Microstructure and mechanical properties of Sn-9Zn-xAl and Sn-9Zn-xCu lead-free solder alloys

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This study investigates microstructures and mechanical properties of the alloys obtained by adding Cu (0.7 % and 0.9 %) and Al (0.7 % and 0.9 %) to lead-free Sn-9Zn eutectic soldering alloy produced by investment casting method. The results show that Cu_5Zn_8 phase has formed in the structure of Cu added alloys and the Al_2O_3 phase has formed due to addition of Al. It was found that small and round-shaped Al_2O_3 phase increased the tensile strength of the new alloy compared to the eutectic alloy. In addition, it was observed that the microhardness of Cu added alloys was lower than that of Sn-9Zn eutectic alloy, but the microhardness of alloys containing Al was higher compared to the other eutectic Sn-9Zn alloy.

Keywords: Sn-Zn lead-free alloys; investment casting; mechanical properties

1. Introduction

Tin-lead (Sn-Pb) alloys are widely used to join and install electronic circuits. These alloys are preferred as soldering alloys in industrial production, especially in electronics sector, due to their low melting temperatures, low cost and good wettability. However, the number of studies on lead-free soldering alloys has been increasing due to adverse effects of lead on environment and human health [1–6]. In addition, the use of soldering alloys containing lead in manufacturing of electronic and microelectronic products has been banned by environmental protection agencies (RoHS and WEEE) [7–10]. Therefore, legislations banning the use of traditional Sn-Pb soldering alloys have primarily aimed to improve the mechanical properties of alternative lead-free alloys in order to make them available to use [11–14]. New alloys intended to be used as soldering material must meet a wide range of criteria such as low cost, good wettability, suitable melting temperature, excellent mechanical and electrical conduction, high corrosion resistance, health and environment friendliness. In recent years, there are increasing number of studies on Sn-Ag [15], Sn-Zn [16], Sn-Bi [17], Sn-Cu [18]

alloys, and ternary alloys as well as quaternary alloys obtained by adding new elements to these alloys as an alternative soldering alloy to Sn-Pb alloys [19, 20].

The Sn-9Zn alloy seems to be the closest alternative soldering alloy to Sn-Pb soldering alloys. This is due to its low melting temperature, health and environment friendliness, excellent mechanical properties, and low cost compared to other lead-free soldering alloys. On the other hand, the most significant disadvantage of the Sn-9Zn alloy is its low oxidation resistance (since Zn is a highly active element) and poor wettability. This property of the Sn-9Zn alloy prevents it from being widely used [11, 13]. With a melting temperature very close to Sn-Pb soldering alloy, Sn-9Zn alloy is widely preferred for production. The most significant disadvantage of the high melting temperature of lead-free soldering alloys intended to be used instead of existing soldering alloys is the necessity of replacing many materials used in printed-circuit cards and thus, many existing devices. This causes an increase in production costs. In addition, full understanding of the effect of third and fourth alloy elements added to the alloy on successful application of Sn-Zn based solders in interconnecting technology, plays an important role in terms of thermal-mechanical reliability of soldering

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assemblies. For this reason, different alloy elements such as Ag, Al, Cu, Cr, In and Ni are added to Sn-Zn alloys. For example, Yang et al. [21] has reported that various intermetallics, such as Al_2Cu formed in the structure of the alloy take part in improving the creep strength of the alloy and preventing dislocation moves. Therefore, in this study, the alloys were produced by investment casting adding Al and Cu to a Sn-9Zn eutectic alloy at different amounts. Microstructures and mechanical properties of the alloys were examined in an attempt to understand the effect of possible intermetallic compounds (IMCs) on their mechanical properties.

2. Materials and method

In this study, alloys with different chemical compositions were produced using investment casting by adding Al and Cu to the Sn-9Zn eutectic alloy at different amounts. Chemical compositions of produced alloys can be found in Table 1.

Table 1. Chemical composition of produced alloys.

Chemical Compositions [wt.%]
Sn-9Zn
Sn-9Zn-0.7Cu
Sn-9Zn-0.9Cu
Sn-9Zn-0.7Al
Sn-9Zn-0.9Al

In order to produce the alloys given in Table 1 using investment casting, wax models of the samples were prepared first. The molds of the wax models to be used for producing tensile samples were prepared using Al-Si alloy in accordance with EN ISO 6892-1 (ASTM E8/E8M - 13a) standard.

A 1 kg capacity wax injection device was used to prepare the wax models of the samples. Wax was injected to the metal mold at 73 °C temperature under 80 kPa pressure. The wax models of the samples were coupled together using an electric soldering iron to form a cluster model. The cluster model was placed in a steel flask with 90 mm diameter.

The chemical compositions given in Table 1 were prepared using elements (Sn, Zn, Cu, Al) of commercial purity. The elements were melted

at different temperatures. Pre-alloying treatment was performed at 350 °C for Sn-9Zn alloy, and at 400 °C for other alloys. Since the melting temperatures of Al and Cu are higher than those of Sn and Zn, the liquid metal was kept in the melting furnace at these temperatures for 1 hour to avoid segregation. In the melting operations, a 1 kg capacity electric furnace and graphite crucible were used.

The pre-alloyed materials were poured into prepared plaster molds in atmospheric environment after the second melting, and the sample production for tensile testing was completed. Temperature measurements during the pouring were done using NiCr-K type mineral insulated thermocouples with a diameter of 0.23 mm.

After the casting procedure was completed, the samples were prepared for microstructure examinations using standard metallographic operations. Metallographically prepared samples were etched in a mixture of 100 mL H_2O , 2 mL HCl, 10 g FeCl_3 for 45 seconds and microstructure examinations were performed. In the microstructure examinations, CARL ZEISS ULTRA PLUS GEMINI (FEG) scanning electron microscope (SEM) and energy-dispersion spectroscopy (EDS) were used. In addition, X-ray diffraction (XRD) examinations were performed with a Rigaku D-MAX RINT-2200 series brand device in order to determine the phases formed during the solidification. Shimadzu HMV microhardness tester was used for hardness measurements. Hardness values were measured applying 50 g load for 20 seconds. The average of five hardness measurements performed on each sample was taken. 1200 grid sandpaper was used for surface cleaning of tensile test samples. After surface cleaning processes, the samples were tested at 1 mm/min load rate using Shimadzu AG-IS brand tester that can be adjusted to 50 kN capacity.

3. Results and discussion

3.1. Microstructural characterization

In the experimental studies, microstructural and mechanical properties of (Al and Cu added) Sn-Zn alloys with different chemical compositions were examined. Microstructure SEM images of Sn-9Zn

alloys with different chemical compositions can be found in Fig. 1.

Fig. 1. SEM images of eutectic Sn-9Zn alloy obtained by adding different amounts of Al and Cu.

As can be seen in the microstructure SEM images in Fig. 1, the matrix structure of the Sn-9Zn alloy contains β -Sn and Zn-rich phases with homogeneous distribution formed in β matrix. In a study by El-Daly et al. [22], Zn-rich areas were reported to form in Sn-Zn eutectic alloy. In the SEM images of alloys produced by adding Cu to the Sn-9Zn eutectic alloy at different amounts (wt.% 0.7 and 0.9), it was found that β -Sn, which is the main matrix, eutectic α -Zn and flower-shaped phases were formed. It can be seen from EDS results (Table 2) that the flower-shaped phase consists of Zn and Cu, and according to XRD results (Fig. 2) shows the formation of Cu_5Zn_8 and CuZn_5 intermetallic compounds (IMCs) in the structure. It was found that the size of IMCs and percentage ratios in the structure increase with increasing the amount of Cu addition. Also, it was observed that the α -Zn phase formed around IMCs has a thinner structure. In investment casting, pores may occur due to low cooling rate. Previously, it was also reported by Garcia

et al. [8] that pores were formed in the microstructure of the alloy.

Fig. 2. XRD results of eutectic Sn-9Zn alloy obtained by adding different amounts of Al and Cu.

In the SEM images of the alloys produced by adding Al to the Sn-9Zn eutectic alloy at different amounts (0.7 and 0.9 wt.%), it was found that Al-rich areas formed in the microstructure. Another study by Das et al. [23] also reported Al-rich areas seen in the microstructure of Sn-Zn-Al alloys. EDS analysis results can be found in Table 2.

It can be seen from the results of EDS analysis given in Table 2 that Al_2O_3 intermetallic phase has formed in the structure of Sn-9Zn-0.9Al alloy. The formation of Al_2O_3 intermetallic phase in the microstructure of the alloy is thought to be caused by liquid metal contact with atmosphere during melting or casting operations. Although these areas were found to be $\text{Al}_6\text{Zn}_3\text{Sn}$ in some earlier studies, this intermetallic phase could not be identified by EDS and XRD examinations [24, 25]. Again, based on EDS (Table 2) and XRD results in Fig. 2 it can be stated that Al_2O_3 intermetallic phase occurred in the alloy. It is also seen that the pores formed in the microstructure of the alloy were produced by adding 0.9 Al to the Sn-9Zn eutectic alloy.

3.2. Hardness results

Movement of dislocations is affected by a microstructure of a material and subsequently affects its hardness. Therefore, microhardness measurements were performed in order to determine

Table 2. Results of EDS analysis [wt.%].

Alloy	Location	Sn	Zn	Cu	Al	O
Sn-9Zn	1	98.96	1.04	-	-	-
	2	96.37	3.63	-	-	-
	3	89.33	10.67	-	-	-
Sn-9Zn-0.7Cu	1	-	65.91	27.13	-	1.25
	2	90.98	3.39	-	-	2.59
	3	67.47	15.47	5.4	-	3.7
Sn-9Zn-0.9Cu	1	-	72.83	19.20	-	1.2
	2	72.56	26.53	-	-	0.91
	3	92.30	6.86	0.84	-	-
Sn-9Zn-0.7Al	1	93.68	3.86	-	2.46	-
	2	99.43	0.52	-	0.05	-
Sn-9Zn-0.9Al	1	37.5	3.93	-	14.88	29.18
	2	91.2	3.61	-	-	2.89

microstructural differences between Sn-Zn and Sn-Zn-xCu/Al alloys produced by investment casting method. Microhardness changes in the alloys can be found in Fig. 3.

Fig. 3. Microhardness changes in Sn-Zn and Sn-Zn-xCu/Al alloys.

It was observed that the hardness of Sn-9Zn-xCu alloys decreased when the addition of Cu increased to 0.7 % or 0.9 %. When the amount of Al in the Sn-9Zn eutectic alloy increased from 0.7 % to 0.9 %, the hardness of the alloy increased as well. In addition to the two-phased structure of Sn-9Zn alloy, a third phase appeared in the structure with the addition of Cu. The hardness of the alloy decreased due to weak areas formed between

the complex-shaped Cu_5Zn_8 IMCs and the matrix. It can be understood from the microstructure SEM images (Fig. 1) that an increase in Cu amount resulted in an increase in the size and amount of Cu_5Zn_8 intermetallic phases. Therefore, a slight increase in hardness was observed for 0.9 % Cu added alloy. When Al was added to the Sn-9Zn eutectic alloy at different amounts, on the other hand, it was seen that the addition of Al increased the hardness of the alloy (compared to the hardness value of Sn-9Zn eutectic alloy). Although the intermetallic phases observed in this study were described as $\text{Al}_6\text{Zn}_3\text{Sn}$ in some earlier studies [23–26], these intermetallic phases could not be identified as a result of EDS analysis and XRD examinations in this study. Again based on EDS and XRD results, it was concluded that Al_2O_3 was this intermetallic phase. It is also seen that the pores formed in the microstructure of the alloy were produced by adding 0.9 Al to the Sn-9Zn eutectic alloy.

3.3. Tensile test results

Tensile tests are performed in order to measure resistance of a material against plastic deformation. The transition from elastic behavior to plastic behavior cannot be easily determined for some materials. Results of the tensile test performed on Sn-9Zn and Sn-9Zn xCu/Al solder alloys can be found in Fig. 4.

Fig. 4. Tensile stress-strain curves of Sn-9Zn, Sn-9Zn-0.7Cu, Sn-9Zn-0.9Cu, Sn-9Zn-0.7Al and Sn-9Zn-0.9Al alloys.

According to the tensile test results given in Fig. 4, the measured tensile strengths of the alloys were 38 MPa (Sn-9Zn), 35 MPa (Sn-9Zn-0.7Cu), 37 MPa (Sn-9Zn-0.9Cu), 45 MPa (Sn-9Zn-0.7Al) and 46 MPa (Sn-9Zn-0.9Al). These results show that when 0.7 % Cu was added to the Sn-9Zn eutectic alloy, the tensile strength decreased while a slight increase in the strength was observed by adding 0.9 % wt. Cu. As the amount of added Cu increased, a slight increase in tensile strength was observed. A comparison of tensile test results with the microstructure images (Fig. 1) and XRD results (Fig. 2) reveals that Cu_5Zn_8 IMC phase is the factor that causes the tensile strength to decrease. As the amount of Cu added to the Sn-9Zn increased, the size of IMCs formed in the structure increased as well. While the tensile strength slightly increased in parallel with the increase in the size of the intermetallics in the structure of the alloys, the percentage elongation decreased slightly. In spite of this, the tensile strength of the 0.9 % Cu added alloy, which had the highest tensile strength among Cu added alloys, was lower compared to the eutectic alloy (Sn-9Zn). This is due to the notch effect observed in the structure of the alloy caused by the third phase (intermetallics) formed in the structure of the alloy during pouring and solidification. Due to this notch effect, high tension areas developed under tension, especially in tips of intermetallics and these high tension areas led to microcracks (under increased tension). These microcracks in the structure grew bigger with the increasing load and caused fractures [27, 28]. Among Al added

eutectic Sn-9Zn alloys, on the other hand, Sn-9Zn-0.9Al alloy had the highest tensile strength. Accordingly, the maximum tensile strength of the alloys increased as the amount of Al added to the Sn-9Zn eutectic alloy increased. SEM images of fractured surfaces of Sn-9Zn and Sn-9Zn xCu/Al alloys obtained as a result of tensile test can be found in Fig. 5.

Fig. 5. SEM images of fractured surfaces of Sn-9Zn and Sn-9Zn xCu/Al alloys.

Since the alloys were prepared and poured in atmospheric conditions, various oxides formed due to the contact of liquid metal with atmosphere during the pouring. Also, the pores formed in slow solidification conditions had some effect on the fracture. In other words, micro and macro defects occurring in the structure of the alloy contribute to fracture. Aluminum oxide formation was observed in the fracture areas of Al added alloys. Due to the tensile stress created during tensile tests, the fracture started from β -Sn and eutectic area, and the areas where intermetallics such as aluminum oxide was present. It was seen from the fracture surfaces of the samples that ductile fracture mode occurred in all alloys. It can be concluded from the SEM images that intermetallic compounds formed during

pouring increased tensile strengths of alloys, while decreased ductility.

3.4. Weibull statistical analysis

Weibull statistical analysis was performed using the data obtained from tensile tests. The Weibull probability distribution was estimated using the graphical method. The Weibull probability distribution of Sn-9Zn and Sn-9Zn xCu/Al alloys can be seen in Fig. 6.

Fig. 6. Weibull modules of Sn-9Zn and Sn-9Zn xCu/Al alloys.

Tensile strength and percentage elongation values obtained from tensile tests were used to determine two-dimensional Weibull distribution and quality index. Two-dimensional Weibull distribution is a simple and useful statistical method used to determine the reliability of materials. The tensile strength data obtained with this method were sorted from low to high and the corresponding ln values (ln tensile and/or ln percentage elongation) were plotted on the x axis of the graph.

Weibull modules of eutectic Sn-9Zn alloy obtained by adding different amounts of Al and Cu were calculated according to tensile test results. The Weibull modules of the Sn-9Zn alloy, 0.7 % Al added alloy and 0.9 % Al added alloy were calculated as 11.77, 10.95 and 17.69 respectively. According to tensile strength formation frequencies (see Table 3), it was found that the increased amount of Al addition positively affects the formation frequency. Das et al. [26] reported that 0.5 % Al addition increased tensile strength and elongation values of the alloy. This increase in tensile strength and elongation values is due to the dispersion hardening that occurs in the structure

of the alloy. The dispersion hardening can be explained as second phases (intermetallics) formed in grain boundaries, hampering dislocation and consequently, increasing the tensile strength of the alloy. It was found that the tensile strength and Weibull module increased as the amount of aluminum added to the Sn-9Zn alloy increased. The Weibull module was calculated as 12.40 with the addition of 0.7 % Cu, and 12.10 with the addition of 0.9 % Cu. Although a slight increase occurred in tensile strength and elongation values, it was not remarkable. Considering tensile strength formation frequencies, the increase in the amount of Cu addition adversely affected the formation frequency.

4. Conclusion

- It was observed that the size of IMC phase increased as the amount of Cu increased and that the α -Zn phase, which occurs in the area between these phases and the main matrix, is thinner.
- It was found from the XRD examination that Cu_5Zn_8 phase formed in the Sn-9Zn-xCu alloys, but CuZn_5 formed only in the Sn-9Zn-0.9Cu alloy.
- It was determined that the hardness value increased as the addition of Cu increased in Sn-9Zn-xCu alloys. However, even the hardest alloy, Sn-9Zn-0.9Cu, did not reach the hardness value of the Sn-9Zn eutectic alloy.
- It was found that the hardness value increased as the Al amount increased in Sn-9Zn-xAl alloys and the hardness values of both Al added alloys were higher compared to the Sn-9Zn eutectic alloy.
- According to results of tensile tests, the highest tensile strength was obtained with the addition of Al to the Sn-9Zn eutectic alloy. It was determined that the percentage elongation value slightly decreased with increasing amount of Al addition.
- It was determined that the Weibull module increased in parallel with the amount of Al addition to the Sn-Zn alloy and

Table 3. Tensile strength and percentage elongation values of Sn-9Zn and Sn-9Zn xCu/Al alloys.

	Sn-9Zn	Sn-9Zn-0.9Cu	Sn-9Zn-0.9Al	Sn-9Zn-0.7Cu	Sn-9Zn-0.7Al
Range of UTS [MPa]	33–41	33–44	45–56	29–40	40–55
Average of UTS [MPa]	36	38	53	35	48
Standard deviation of UTS	3.25	3.60	3.21	3.22	5.16
Range of E [%]	6.80–13.52	3.6–14.06	6.77–13.31	8.28–16.82	9.04–11.53
Average of E [%]	8.95	7.96	10.23	11.68	10.77
Standard deviation of E [%]	2.32	4.03	2.30	3.35	0.82
Weibull moduls	11.7	12.10	17.69	12.40	10.95

the addition of Al had a positive effect on the tensile strength and reliability of the alloy.

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