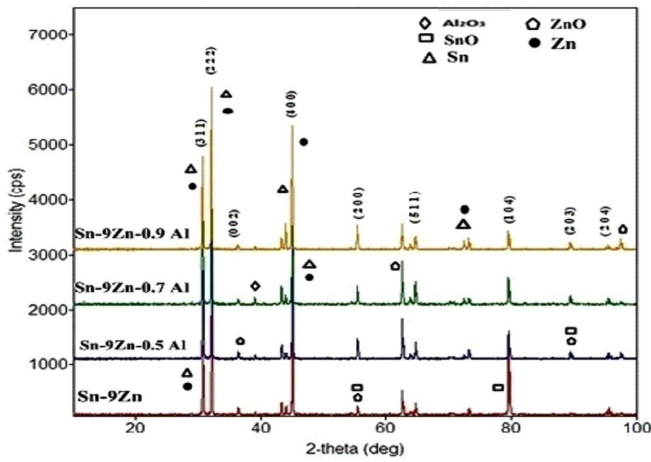


Fig. 2. XRD results of the Sn-9Zn and Sn-9Zn-xAl alloys.

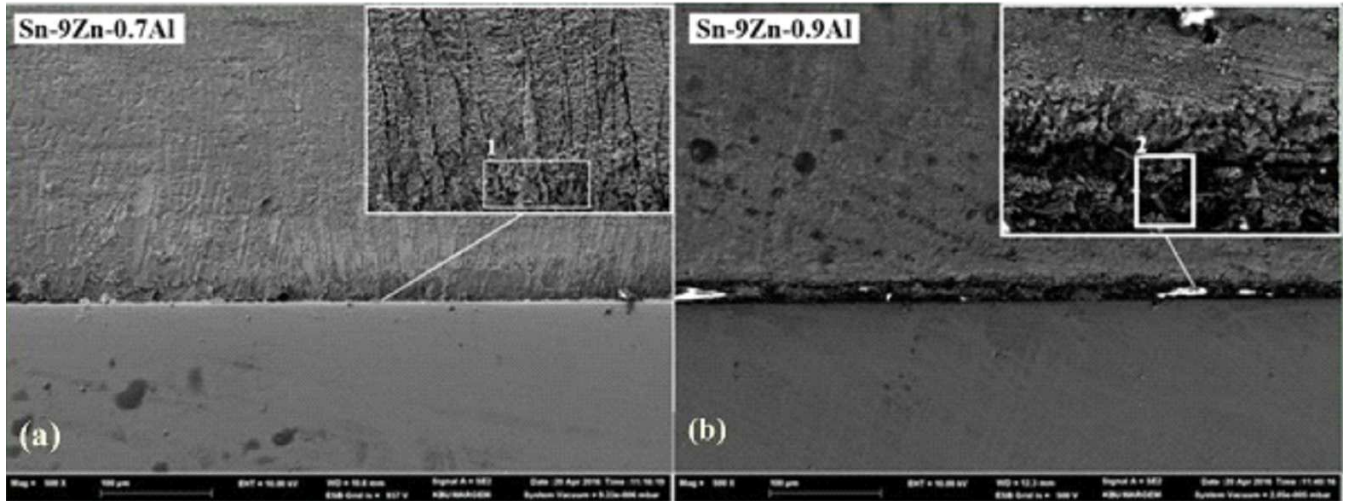


Fig. 3. SEM images of the Sn-9Zn-xAl alloy after the drop process.

In Fig. 2 there are given XRD results of the eutectic Sn-9Zn alloys with added different amounts of Al. It was determined that ZnO, SnO, and Al₂O₃ phases were formed in the alloy structure according to the XRD results. The most important problem with Sn-Zn based solders was that these alloys have low level of oxidation resistance [8]. Zn is highly inclined to oxidation; and Zn displays more inclination to oxidation at high temperatures in comparison with Sn [9]. Figure 3 shows the SEM images of Sn-9Zn-xAl alloy afterwards of drop process. EDS results of Sn-9Zn-xAl alloys are displayed in Table I.

TABLE I
EDS results of the Sn-9Zn and Sn-9Zn-xAl alloys [wt.%].

Alloy	Image	Sn	Zn	Al	O
Sn-9Zn-0.7Al	Fig. 3a (1)	77.53	11.70	1.41	9.36
Sn-9Zn-0.9Al	Fig. 3b (2)	44.09	22.75	1.77	31.39

According to given in Fig. 3a and b SEM images, it could be understood that shiny regions with light colour were oxides based on both the EDS and the XRD analysis. Melting temperature of Sn-9Zn eutectic alloy was so close to the Sn-Pb solder alloy. However, Zn is active to the oxidation and it causes solder surface to oxidize easily by reducing surface tension and by reducing wettability of Sn-Zn solders during dropping [10]. Figure 4 exhibits contact angle results of the Sn-9Zn-xAl (0.5-0.9Al) alloys at 215 °C.

According to the contact angle measurement results of Sn-9Zn-xAl (0.5-0.9Al) alloys given in Fig. 4 with respect to 215-230-250 °C, it was determined that addition of Al into the Sn-9Zn lead-free solder alloy adversely influenced wettability. The main cause of this was that addition of Al and increasing temperature resulted in formation of SnO, ZnO, and Al₂O₃ phases as accompanied by atmospheric environment.

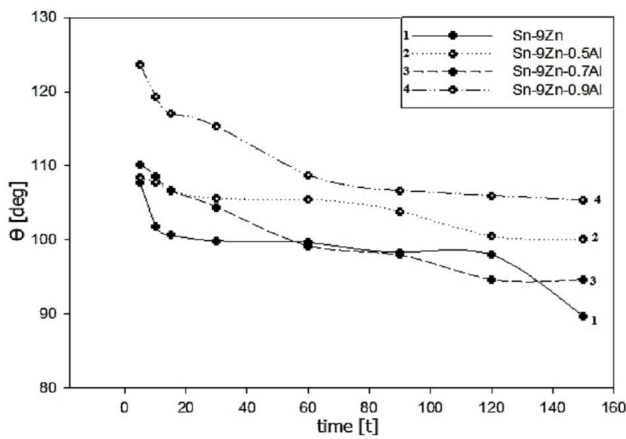


Fig. 4. Wetting results of the Sn-9Zn and the Sn-9Zn- x Al at 215 °C.

4. Conclusion

Sn-9Zn alloys exhibit lamellar eutectic structure. In microstructure examinations, it was determined that there were Zn-rich regions formed in the structure (acicular and dark-colored regions); and that addition of Al thinned these Zn-rich regions. Furthermore, oxidations were formed in the Sn-9Zn- x Al alloys at three different temperatures (SnO, ZnO, and Al₂O₃) (white

and shiny regions). As a result of the characterization studies (SEM, EDS, and XRD), wetting capabilities of Sn-9Zn and Sn-9Zn- x Al alloys were at low level due to oxidization.

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