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Effect of Al Addition on Microstructure, IMCs and Wettability of Sn-2Ag-0.5Cu-1In-xAl Lead Free Solder Alloy

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Abstract. The present study investigated the effect of adding a small amount of Al on the wettability, microstructure, formation of intermetallic compounds (IMC'S) and melting temperature of SAC205-1In lead free solder alloys, the quinary lead free solder alloys SAC205-1In-(x)AL with (x = 0.3 wt.%, 0.5 wt.%, 0.7 wt%, 0.8 wt%, 0.9 wt%) were produced. The X-ray diffraction results (XRD) showed the formation of new IMCs into the alloy at the SAC205-1In-xAl/Cu interface; intermetallic compounds of Cu_3Sn, Cu_6Sn_5, Ag_3Sn, Ag_3Al, Ag_2Al, Al_2Cu and Cu-Al were observed. According to the scanning electronic microscope (SEM) analysis, the intermetallic components generated at the interface of each lead free solder alloy grew increasingly apparent as the temperature value increased. The contact angles of the Pb free solder alloys on the copper (Cu) substrate were measured using the sessile drop technique at specified temperatures (275 °C, 300 °C and 325 °C). The wetting tests' findings indicate that adding aluminum (Al) improves the Sn-2Ag-0.5Cu-1In solder's wetting characteristics. According to the study, SAC205-1In-0.3Al showed the best wettability among all solder alloys produced on a Cu substrate at a temperature of 325°C. By optimizing Sn-Al in the range of 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, 0.8 wt.% and 0.9 wt. % and also possible to reduce the production cost of solder alloys.

Keywords: wettability, sessile drop method, melting temperature, microstructure

Introduction

Sn-Pb solder alloys have been used mainly in electrical and electronic equipment. However, due to lead toxicity, they are being retired. As a response to the directives of restriction of hazardous substances (RoHS) starting in July 2006 (Gancarz *et al*, 2013; Waste Electrical and Electronic Equipment, 2012). Lead can accumulate in the body over time by binding to proteins and interfering with normal bodily functions (Monsalve, 1984). Over the past two decades, lead free solder materials have been the focus of significant growth in the electronics industry (Ismail *et al*., 2022). Several alloying elements and nanoparticles are added to (tin-silver-copper) SAC solders for improved characteristics, including In, Ti, Fe, Zn, Bi, Ni, Sb, Ga, Al and rare earths (Sun and Zhang, 2015). The wetting test results indicate that adding 1wt% of Indium (In) enhances the wetting characteristics of SAC305 alloy. (Erer and Uyanik, 2019). In the SAC-In/Cu contact, intermetallic compounds of Cu_3Sn, Cu_6Sn_5 and Ag_3Sn were observed. The additions of Bi and Sb to the ternary SAC solder alloy were used to test the surface tension and contact angle as a metric for wettability (Moser *et al*., 2008). Dheeraj Jaiswal, Dileep Pathote, Vikrant Singh and Behera investigated the effect of Al adding on the electrochemical behaviour of Sn0.7Cu-xAl (x = 0, 1, 2 and 3 wt.%). Adding (Al) to the Sn-0.7Cu alloys improved the micro-structure of the alloys (Jaiswal *et al*., 2022). As the amount of Al increased, the wettability of solders reduced but it remained within acceptable limits. Al had facilitated the construction of Ag-Al and Cu-Al IMC improved β-Sn dendrites and inhibited the growth of Ag_3Sn and Cu_6-Sn_5 IMC (Maslinda *et al*., 2016). According to reports, the SACBi-0.1Al solder alloy offers the best wetting angle (38.44 at 325 °C) and melting temperature (212.5 °C). Upon examining the micro-structural properties, it is observed that the CuAl IMC phase, which is rich in Al which has replaced Cu_6Sn_5 and Ag_3Sn IMCs (Oguz and Erer, 2023). It has been observed through differential scanning calorimeter analysis (DSC) measurements that the melting point of SAC decreases with the addition of indium (Fallahi *et al*., 2012). Aluminum enhances the wettability of the Sn-Cu-Al solder alloy (Yang *et al*., 2015). According to the investigations presented, the wettability of the SAC105 solder alloy on the Cu substrate is moderately improved by adding Al (Sabri *et al*., 2015). The addition of Al has reduced the undercooling of SAC105 solder. Cu_3A_{12} IMC was identified by adding 0.1 and 0.5 wt%

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Al to SAC105 (Leong, and Haseeb, 2016). The SAC105 solder's melting point does not dramatically alter with the addition of Al nanoparticles but the wettability and mechanical properties of SAC105 solder have improved (Sun *et al*., 2016). This study investigates the effects of aluminum addition on the wettability of the Pb-free solder alloy SAC205-1In and to produce quinary lead free solder alloy ((96.5-x)wt.%Sn–2wt.%Ag-0.5wt.%Cu-1wt.%In– (xwt.%)Al, where x = 0.3, 0.5, 0.7, 0.8 and 0.9 wt% and studying the performance of the new alloys and their physical properties, Inter-metallic phases, micro-structures and melting temperatures of alloy using XRF X-ray fluorescence analysis, X-ray diffraction (XRD), differential scanning calorimeter (DSC), scanning electron microscope and energy dispersive X-ray spectroscopy (SEM + EDX).

Material and Methods

In this study, we added varying amounts of Al (0.3 wt.%, 0.5 wt.%, 0.7 wt.%, 0.8 wt.% and 0.9 wt.%) to the SAC205-1In alloy to create quinary lead free solder alloys. We evaluated the wetting properties of these alloys using the sessile drop method. We dropped the solder alloys onto a pure copper substrate (99.85% purity) at 275 °C, 300 °C and 325 °C X-ray diffraction (XRD), scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM + EDX) were then used to evaluate the performance of the new alloy, micro-structure and IMC formation at the SACIn-xAl/Cu interface.

Results and Discussion

Figure 1 illustrates the relationship between contact angle, temperature and time. The contact angles of various solder alloys, namely SAC205-1In-0.3Al, SAC205-1In-0.5Al, SAC205-1In-0.7Al, SAC205-1In-0.8Al and SAC205-1In-0.9Al, change gradually over time instead of suddenly decreasing with temperature. The lowest average contact angle for SAC205-1In-0.3Al solder alloy at 325 °C was 42.87 and followed by SAC205-1In-0.5Al solder alloy at 43.06, SAC205-1In-0.7Al solder alloy at 50.45, SAC205-1In-0.8Al solder alloy at 43.94 and SAC205-1In 0.9Al solder alloy at 44.78. as shown in Chart 1 and Table 1.

The experiments were conducted on a solder droplet on Cu substrate at temperatures of 275°C, 300 °C and 325 °C for different solder alloys produced on Cu substrate. According to Tables 1 and 2, the lead free solder alloy SAC205-1In-0.3Al had the lowest melting temperature of 214.3 °C, as determined by diffraction scanning calorimeter (DSC) analysis. Additionally, it had the lowest contact angle rate of 42.87° at a temperature of 325 °C.

Table 1. Displays the contact angle rate of SAC205-1In-xAl at 275 °C, 300 °C and 325 °C.

Lead free solder alloys	Avg. contact angles at temperatures		
	275 °C	300 °C	325 °C
SAC205-1In-0.3Al	52.61	45.64	42.87
SAC205-1In-0.5Al	52.3	49.07	43.06
SAC205-1In-0.7Al	63.93	53.25	50.45
SAC205-1In-0.8Al	52.55	49.85	43.94
SAC205-1In-0.9Al	52.57	48.56	44.78

The influence of melting temperature at various temperatures (275°C,300 °C,325 °C) on the contact angle of lead free solder alloys SACIn-xAl (x=0.3wt.%, 0.5 wt.%, 0.7 wt.%, 0.8 wt.% and 0.9 wt.%) was investigated using the sessile drop method in an environment of argon. Due to the experimental results, equilibrium contact angles (θ) dropped proportionately as temperature increased.

Based on the DSC analysis, the melting temperature for five different SAC205-1In-XAl solder alloys was determined. The values for SAC205-1In-0.3Al, SAC205-1In-0.5Al, SAC205-1In-0.7Al, SAC205-1In-0.8Al and SAC205-1In-0.9Al which found to be 214.30 °C, 219.70 °C, 219.30 °C, 219.10 °C and 220.50 °C, respectively. As indicated in Table 2, the SAC205-1In-0.3Al alloy had the lowest melting temperature among all the alloys produced in this study and was even lower than the SAC205-1In and SAC305 alloys produced previously. The melting temperature of SAC305 and SAC205-1In ranged between 217-219 °C (Oyuz and Err, 2023; Serkan *et al*., 2022).

The XRD, SEM analysis shows the formation of IMC'S Ag_3Sn, Ag_2Al, Ag_3Al, Al_2Cu, Al Cu, Cu_3Sn and Cu_6Sn_5 onto the interface of drop solder/Cu substrate as shown in Fig. 2-7. SEM analysis was employed to analyze the IMCs produced at the solder-to-Cu substrate interface. Each IMC was investigated separately for three experimentally measured temperature values at 275°C, 300°C and 325°C. It is common knowledge that an

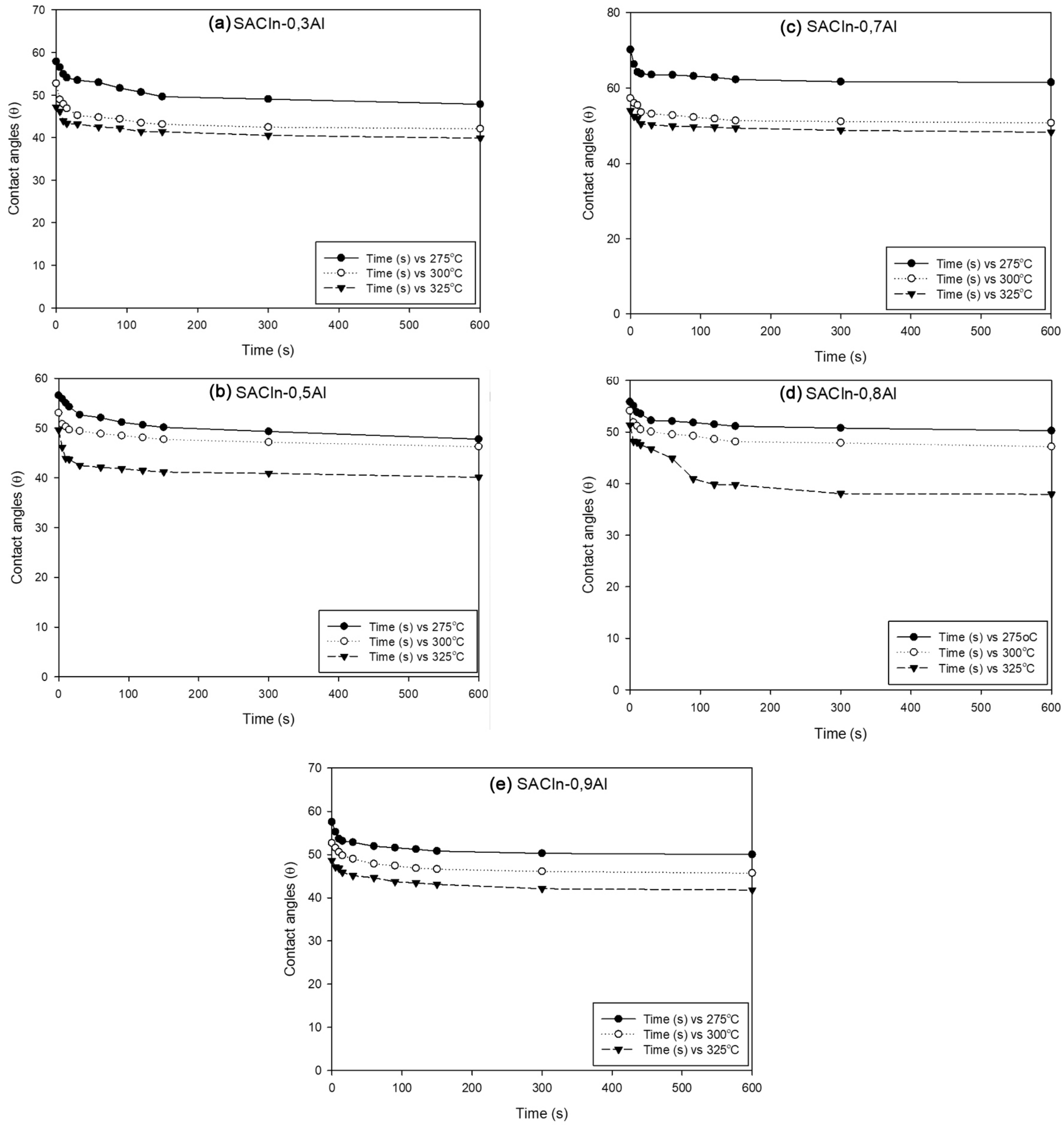

Fig. 1.(a,b,c,d,e) shows the average of contact angles (both left and right) from three positive experiments at different time intervals, including 5th, 10th, 15th, 30th, 60th, 90th, 120th, 150th, 300th and 600th sec.

alloy's mechanical performance is greatly influenced by its micro structural characteristics. Therefore, it is essential to comprehend the microstructural characteristics of the Sn-Ag-Cu-In-xAl, a quinary lead-free solder alloy, to comprehend its mechanical reliability and efficiency. Cu_6Sn_5 and Cu_3Sn are important intermetallic components in the solder alloy's mechanical properties. The primary metallic phase formed between the solder and the Cu substrate is CuSn. During the soldering process, Cu_6Sn_5 is first formed at the interface, followed by Cu_3Sn between Cu_6Sn_5 and the Cu substrate, with a lower thickness than the Cu_6Sn_5 layer. The literature indicates that the primary CuSn phases related to Al-added SAC solder alloys are suppressed and the groups of Al content inhibit the CuSn steps. It has been observed that β-Sn, CuAl and SnCu phases were formed in regions close to the Cu_6Sn_5 phase. Upon examining the SEM analyses, it was observed that the intermetallic components formed at the interface became more prominent as the temperature value increased for each

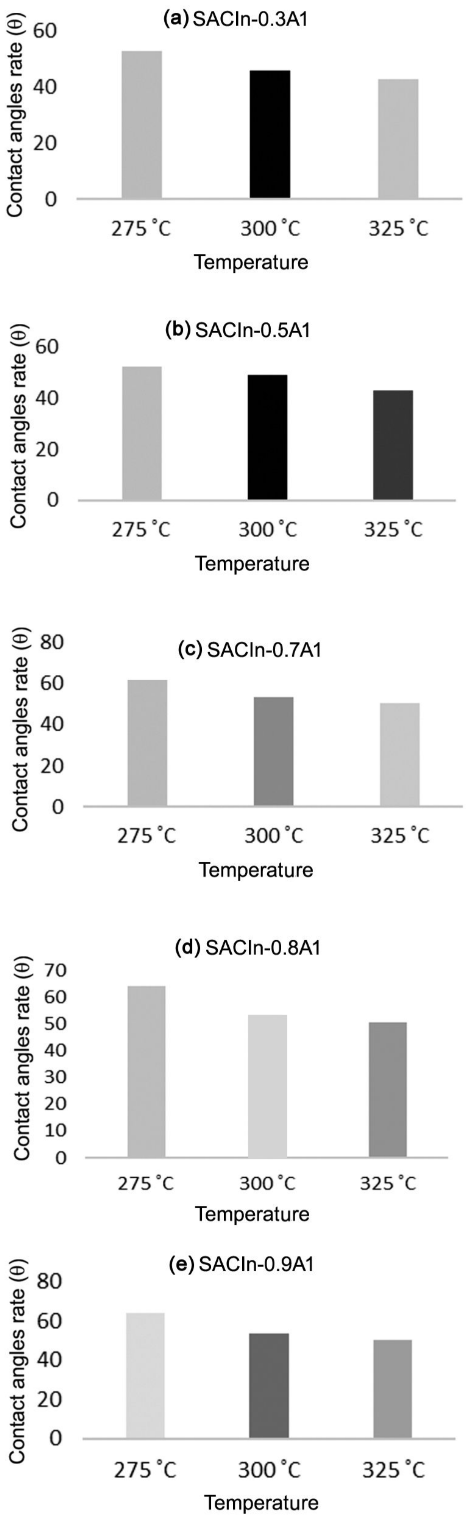

Chart 1. shows the contact angle rates of lead-free solder alloys produced at 275 °C, 300 °C, and 325 °C.15th, 30th, 60th, 90th, 120th, 150th, 300th and 600th sec.

Table 2. Shows the melting temperatures of the solder alloys SAC205-1In-xAl which was determined by DSC analysis.

Lead free solder alloys	Melting temperature °C
SAC305	219.1 (Oguz, 2023; Serkan *et al*., 2022)
SAC205-1In	217.7 (Oguz, 2023; Serkan *et al*., 2022)
SAC205-1In-0.3Al	214.3
SAC205-1In-0.5Al	219.7
SAC205-1In-0.7Al	219.3
SAC205-1In-0.8Al	219.1
SAC205-1In-0.9Al	220.5

lead-free solder alloy (Wnag *et al*., 2015; Shnawah *et al*., 2012). Dark gray structures represent the SnCu phase, black dotted structures represent the CuAl phase and white dendrite structures represent the SnAg phase. As the temperature increased, the thickness of the SnCu and CuAl phases increased and became more pronounced. Similarly, the size of the Cu_3Sn and Cu_6Sn_5 phases increased with the increase in temperature (Fig. 2-7).

The mechanical features of the joint reliability may be negatively impacted by Cu_6Sn_5 IMC (Pandher *et al*., 2007). but on its positive side, it has strong resistance to stop corrosion by creating a protection barrier on copper surfaces. Cu_3Sn IMC'S improves electrical conductivity and has a strong resistance against corrosion. Many alloys have been studied and debated in the literature as alternatives to high Ag SAC alloys. Utilizing low Ag alloys, Lower Ag leads to less Ag_3Sn IMC in the bulk alloy and a corresponding decrease in mechanical strength. It seems evident that lower Ag alloys might be more capable to withstand the effects of high strain rate deformation (Hodulova *et al*., 2011). In the bulk solder alloys, Cu-Al and Ag-Al IMC have formed faster due to the presence of Al. After forming Cu-Al and Ag-Al IMC, less Cu and Ag were available to form IMC with Sn in bulk solder (Maslinda *et al*., 2016). The excellent thermal and electrical conductivity of CuAl IMC makes it a popular choice for conductive or binding compounds. According to the SEM analyses, the intermetallic compounds generated at the interface became increasingly noticeable as the temperature value increased for each lead free solder alloy.

Conclusion

The experiment results indicated that the contact angles (θ) decreased proportionally to the temperature. At a

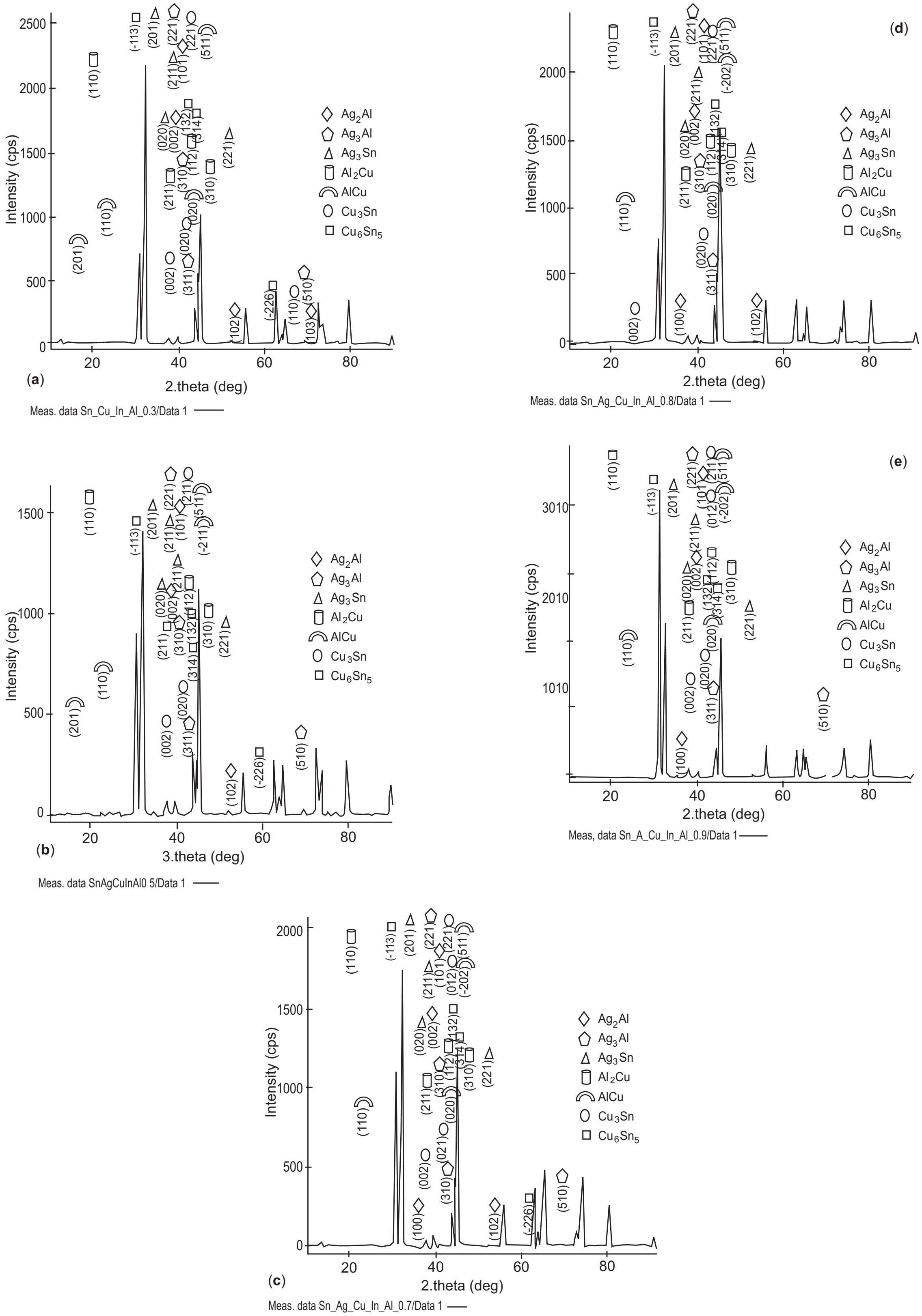

Fig. 2. XRD analysis of lead-free solder alloys SACIn-xAl shows the formation of intermetallic compounds: (**a**) SACIn-0.3Al, (**b**) SACIn-0.5Al, (**c**) SACIn-0.7Al, (**d**) SACIn-0.8Al, (**e**) SACIn-0.9Al.

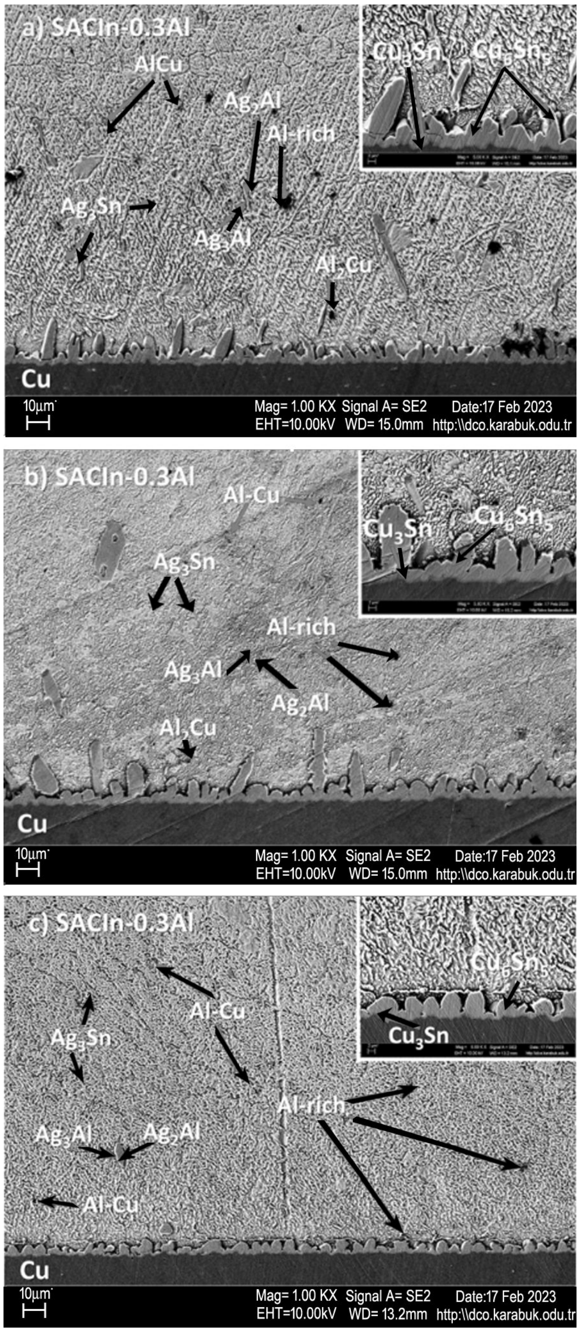

Fig. 3. SEM analysis of SAC205-1In-0.3Al at different temperatures: (**a**) 275°C, (**b**) 300°C, (**c**) 325 °C.

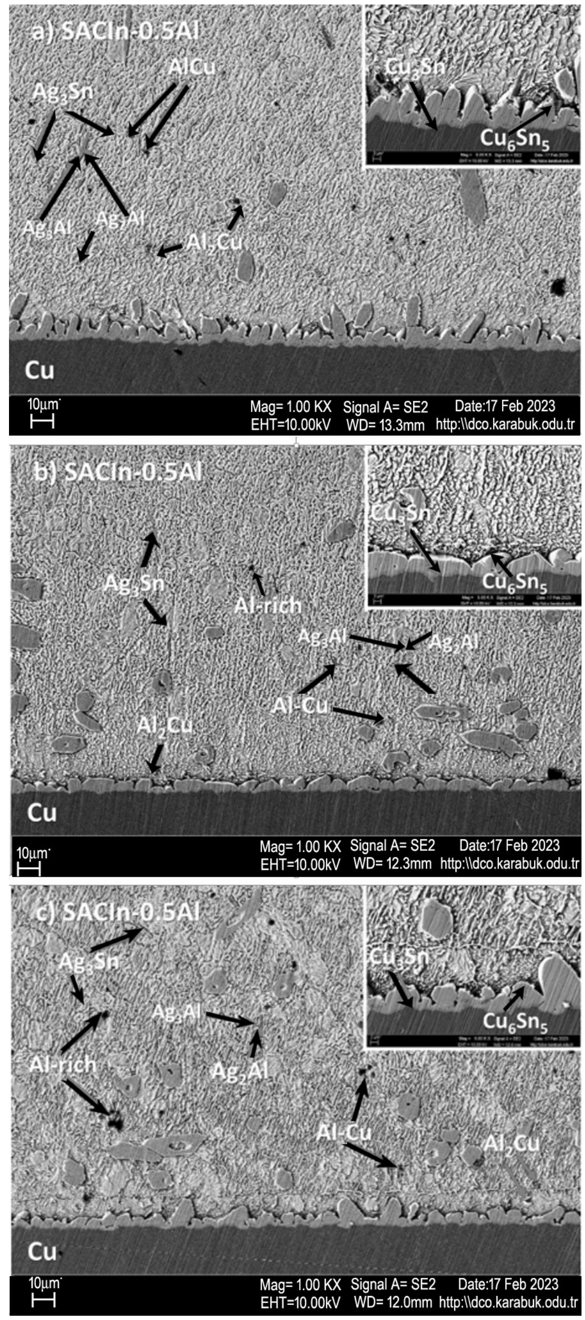

Fig. 4. Fig. 4. SEM analysis of SAC205-1In-0.5Al at different temperatures: (**a**) 275 °C, (**b**) 300 °C, (**c**) 325 °C.

temperature of 325 °C, the average contact angles of the lead-free solder alloys SACIn-0.3Al, SACIn-0.5Al, SACIn-0.7Al, SACIn-0.8Al and SACIn-0.9Al were measured after 600 seconds from the moment of the solder drop. The measurements were 39.88, 40.12, 48.32, 37.95 and 41.82, respectively, as shown in Fig 1. Among all the alloys, SACIn-0.3Al had the lowest contact angle rate (42.87), as indicated in Table 1. The SAC-In-0.3Al alloy also recorded the lowest melting temperature, which was 214.3 °C. This temperature is even lower

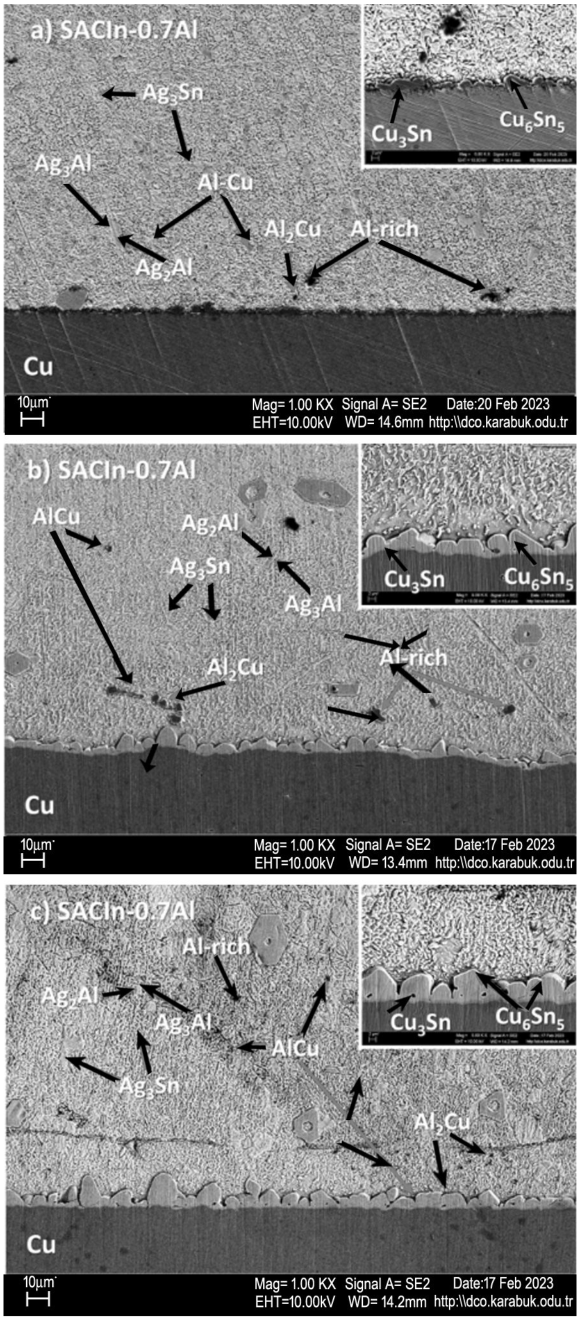

Fig. 5. SEM analysis of SAC205-1In-0.7Al at different temperatures: (**a**) 275 °C, (**b**) 300 °C, (**c**) 325 °C..

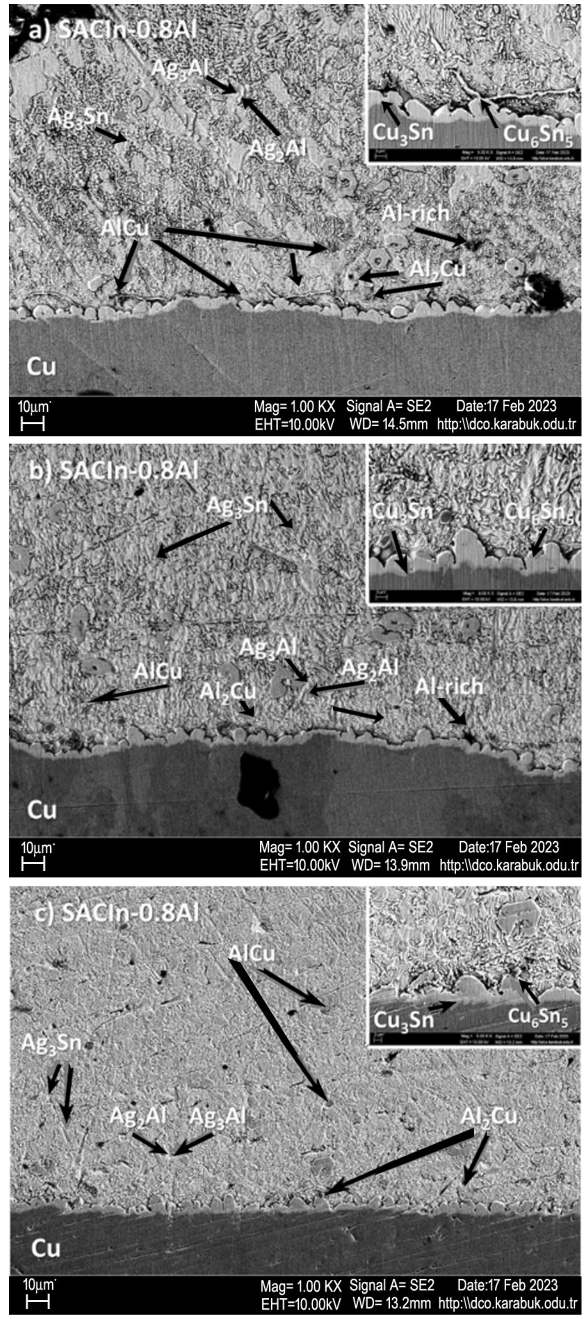

Fig. 6. SEM analysis of SAC205-1In-0.8Al at different temperatures: (**a**) 275 °C, (**b**) 300 °C, (**c**) 325 °C.

than the melting temperature of SAC305 and SAC205-1In, as well as all manufactured solder alloys in this study. The addition of aluminum enhanced the wettability and melting temperature of SAC205-1In-xAl. Furthermore, adding aluminum led to a less interdendritic (eutectic) region, as Cu-Al and Ag-Al IMCs were more likely to form. At the same time, Cu_6Sn_5 and Ag_3Sn IMCs were suppressed. CuAl IMCs are an ideal choice for conductivity or binding compounds due to their thermal solid and electrical conductivity.

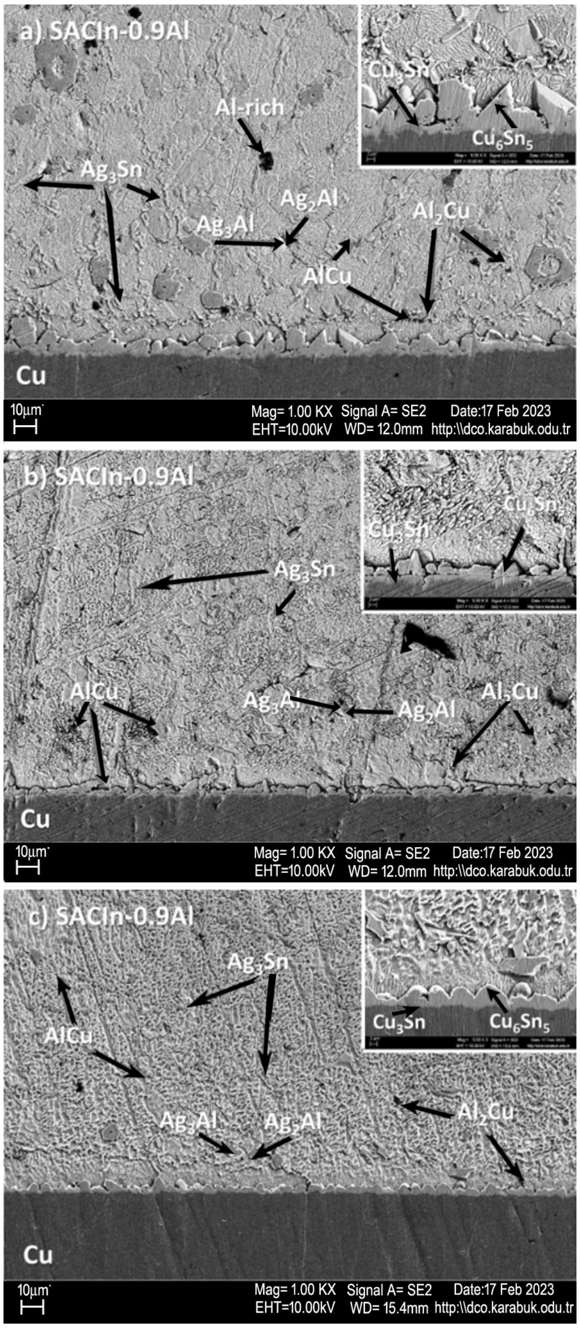

Fig. 7. SEM analysis of SAC205-1In-0.9Al at different temperatures: (**a**) 275 °C, (**b**) 300 °C, (**c**) 325 °C.

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Conflict of Interest. The authors declare they have no conflict of interest.

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