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Letter

Influence of thermal aging on microhardness and microstructure of Sn–0.3Ag–0.7Cu–*x*In lead-free solders

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ABSTRACT

Sn–0.3Ag–0.7Cu is a low-silver lead-free solder, and provides a thinner brittle Ag_3Sn intermetallic layer during soldering process. In this paper, effects of thermal aging on microhardness, and microstructure of Sn–0.3Ag–0.7Cu–*x*In lead-free solders were investigated. Indium was added to lower the melting temperature, and varied from 0.0 to 3.0 wt%. The solders were thermally aged at 100 °C for 1, 10, 100, and 1000 h. Results showed that microhardness of the solders decreases as the aging time increases, and average grain size of the microstructure is larger with the increase of the aging time. It was also found that the higher In content in the solder provides the greater decreasing rate of its microhardness.

1. Introduction

In order to reduce toxic substances, the European Union has legislated the RoHS directive to force electronics industry to use Pb-free solder alloys. There are many Pb-free solder alloys that are of interest such as, Sn–Ag, Sn–Cu, Sn–Zn, and Sn–Ag–Cu solder alloys. The Sn–Ag–Cu (SAC) family of alloys is a very attractive candidate because of its advantages in mechanical properties and its good soldering ability. Thus, the SAC solder alloys have been proposed by many consortiums as a replacement for the traditional Sn–Pb eutectic solder alloy. However, some properties of SAC solder alloys are inferior to those of the Sn–Pb solder alloy, especially the high melting temperature of SAC solder alloys. Adding an alloying element to the solder alloys is a mean to lower the melting temperature. However, the alloying element might have other effects on properties of the alloys, such as mechanical properties and microstructure [1–8].

The alloying element employed to lower the melting temperature of solder alloys must be conformed to the RoHS directive, and possesses a low melting point, such as bismuth (Bi), gallium (Ga), and indium (In) [7,9]. Previous investigations reported that Bi, Ga, and In can be employed to lower solidus and liquidus temperatures of solder alloys, but adding of these elements also affected their microstructure and other properties [1–6,9–11].

Thermal aging can be used to simulate alteration of microstructure and properties of solder under working environment. As a microelectronic package increasingly demands smaller pitch, smaller solder bumps and higher electric current per solder bump, solder joints are exposed to very high thermal stresses and temperature. At high temperature, the microstructure of solders would significantly change, and consequently their mechanical properties would be affected. For that reason, effect of thermal aging on microstructure and mechanical properties of various types of solders has been studied [12–18].

Sn–0.3Ag–0.7Cu solder is a low-Ag lead-free solder alloy in the SAC family. This solder possesses a major advantage in that it provides a thinner brittle Ag_3Sn intermetallic layer during soldering process due to their low Ag content [19,20], and recently, its high melting temperature can be overcome by adding a small amount of indium [11]. In this research, influence of thermal aging on microstructure and microhardness of the Sn–0.3Ag–0.7Cu–*x*In was investigated.

2. Experimental procedures

In this experiment, Sn–0.3Ag–0.7Cu–*x*In solders with different In contents were studied. All solder alloys and their compositions are shown in Table 1. The compositional elements were melted in a graphite crucible, and then cast into a cylindrical ingot in a copper mold. The composition of each solder alloy was confirmed by an optical emission spectroscopy Spark-OES model Spectrolab M-8.

Thermal aging of solder alloys was performed in an oil bath at 100 °C for 1, 10, 100, and 1000 h, and the oil used was a silicone oil. After that the specimen was air-cooled to room temperature. The oil bath used in this experiment was Haake Phoenix II model P2-B5 with temperature accuracy of ±0.01 °C.

Microhardness of each solder alloy was tested using a Vickers microhardness tester with 2.9 N indentation force, and 10 s holding time. The machine used in this study was Mitutoyo H-M113. Microstructure of each solder alloy was studied using an electron probe micro-analyzer (EPMA) to obtain the microstructure and distribution of elements in the alloy. The EPMA used in this experiment was Shimadzu

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Table 1
Solder alloys and their compositions.

Solder	Composition (wt%)			
	Sn	Ag	Cu	In
Sn–0.3Ag–0.7Cu	99.0	0.3	0.7	0.0
Sn–0.3Ag–0.7Cu–1.0In	98.0	0.3	0.7	1.0
Sn–0.3Ag–0.7Cu–2.0In	97.0	0.3	0.7	2.0
Sn–0.3Ag–0.7Cu–3.0In	96.0	0.3	0.7	3.0

model EPMA 1610. Acceleration voltage for the EPMA was 15 kV with beam size of 1 μm. All samples were examined at 500× magnification. An optical microscope and a scanning electron microscope (SEM) were employed to examine microstructure of the solder alloys. The Hitachi S-4700 SEM coupled with an energy dispersive X-ray spectroscopy (EDX) was used to determine chemical composition of phases presented in the solder alloys. The EDX was manufactured by IXRF Systems. Before the microstructural examinations, the solder alloys were etched using 5 vol.% $FeCl_3$ solution to reveal their microstructure.

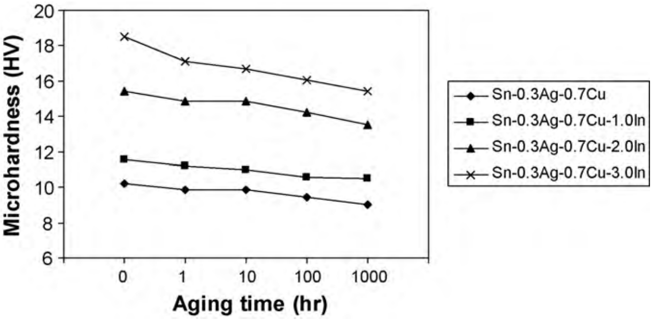

Fig. 1. Microhardness of solder alloys.

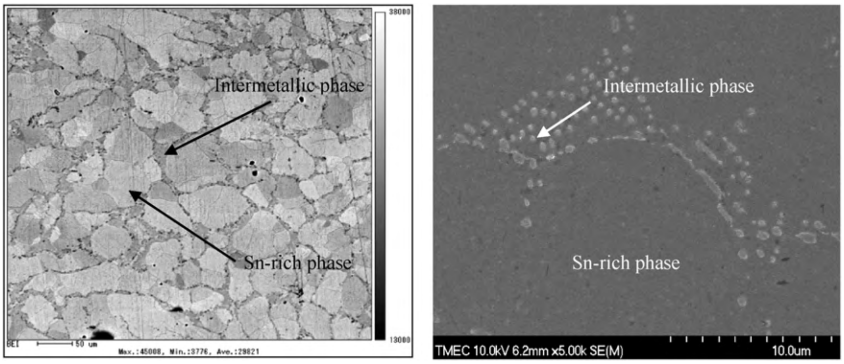

Fig. 2. Microstructure of Sn–0.3Ag–0.7Cu.

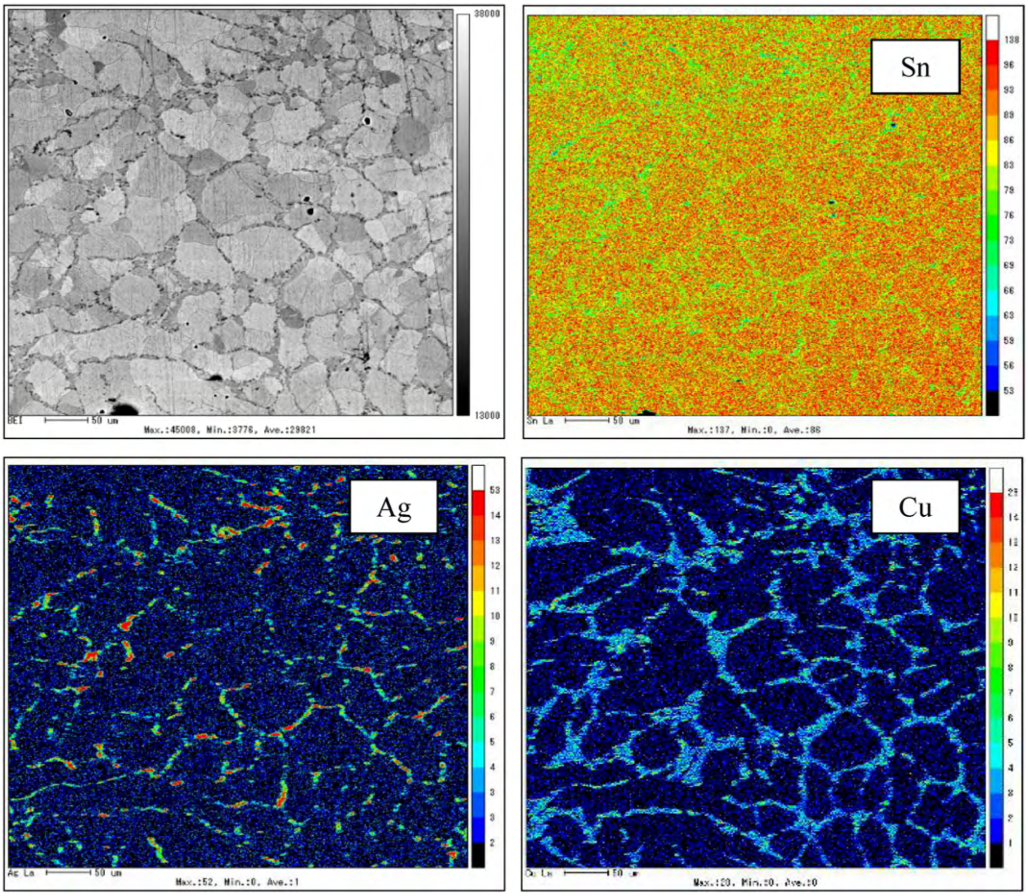

Fig. 3. Element distribution in Sn–0.3Ag–0.7Cu.

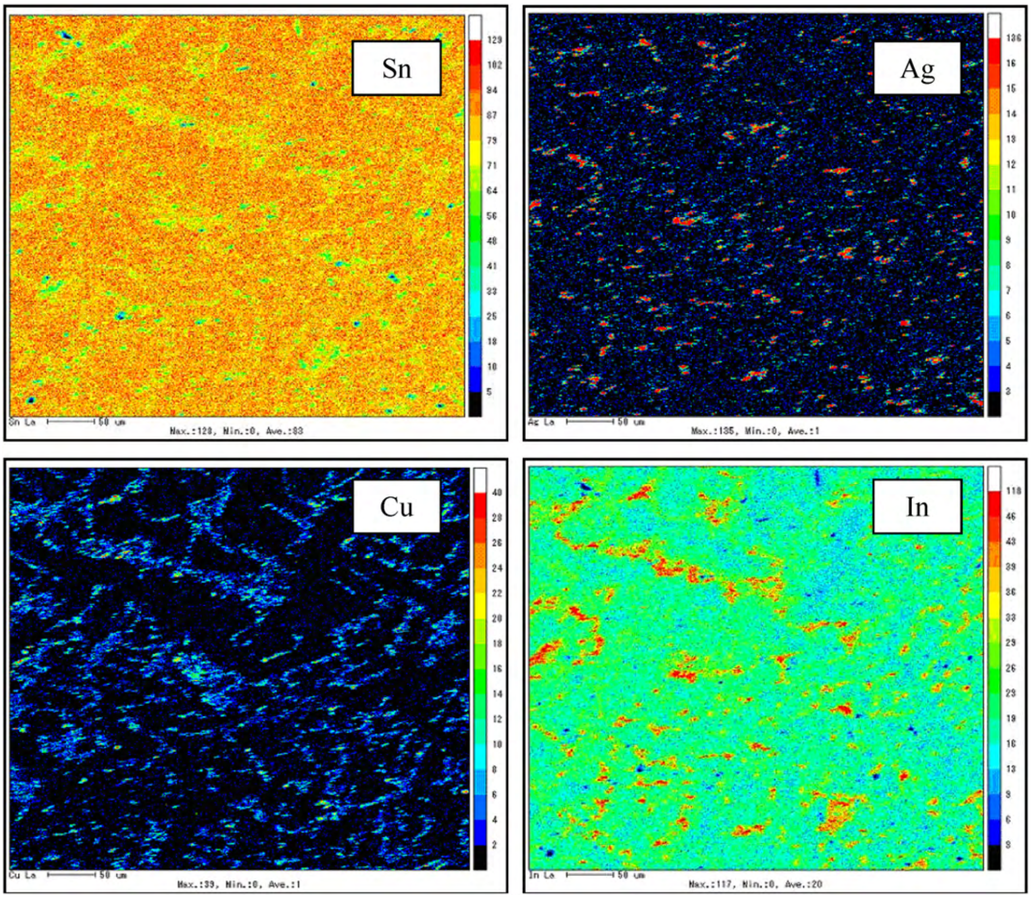

Fig. 4. Element distribution in Sn–0.3Ag–0.7Cu–3.0In.

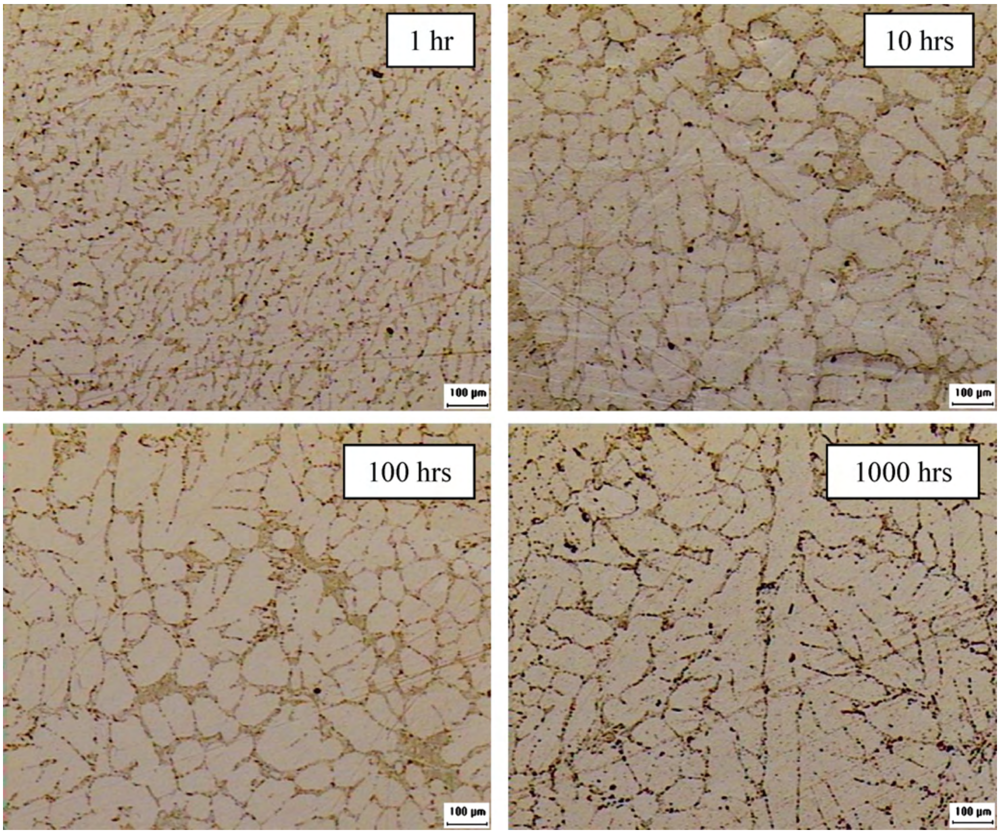

Fig. 5. Microstructure of Sn–0.3Ag–0.7Cu after aging for 1, 10, 100, and 1000 h.

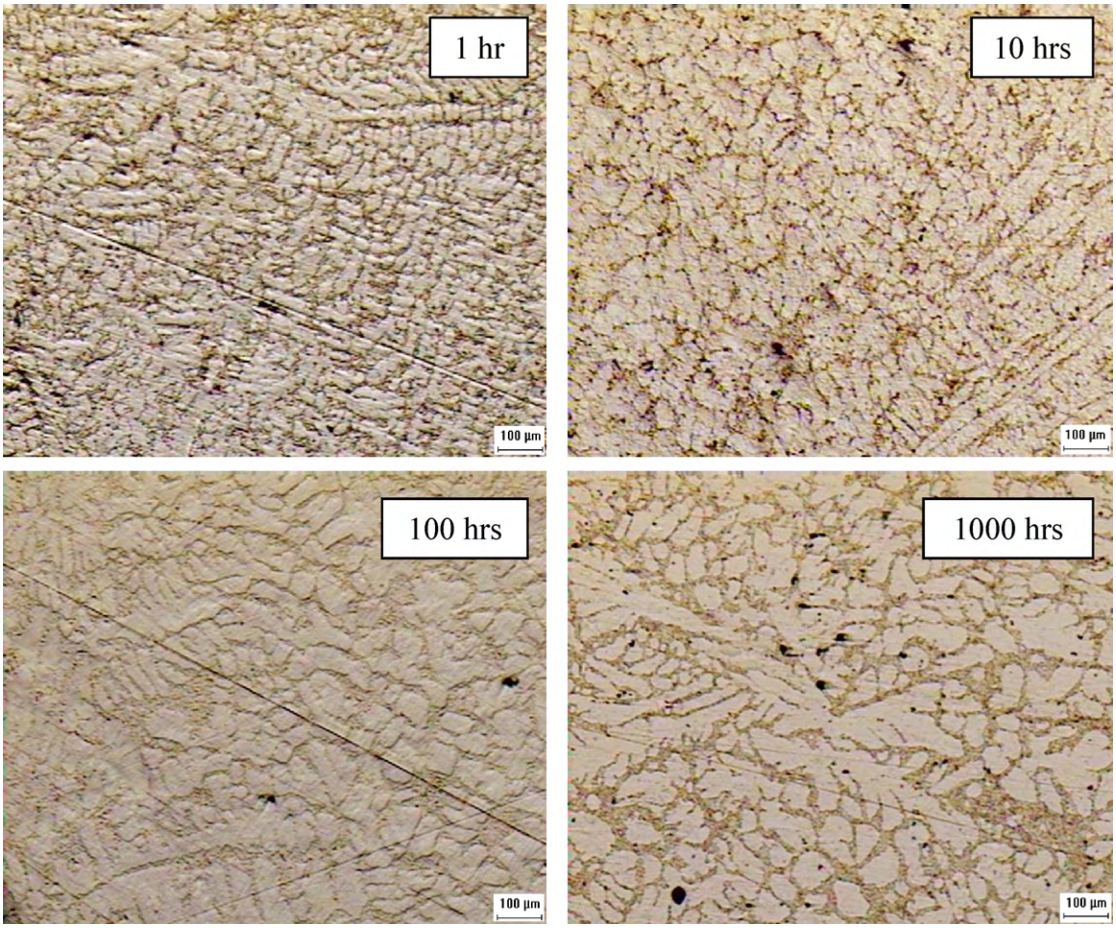

Fig. 6. Microstructure of Sn–0.3Ag–0.7Cu–3.0In after aging for 1, 10, 100, and 1000 h.

3. Results and discussion

Microhardness of each solder alloy is shown in Fig. 1. Microhardness of the original Sn–0.3Ag–0.7Cu solder alloy was 10.23 HV, and it was found that the microhardness of the as-cast solder alloys is increased with the increase of In content as described in the previous work [11]. After thermal aging, it was obvious that the microhardness of solder alloys is decreased as the aging time increases. Moreover, from Fig. 1, the plot between microhardness and aging time of solder alloy with a higher In content has a steeper slope. This means that the microhardness of solder alloy with a higher In content decreased with a higher rate than that of solder alloy contained a lower In composition. The reason for explaining this microhardness reduction mechanism is not clear. Further investigation on this phenomenon will be performed.

From the microstructure examination, it was found that Sn-rich phase is the basic microstructure of the original Sn–0.3Ag–0.7Cu, and there are intermetallic particles around the Sn-rich phase as shown in Fig. 2. From EDX analysis, the intermetallic compounds found were mainly Cu_6Sn_5, and Cu_3Sn. After adding In into the original solder, it was found that the solder alloy has more uniform distribution of the intermetallic particles as shown in Figs. 3 and 4, and more details on this phenomena was explained the previous investigation [11].

The decrease of microhardness of the solders can be explained by the alteration of microstructure due to thermal aging. As illustrated in Figs. 5 and 6, the average grain size of the Sn-rich phase was larger as the aging time increased. It is well known that the larger grain size provides the lower mechanical strength and hardness.

4. Summary

Influence of thermal aging on microstructure and microhardness of the Sn–0.3Ag–0.7Cu–*x*In was investigated. Aging temperature was set at 100 °C with the aging time of 1, 10, 100, and 1000 h in an oil bath. After aging, alteration of microstructure and microhardness was clearly observed. The average grain size of the solder was larger. The longer the aging time, the larger the grain size. It was also found that the higher In content in the solder provides the greater decreasing rate of its microhardness.

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