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DOI	http://dx.doi.org/10.12739/NWSA.2017.12.4.2A0123
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WETTING BEHAVIORS AND INTERFACIAL PROPERTIES OF SAC300, SAC305 AND SAC0307 TERNARY Pb-FREE SOLDER ALLOYS

ABSTRACT

The wetting behavior and interfacial properties of molten SAC300, SAC305 and SAC0307 (Sn-Ag-Cu) Pb-free solder alloys were investigated by sessile drop technique at various temperatures (250, 280 and 310°C) on Cu substrate in Ar atmosphere, as well as its dependence on time. The contact angles of the Pb-free solder alloys on Cu substrate do not decrease sharply with increasing temperature but change with time. The contact angles were measured for SAC305, SAC300 and SAC0307 alloys and the lowest θ was obtained as 41.90° for SAC305 alloy at 310°C. The melting temperatures were examined which for SAC305 Pb-free alloy is lower than those for SAC300, SAC0307 Pb-free alloys. The formation of intermetallic compounds (IMC) between the Pb-free solder alloys and the Cu substrate was observed.

Keywords: Pb-free Solder Alloy, Contact Angle, Sessile Drop Technique, IMC

1. INTRODUCTION

Due to polluting effects on environment and harming human health, the electronics industry is also enforced by RoHS directive of European Union to reduce the usage of toxic substances [1]. Because of the toxicity of the traditional Sn-Pb solder alloy, researchers have actuated widely to find alternative Pb-free solder alloys especially suitable for electronics industry [2]. The solders with high-melting temperatures are effectively used in electronics industry and device manufacturing [3]. In modern microelectronic technology, soldering plays an important role. In both of circuit-board and flip-chip technologies, solder is used to connect apparatus to printed-circuit boards. In the soldering process, the molten solder and metal surface are connected to each other with a metallurgical bond [4]. Thus, the ability of molten solder alloys to flow or spreading on the solid metal surface is important for the formation of healthy metallurgical bond. The phenomenon of liquid spreading on a solid surface is also referred as wetting. In fact that, wettability is defined as the tendency for liquid to spread on a solid surface [4 and 6]. The solderability is directly related to the wettability of two surfaces being joined. The efficiency of manufacturing and reliability of electronic devices depend upon the quality of solderability thus wettability [7]. Wettability generally involves the measurement of contact angles as the primary data, which specifies the degree of wetting when a solid and liquid interact. Thus, the measurement of the contact angle gives an estimate on wetting behaviour. To determine the wettability of a solid metal substrate by molten solder alloy, Young's equation is conventionally used:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

How to Cite:

Erer, A.M., (2017). Wetting Behaviors and Interfacial Properties of SAC300, SAC305 and SAC0307 Ternary Pb-Free Solder Alloys, **Technological Applied Sciences (NWSATAS)**, 12(4):163-169, DOI:10.12739/NWSA.2017.12.4.2A0123.



where θ is the contact angle in degree; γ_{sv} is the surface tension of the solid-vapour; γ_{sl} is the surface tension between the liquid and the solid; γ_{lv} is the surface tension of the liquid-vapour. A small contact angle ($<90^\circ$) corresponds to high wettability, while the large contact angle ($>90^\circ$) corresponds to low wettability [8]. A Pb-free solder alloy drop spreads to enlarge on the Cu substrate and comes to rest making an angle. Under equilibrium conditions this angle is called contact angle which is decided by the surface and interfacial tensions. It is usually accepted that the smaller the contact angle, the better the wettability. The process of wetting and spreading includes the flow of fluid over the surface of a solid. That flow is influenced by number of factors such as viscosity, work of adhesion, melting temperature, thickness of intermetallic compounds (IMCs), surface tension and spreading, etc [9]. The formation and growth of IMCs between molten solder alloy and substrate have influence on the efficiency of Pb-free solder alloys [10]. In order to attain perfect wettability of Pb-free solder alloys as substitutes for Sn-Pb solder alloys, Sn-Ag-Cu Pb-free alloy systems have been studied in the previous works [1, 5, 6, 9, 11, 13, 16, 18, 20, 21, and 23]. However, the effects of contact angles and interfacial reactions on wettability must also be compared. The purpose of this work is to investigate and to compare the wettability of SAC300, SAC305 and SAC0307 Pb-free solder alloys on Cu substrate in Atmosphere at various temperatures 250, 280 and 310°C.

2. RESEARCH SIGNIFICANCE

Wetting behaviours of SAC300, SAC305 and SAC0307 Pb-free solder alloys on Cu substrate were investigated by these sessile drop technique in Ar atmosphere. Interfacial properties were also investigated for the Pb-free solder alloys. It was seen that two intermetallic layers (Cu_6Sn_5 and Cu_3Sn) were commonly found at the interfacial zone of Sn-Ag-Cu Pb-free solder alloys and the Cu substrate. According to DSC analysis results, SAC305 alloy has the lowest melting temperature (217,8 °C) than other alloys. The experimental results showed that equilibrium contact angles (θ) proportionally decreased with increasing temperature and time. The lowest θ was obtained as 41,90° for SAC305 alloy at 310 °C. Thus, the SAC305 alloy exhibits better wetting behaviour than the SAC 300 and SAC0307 alloys.

3. MATERIALS, EXPERIMENTAL PROCEDURES AND METHOD

In this study, SAC300, SAC305 and SAC0307 Pb-free solder alloys and oxygen-free Cu were chosen as the soldering materials and the substrate, respectively. The chemical compositions of the studied Pb-free solder alloys are listed in Table 1.

Table 1. Chemical composition of Pb-free solder alloys (wt.%)

Pb-free alloys	Ag	Cu	Sb	Bi	Pb	As	Sn
SAC300	3.05	0.05	0.12	0.1	0.1	0.03	Rest
SAC305	2.98	0.52	0.1	0.1	0.1	0.03	Rest
SAC0307	0.35	0.73	0.05	0.05	0.1	0.01	Rest

The sessile drop technique was used in the wettability testing's [2 and 13]. By means of this technique, the SAC300, SAC305 and SAC0307 solder alloy was dropped on copper substrate at various temperatures of 250, 280 and 310°C. Casio Pro EX-F1 (1200 fps) Model camera used to catch views of drops at the 5th, 10th, 15th, 30th, 60th, 90th, 120th, and 150th seconds and these images were transferred into AutoCAD 2010 to measure contact angles of each drop from the right and left profiles [11]. As a result of these processes repeated for each



temperature, mean angle values were calculated and new diagrams were drawn through the Sigma Plot 12.0 Software. Standard metallographic processes were carried out for microstructure examinations. Prepared specimens were etched with 100ml H₂O, 2ml HCl, 10g 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). In order to determine melting temperatures of alloys, the DSC analysis were carried out on specimens in maximum 30mg weight and at 40-300°C temperature range (5 min). The morphology of the interface of Sn-Ag-Cu/Cu was also analysed.

3. RESULTS AND DISCUSSIONS

3.1. Temperature effects on contact angle

Figure 1 shows the relationship between the contact angle and the temperature and the time. For SAC300, SAC305 and SAC0307 Pb-free solder alloys, the contact angle does not decrease suddenly with temperature but changes with time. A sharp decrease in the contact angle is observed for the Pb-free solder alloys at each temperature for approximately the first 30 s. The values of contact angle exhibit the degree of wettability [14]. Table 2 lists the equilibrium contact angles of the SAC305 Pb-free solder alloy on Cu substrate at each temperature for the present work and for the others reported elsewhere.

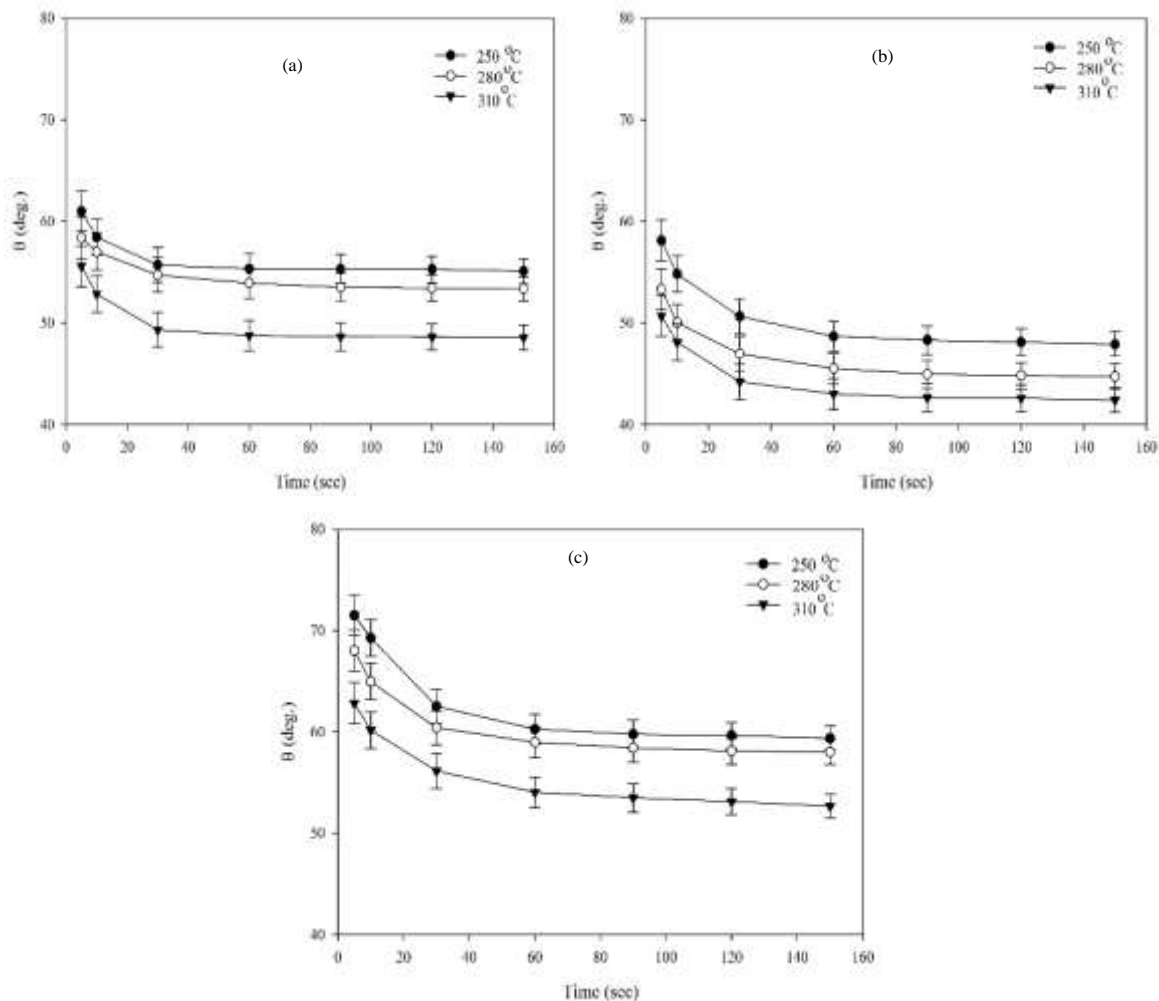


Figure 1. Time dependence of the contact angle of molten Pb-free solder alloys on Cu substrate at various temperatures for (a) SAC300, (b) SAC305 and (c) SAC0307

Table 2. The equilibrium contact angles of SAC305 Pb-free solder alloy on Cu substrate at each temperature

Pb-free Alloy	Contact Angle								Ref.
	217°C	230°C	250°C	280°C	300°C	310°C	350°C	400°C	
SAC305	53.5°	-	-	-	-	-	-	-	10
	-	32.5°	29.3°	-	27.3°	-	-	26.65°	15
	53.5°	-	49.6°	-	47.2°	-	47.2°	-	16
	-	-	49.1°	45.1°	-	41.9°	-	-	P.Work

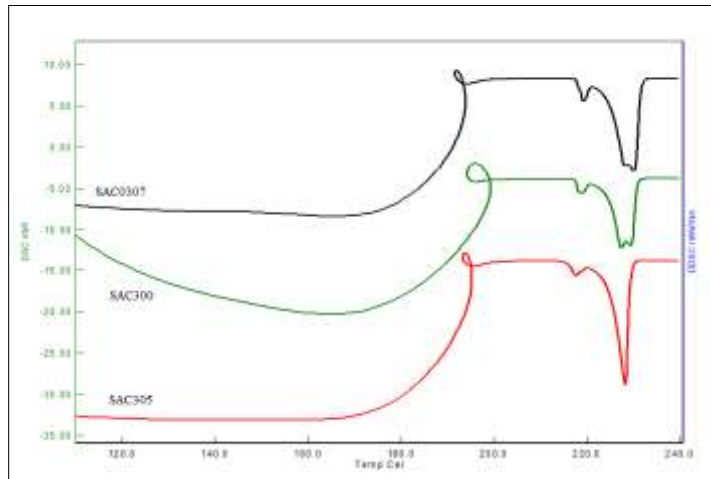


Figure 2. DSC analysis results of SAC300, SAC0307 and SAC305 alloys

Figure 2 shows DSC analysis results of SAC300, SAC0307 and SAC305 alloys. As can be seen from Figure 2 that the melting temperature of SAC305 is lower than those of SAC300 and SAC0307. Besides, due to its lowest melting temperature (217.8°C) [10, 12, 15, and 22], SAC305 has the longest wetting time (90s) [12]. Thus, the wettability of SAC305 Pb-free solder alloy is better than those of SAC300 and SAC0307 Pb-free solder alloys.

3.2. Interfacial Properties

During the soldering process, SAC300, SAC305 and SAC0307 Pb-free solder alloys melt and get into contact with Cu substrate. Furthermore, Sn in the molten solder alloys reacts with Cu to form intermetallic compounds (IMCs) on the interface. The IMCs promote the bonding between the solder alloys and Cu [16 and 23].



Figure3. SEM images of the Pb-free solder/Cu interface at 310°C on Cu substrate for (a) SAC300 (b) SAC305 and (c) SAC0307

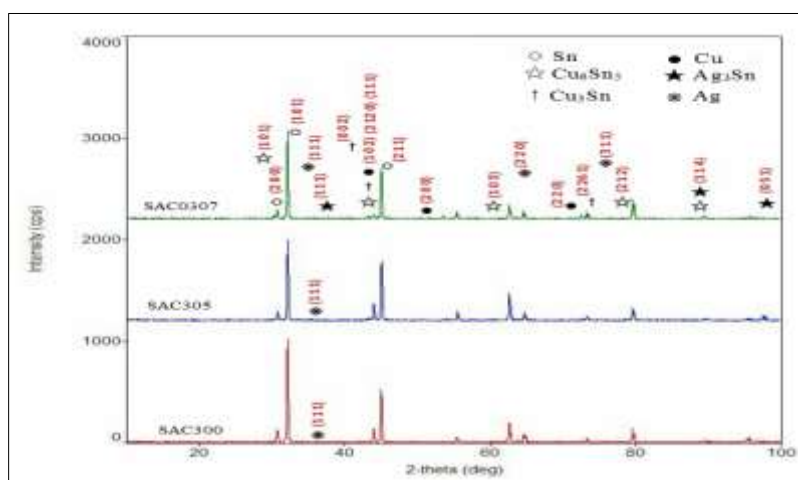
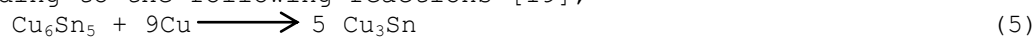


Figure4. XRD analysis results of SAC300, SAC305 and SAC0307 Alloys

From SEM and XRD analysis given in Figure 3a-c and Figure 4, Cu-Sn IMCs are seen in the Pb-free solder alloys and Cu interface. Interfacial reactions between the Cu substrate and the three molten Pb-free solder alloys of SAC300, SAC305 and SAC0307 lead to two types of IMCs, Cu_6Sn_5 and Cu_3Sn . While the Cu_6Sn_5 is adjacent to the solder alloys, the Cu_3Sn is adjacent to the Cu substrate [4, 17 and 18]. The scallop type Cu_6Sn_5 was formed through the interfacial reactions between Sn-Ag-Cu/Cu systems. The formation of Cu-Sn IMCs is realised by the continuous growth of Cu_6Sn_5 . On the other hand, the formation and growth of Cu_3Sn is realised in the interface of Cu_6Sn_5 and Cu substrate. The formation of Cu_3Sn is controlled by the phase stability according to the following reactions [19];



Vianco [19] reported that Cu_6Sn_5 intermetallic was formed during soldering and Cu_3Sn was formed during solid-state ageing between Cu_6Sn_5 and Cu substrate. It is clear that the thickness of IMCs is established by the relative movement of two interfaces; IMCs/liquid solder and solid/IMCs [21]. Lee and Mohamad [21] reviewed the reactions of Sn-Ag-Cu/Cu interface in detail and mentioned the importance of Sn-Ag-Cu Pb-free solder alloys in electronic industry. They concluded that thin, continuous and uniform IMC layers are main requirement for good bonding. Without IMCs, the solder/substrate interface is poor as metallurgical interaction does not take place in the bonding. Nevertheless, thick IMCs at the solder/substrate interface may reduce the reliability of the solder interface because of their inherent brittle nature. In addition, thick IMCs are likely to lead to structural defects which deteriorate the physical properties. Both the Cu_6Sn_5 and Cu_3Sn intermetallic phases were found at the interface depending on soldering conditions. It is expected that the thickness of Cu_3Sn is smaller than Cu_6Sn_5 . That is because Cu_3Sn is grown by solid-state diffusion. Chen et al. [23] investigated the available phase diagrams of Pb-free solders, and the materials systems including the solders and the substrates. They stated that the thick IMC layer should be avoided during the soldering. The authors concluded that increasing IMCs thickness results from increasing soldering time. Thus, the Cu_3Sn thickness increases with decreasing Cu_6Sn_5 thickness despite the fact that Cu_6Sn_5 generally grows with increasing soldering time [24].

4. CONCLUSION

In summary, wetting behaviours of SAC300, SAC305 and SAC0307 Pb-free solder alloys on Cu substrate were investigated by this sessile



drop technique in Ar atmosphere. Interfacial properties were also investigated for the Pb-free solder alloys. It was seen that two intermetallic layers (Cu_6Sn_5 and Cu_3Sn) were commonly found at the interfacial zone of Sn-Ag-Cu Pb-free solder alloys and the Cu substrate. According to DSC analysis results, SAC305 alloy has the lowest melting temperature (217.8°C) than other alloys. The experimental results showed that equilibrium contact angles (θ) proportionally decreased with increasing temperature and time. The lowest θ was obtained as 41.90° for SAC305 alloy at 310°C . Thus, the SAC305 alloy exhibits better wetting behaviour than the SAC 300 and SAC0307 alloys.

ACKNOWLEDGEMENTS

This work was supported by Scientific Research Projects Coordination Unit of Karabük University. Project Number: KBÜBAP-17-YD-314.

NOTE

This work is presented at 5-8 September 2017, 2nd International Science Symposium (ISS2017) in Tbilisi/Georgia.

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