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Wetting of Al pads by Sn–8.8Zn and Sn–8.7Zn–1.5(Ag, In) alloys

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Abstract Wetting of Al (99 %) pads by Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag (wt%) alloys was studied by means of the sessile drop method. The tests were carried out at 250 °C, using Amasan ALU33® flux, for up to 60 min. We used a setup that allows fast transfer of a sample to and from the hot zone of the furnace. Solidified alloy-substrate couples were cross sectioned and examined by scanning electron microscopy and energy dispersive X-ray analysis. The studied alloys wet Al pads as the wetting angles, determined after cleaning the flux residue from solidified alloy-substrate couples, are lower than 35 degrees. Wetting angles of Sn–8.7Zn–1.5Ag (wt%) alloy are higher and wetting areas are smaller than those of the remaining alloys, possibly due to a small gap between the melting and test temperatures. There is no clear dependence of the wetting angle and spreading area on time. Microstructures of cross-sectioned samples indicate that alloys dissolve the substrate and penetrate along grain boundaries. Since there is no significant difference between the same solder/Al interfaces at different wetting times, it is assumed that the microstructure evolves in <5 min.

Introduction

The soldering of aluminum to aluminum and other metals [1, 2] is of great practical importance because of its broad range of applications. Aluminum is a low-density durable metal of high electrical and thermal conductivity. It is therefore suitable to be used in the manufacture of parts of heat exchangers such as air conditioners, radiators in electronic devices, etc. [2]. However, the soldering of aluminum is not an easy task due to the thin oxide film which forms immediately on fresh aluminum surfaces exposed to air. Typically, liquid metals and alloys do not wet aluminum until this oxide film is destroyed. Al–Si eutectic alloy is often used for brazing aluminum at temperatures above 500 °C [3]. Unfortunately, these temperatures are rather high considering the melting temperature of aluminum (660 °C), also brittle Si-rich precipitates tend to form in such joints. More recently, ultrasonic-assisted soldering was proposed [4], yet this technique cannot easily be applied to the commonly used soldering equipment. Alternatively, the soldering of aluminum can be achieved using solders based on Sn or Zn [5] and a specific flux with the Sn-based solders being the preferred choice due to their lower melting temperature. Sn–Zn near-eutectic solders are particularly interesting because of their low melting temperature (~199 °C), good mechanical properties, and low cost [6]. Silver and indium are among alloying additions [7] that are supposed to further improve the wetting properties of Sn–Zn alloys. Recently, Huang et al. [2] studied reflow-soldered aluminum–copper joints obtained with Sn–9Zn–*x*Ag solders at a reflow temperature of 260 °C. They found that the solder/3003 Al (98.8 wt% Al) interface was not smooth with fine Zn and coarsened $AgZn_3$ precipitates in the Sn-rich matrix and with some Al particles detached from the substrate. Wang et al. [1] found the Sn–9Zn/Al interface to be smooth after hot-dipping 6061 Al bars (98 wt% Al) for 5 s into a Sn–9Zn solder bath at 200 °C.

In this work, Sn–8.8Zn, Sn–8.7Zn–1.5In, and SSn–8.7Zn–1.5Ag (wt%) alloys and pure Sn (only as a reference for interfacial microstructure) are used to study the wetting of Al (99 %) substrates in the presence of flux. The aim of this work is to study the effect of wetting time on the microstructure evolution of solder/Al couples.

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Experimental

Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag (wt%) alloys and pure Sn (99.999 %) were used for a study of the wetting on Al (99 %) substrates by means of the sessile drop method (SD). Alloys were prepared by melting in proportions pure metals (99.999 %) in graphite crucibles under Ar (99.9992 %)-protective atmosphere. Such conditions were selected to avoid oxidation of the prepared alloys. Liquid alloys were sucked into quartz capillaries of uniform 2-mm inner diameter and after solidification cut in 3-mm long pieces for wetting tests. No Si was detected from EDS analysis with the theoretic detection limit of 0.1 wt% [8]. Both the samples and substrates (25 × 20 × 0.2 mm) before the wetting tests were degreased with acetone, except for degreasing the substrates were not subjected to any special surface treatment. The wetting tests were carried out at 250 °C for up to 60 min with the setup described in detail in [9]. The setup enables rapid transfer of the sample into and out of the hot zone of the furnace, allowing precise control of the hold time of the test. Wetting tests were performed using ALU33® flux applied to the solder sample and surrounding part of the substrate. The flux components are aminoethylethanolamine ($C_4H_{12}N_2O$) and ammonium fluoroborate (NH_4BF_4). According to ISO 9454-1, this is the 2.1.2-type flux, i.e., organic, water-soluble, and activated with halides. The role of the flux is to break and remove the oxide film from an aluminum surface. The reported wetting angles and spreading areas of three alloys were determined from six independent measurements on solidified samples after washing flux residue with tap water. Sn/Al couples were only subjected to microstructure characterization. After the wetting tests, selected solidified solder/substrate couples were cut perpendicular to the plane of the interface, mounted in conductive resin and polished for microstructural characterization. A thin layer of carbon was sputtered on the samples' surface to protect it against oxidation. The microstructural and standardless EDS analysis was performed at 20 kV and a working distance of 10 mm by means of FEI XL30 ESEM using the Energy Dispersive X-Ray Spectrometer EDAX Genesis 4000. The DSC analysis of Sn–8.7–1.5In and Sn–8.7–1.5Ag alloys was performed using DSC DuPont 910 at a heating rate of 10 °C/min.

Results and discussion

Wetting behavior

Figure 1 presents the wetting angle between the alloys and the Al substrate, determined on solidified samples after cleaning the flux residue, while Fig. 2 shows the area of the substrate covered by spread solder. The angles are lower than 35° (Fig. 1) which indicates very good wetting, according to the classification of wetting given by Klein-Wassink [10]. Of the samples that are the subjects of this study, the angles of alloys containing Ag are significantly higher than those of the remaining alloys (Fig. 1), whereas its spreading area after 5 min of wetting is the smallest; after 60 min of wetting, it is nearly the same as the spreading area of Sn–8.8Zn and Sn–8.7Zn–1.5In alloys (Fig. 2). On the other hand, Huang et al. [2] determined spreading areas of Sn–9Zn–*x*Ag solders on Al substrates and found that the spreading area of Sn–9Zn–1.5Ag solder is larger than the spreading areas of Sn–9Zn and Sn–9Zn–*x* Ag solders containing 1, 2, and 3 wt% of Ag. According to a literature survey, there are no data on wetting angles of Sn–Zn–(Ag, In) alloys on Al substrate to compare with. The reason for the different wetting behavior of the Sn–8.7Zn–1.5Ag alloy might be that the addition of silver increases the melting temperature of Sn–Zn thus reducing the gap between the melting temperature of a solder and the soldering temperature [11]. Another reason for the higher wetting angle and smaller spreading area of

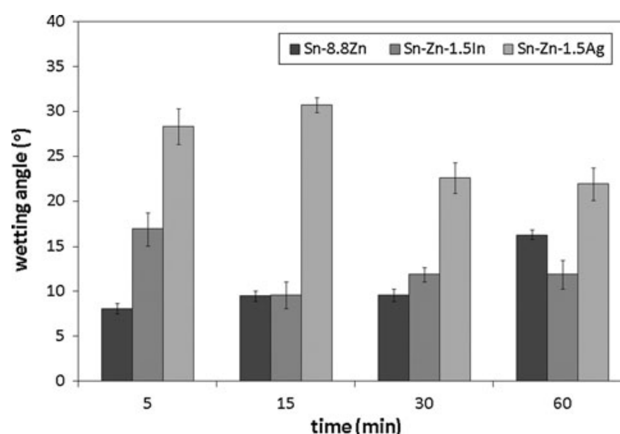

Fig. 1 Wetting angles of Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag on aluminum after wetting at 250 °C for 5, 15, 30, and 60 min

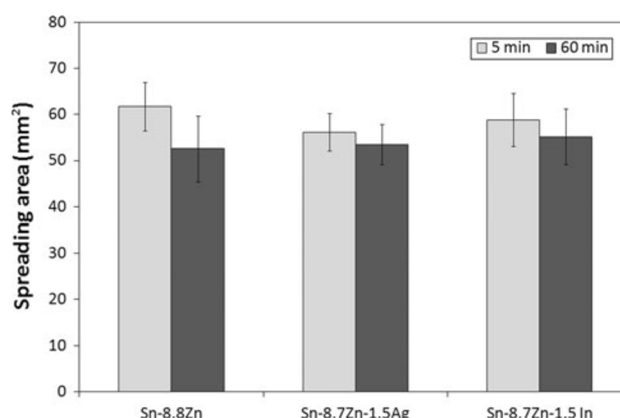

Fig. 2 Spreading area of Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag on aluminum after wetting at 250 °C for 5 and 60 min

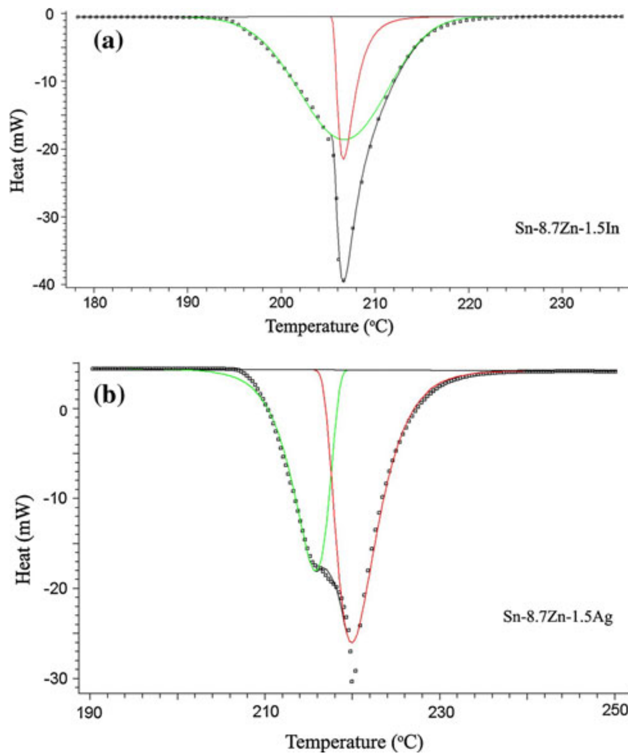

Fig. 3 DSC curves for the solders: **a** Sn–8.7Zn–1.5In, **b** Sn–8.7Zn–1.5Ag. *Squares* denote experimental data, *green* and *red lines* denote separated peak-1 and peak-2, respectively (Color figure online)

Sn–8.7Zn–1.5Ag solder might be its higher viscosity compared to other solders due to the small difference between liquidus and soldering temperature. The liquidus temperatures of Sn–8.7–1.5In and Sn–8.7–1.5Ag alloys calculated based on the data from the SOLDERS database [12] are 207.3 and 299.8 °C, respectively. DSC measurements were run for both alloys and the DSC curves shown in Fig. 3 were analyzed with the software provided by the producer of the DSC calorimeter. Complex peaks shown in Fig. 3 were separated with Fraser transform and the data obtained from this separation are presented in Table 1, where the endset of peak-2 corresponds to the liquidus temperature. According to the present DSC results, liquidus temperatures of both alloys are 209.1 and 226.1 °C, respectively. Good agreement is found between the experimental and calculated values for Sn–8.7–1.5In; while for the Sn–8.7–1.5Ag alloy, the experimental and calculated values disagree. In fact, our result for Sn–8.7–1.5Ag is much closer to the 207.3 °C reported for Sn–9Zn–1.5Ag solder [2].

Interfacial microstructure

The microstructure of the cross-sectioned solder/Al interfaces after 5 and 60 min of wetting are shown in Fig. 4a, b Sn–8.8Zn, Fig. 4c, d Sn–8.7Zn–1.5In, Fig. 4e, f Sn–8.7Zn–1.5Ag, respectively. In Fig. 4g, h, the Sn/Al interface obtained in the same wetting conditions is shown for comparison. There are no intermetallic compound layers formed at the alloy/Al interface, and the interface is not smooth due to the dissolution of Al by the solders, which is confirmed by EDS analysis (Table 2). We have also observed dissolution of Al substrate by the Sn–8.8Zn alloy in our preliminary work [13]. It is well seen, particularly in Fig. 4a, c, that the solders groove and penetrate the substrate along the grain boundaries, which in some cases leads to the detachment of Al grains from the substrate. It should be noted that the concentrations of Al in the solders along Al grain boundaries (points A1, D1, G1, and H1) are higher than expected since at 250 °C maximum solubility of Al in Sn and Al in Sn–9Zn alloy is <1 wt% [14]. The interaction volume at 20 kV is relatively large which means it is likely that, in some spots, the signal was also collected from the surrounding volume. This, and the fact that standardless analysis can include errors up to 20 %, means that the EDS results (Table 2) in the vicinity of grain boundaries are qualitative rather than quantitative.

Detachment of Al grains from the substrate was observed before by Huang et al. [2] in the case of the Sn–9Zn–Ag/3003 Al interface and by Li et al. [15] in the case of the Sn/2024 Al interface. Although we could observe what appears to be Al grains separated from other grains by solders, we did not observe the migration of Al grains toward the bulk of solders reported by Li et al. [15] for 2024 Al alloy substrate and liquid Sn. Such migration of grains toward the bulk of Sn solder is likely due to the much lower density of Al in comparison with liquid Sn. It seems, regardless of higher temperature of soldering [15], that stirring of the liquid Sn in the case of ultrasonic-assisted soldering [15] is causing the migration of grains. The depth of most of the grooves in Fig. 4 (perpendicular to the interface) does not exceed 10 µm, but there is no clear difference between wetting times of 5 and 60 min.

Table 1 DSC measurement results of the Sn–8.7Zn–1.5In and Sn–8.7Zn–1.5Ag alloys

Alloy	Peak separation	Part area (%)	Onset (°C)	Endset (°C)
Sn–8.7Zn–1.5Ag	Peak-1 (green line)	39.2	210.4	218.6
	Peak-2 (red line)	60.8	216.7	226.1
Sn–8.7Zn–1.5In	Peak-1 (green line)	80.0	197.1	215.7
	Peak-2 (red line)	20.0	205.5	209.1

Peaks separated with Fraser transform

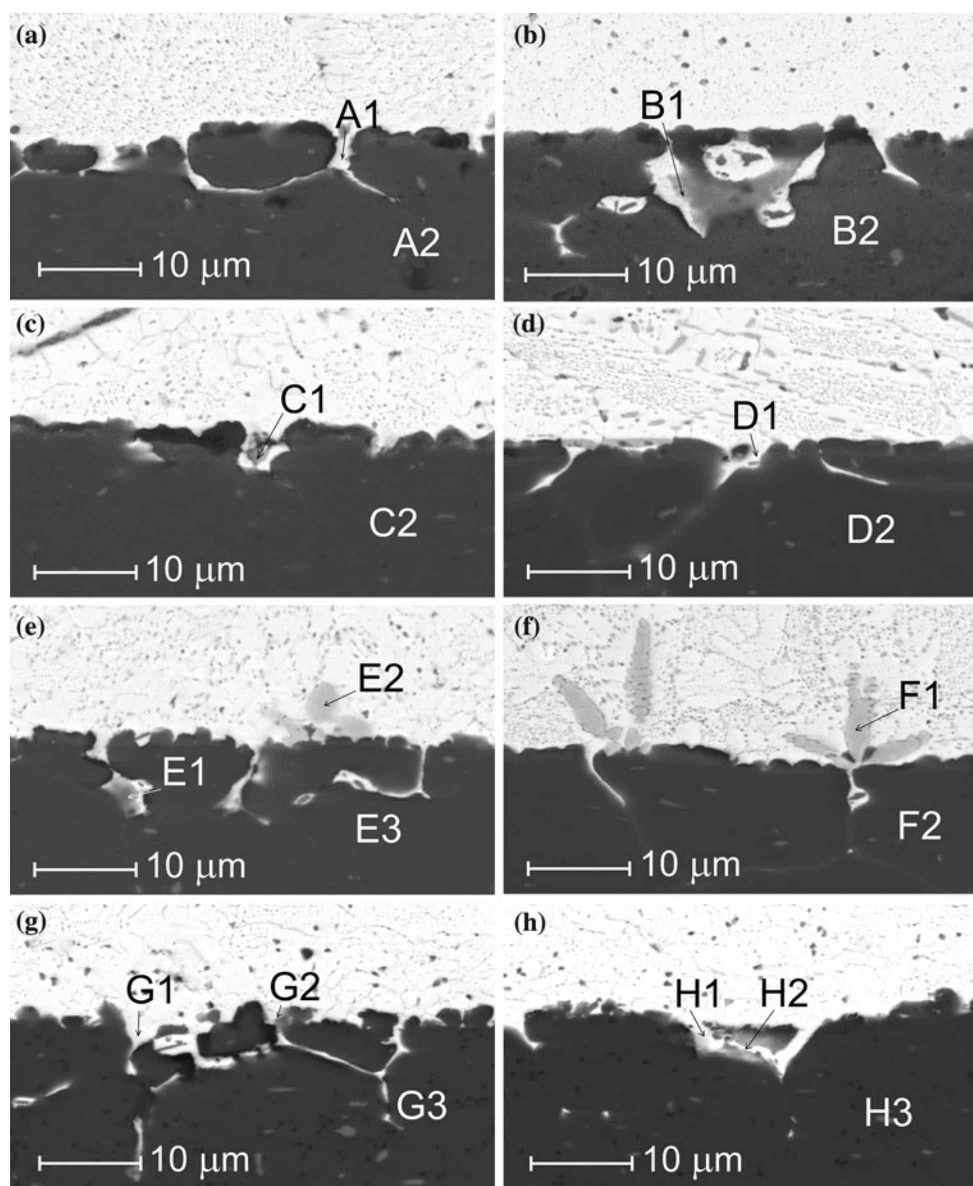

Fig. 4 BSE micrographs of solder/Al interface, respectively: **a** Sn–8.8Zn/Al, 5 min; **b** Sn–8.8Zn/Al, 60 min; **c** Sn–8.7Zn–1.5In/Al, 5 min; **d** Sn–8.7Zn–1.5In/Al, 60 min; **e** Sn–8.7Zn–1.5Ag/Al, 5 min; **f** Sn–8.7Zn–1.5Ag/Al, 60 min; **g** Sn/Al, 5 min; **h** Sn/Al, 60 min

In the case of Sn–8.8Zn and Sn–8.7Zn–1.5In alloys, there are large needle-like precipitates of Zn with small dissolution of Al. In the case of Sn–8.7Zn–1.5Ag/Al couples, discontinuous precipitates of $AgZn_3$ intermetallic compound with some Sn dissolved are observed. Some of those precipitates are adjacent to the interface, while others are detached (Fig. 4f). Song and Lin [16] studied the behavior of intermetallics in liquid Sn–8.87Zn–1.5Ag solder. In the samples isothermally heated at 250 °C for up to 60 min, they observed sedimentation of the intermetallic precipitates ($AgZn_3$ and Ag_5Zn_8) in time. In the absence of stirring that would affect the movement of precipitates, they tend to move toward lower region of the melt because of a density higher than that of Sn–Zn melt [16]. Our findings on the interfacial microstructure of Sn–8.8Zn and Sn–8.7Zn–1.5Ag alloys on Al substrate are in agreement with microstructures observed by Huang et al. [2] although in their case substrates were in contact with liquid solders for at most 2 min, depending on the solders melting temperature. The fact that the interface after 60 min of wetting (b, d, f, h) does not differ much from the interface after 5 min of wetting (a, c, e, and g) indicates that the observed interfacial microstructure evolves in <5 min of wetting. Also, obvious similarities of the solder/Al interfaces and that of Sn/Al suggest that it is Al dissolution in liquid Sn which is responsible for the interfacial microstructure evolution.

Table 2 The results of EDS analysis of Sn–8.8/Al, Sn–8.7Zn–1.5In/Al, Sn–8.7Zn–1.5Ag/Al, and Sn/Al couples in the points indicated in Fig. 4

Point	Composition (wt%)				
	Al	Sn	Zn	Ag	In
A1	11.8	82.5	5.7		
A2	100.0				
B1	12.5	82.4	5.1		
B2	100.0				
C1	10.7	80.8	5.3		3.2
C2	100.0				
D1	4.5	89.1	4.3		2.1
D2	100.0				
E1	22.3	72.7	5.0		
E2		3.2	70.1	26.7	
E3	100.0				
F1		4.9	67.8	27.3	
F2	100.0				
G1	4.0	96.0			
G2	10.3	89.7			
G3	100.0				
H1	5.7	94.3			
H2	9.1	90.9			
H3	100.0				

Conclusion

A study of wetting of aluminum by Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag alloys was performed by means of the sessile drop method at 250 °C for a wetting time of 5–60 min. The tests were performed in the presence of ALU33® flux. The studied alloys wet aluminum as the wetting angles, determined after cleaning the flux residue from solidified alloy-substrate couples, are lower than 35°. Wetting angles of Sn–8.7Zn–1.5Ag (wt%) alloy are higher and spreading areas are smaller than those of Sn–8.8Zn and Sn–8.7Zn–1.5In alloys. The different wetting behavior of Sn–8.7Zn–1.5Ag alloy is caused by the small difference between the melting and test temperatures and possibly by the higher viscosity of the liquid alloy. Under the present experimental conditions, alloys and Sn dissolve the Al substrate, but there is no clear difference between short (5 min) and long (60 min) wetting time. Based on the present results and literature data, it can be assumed that the interfacial microstructure of Sn–8.8Zn, Sn–8.7Zn–1.5In, and Sn–8.7Zn–1.5Ag on Al substrates evolves in <5 min. However, this should be further investigated in future studies.

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