THE INFLUENCE OF HEAT TREATMENT ON PROPERTIES OF LEAD-FREE SOLDERS

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Resume

The article is focused on the analysis of degradation of properties of two eutectic lead-free solders SnCu0.7 and SnAg3.5Cu0.7. The microstructures of the intermetallic compound (IMC) layers at the copper substrate - solder interface were examined before and after heat treatment at 150 °C for 50, 200, 500 and 1000 hours. The thickness of IMC layers of the Cu_6Sn_5 phase was growing with the increasing time of annealing and shown the typical scallops. For the heat treatment times of 200 hours and longer, the Cu_3Sn IMC layers located near the Cu substrate were also observed. The experiments showed there is a link between the thickness of IMC layers and decrease of the shear strength of solder joints. In general, the joints made of the ternary solder showed higher shear strength before and after heat treatment in comparison to joints from solder SnCu0.7.

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1. Introduction

Soldering of metallic materials remains still an advanced technology, despite that it is the oldest technology of materials joining. Mostly it is utilized in the fields where welding is not possible to use. Soldering can be found in automotive industry, in nuclear power industry, in space and aircraft industry as well as in many other industrial applications. That is why soldered joints must satisfy variety of requirements such as high or low temperatures resistance, high corrosion resistance, strength and toughness requirements, etc.

Tin-lead solders of eutectic or near eutectic composition were widely spread practically in all soldering applications, however, due to legislative limitations related to the toxicity of lead, now in industry it is possible to utilize only the lead-free solders [1, 2]. Sn-Ag-Cu alloys became most favourite lead-free solders [3]. There are several criteria for selection of appropriate lead-free solder alloys. Basic criteria are environmental, physical, mechanical, technological and economical [4, 5]. During soldering process the intermetallic compound (IMC) layers of the Cu_6Sn_5 and Cu_3Sn composition are created [6 - 8]. It is well known, that the strength of a soldered bond is provided by means of IMC layer [9]. The presence of such IMC layer between the solder alloy and substrate material indicates formation of proper metallurgical bond. However, owing to the low fracture resistance of IMC compounds and due to different physical properties (e.g. linear expansion coefficient and Young modulus of elasticity) of the IMC compounds and the solder itself the thickness of such IMC layer is very important [10]. Very thick IMC layer will decrease interface integrity [11]. That is why the growth of the IMC layer is unwanted. It is known that their growing is time-temperature depended process, and the interface solder - IMC compound becomes the source of formation and spreading of cracks if such layer has been grown to a significant size. This growth can be started even at room temperature. Each increase of the IMC layer decreases the mechanical as well as the electrical properties and ultimately causes degradation and dysfunction of the soldered joint [12 - 14].

The goal of this contribution is to compare selected properties of Sn-Cu and Sn-Ag-Cu eutectic alloys, which can be utilized as environmentally acceptable alternative alloys instead of the lead containing solders. This study is focused on the influence of heat treatment on the growth of IMC layers and on the related changes in their mechanical properties.

2. Material procedures

2.1 Experimental alloys

For experiments the eutectic lead-free solders Sn-Cu and Sn-Ag-Cu were utilized. These solders were prepared from pure metals Sn, Ag and Cu of chemical purity of 99.99 %. Precisely weighted amounts of pure metals were melted in an alumina crucible in the vacuum induction furnace under protective atmosphere of pure Ar. The metals were during melting stirred by silica glass rod. The melt was cast on the stainless steel pad, where rapidly solidified. The chemical composition and melting temperature of the prepared solders are in the Table 1.

2.2 Preparation of samples for heat treatment

Samples for heat treatment and microstructural analysis were prepared from mixed alloys by soldering on the Cu substrate. The dimensions of Cu substrate were 20×20 mm and 0.8 mm thick. The surface of the Cu substrate was metallographic prepared by grinding with wet 600 and 1200 grit silicon carbide paper. After the wet grinding all plates were cleaned by alcohol. Flux, colophony, and solder were put onto the prepared Cu plates and afterwards the solder was melted on hot plate. The working temperature was 270 °C which was of 40 °C to 50 °C above the melting temperature of the solders.

The samples for microstructural analysis were prepared by standard metallographic procedure, polished and etched with a solution of 5 % HNO3 + 2 % HCl + methanol. Etching time was 2 - 5 seconds.

To prepare the soldered joints, the solder alloy and the flux were placed between two copper sheets and heated on the hot plate. To ensure fixity during the soldering process a special tool made from aluminium was applied [15]. Copper sheets of 20×10×0.8 mm were cut and shortly polished on 1200 SiC abrasive paper and cleaned by alcohol. Soldering temperature was 270 °C and holding time was 10 s. Finished joints were subsequently cooled on a stainless steel pad. For the mechanical testing FPZ 100/1 Universal Testing Machine was used. Tests were carried out with the deformation rate of 2 $mm.min^{-1}$ at a room temperature.

The samples prepared for the heat treatment experiments in solid state (thermal ageing tests) were annealed at 150 °C for 50, 200, 500 and 1000 hours. After heat treatment experiments these samples were also prepared for microstructural analysis as is described above.

3. Results and discussion

The intermetallic compound (IMC) layers of the Cu_3Sn and Cu_6Sn_5 at the copper - solder interface, Fig. 1, were examined before and after heat treatments on the sectioned samples after their metallographic preparation.

Table 1

Chemical composition of the used solders and their melting temperatures.

Lead-free solder	Chemical composition (wt.%)			Melting temperature (°C)
	Sn	Cu	Ag	
SnCu0.7	99.3	0.7	-	227
SnAg3.5Cu0.7	95.8	0.7	3.5	217

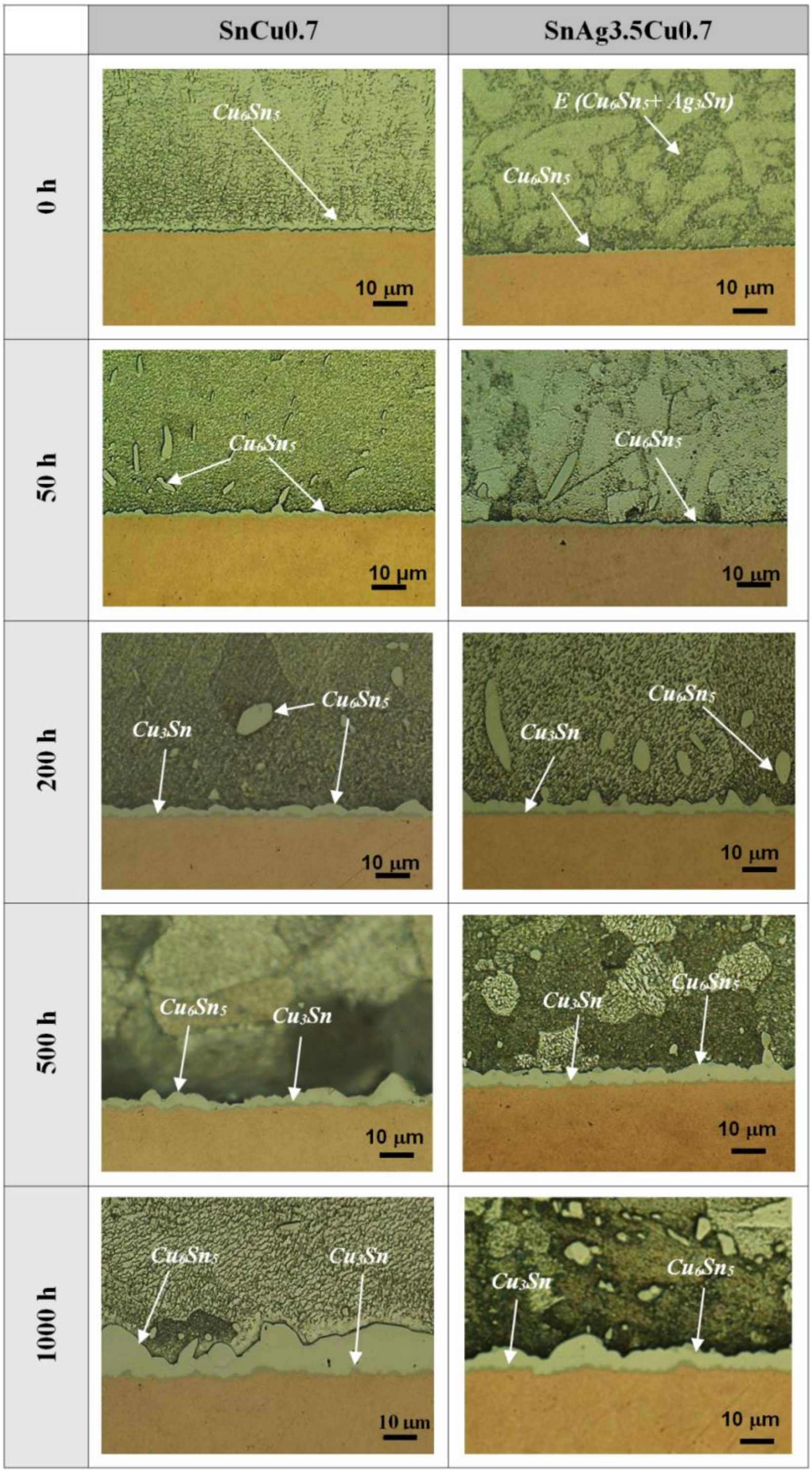

Fig.1. Microstructure after different heat treatment time.

(full colour version available online)

As expected, immediately after soldering a thin IMC layer was created. Mookam and Kanlayasiri [16] reported that as the first IMC layer of Cu_3Sn is created due to a lower Gibbs free energy of formation than exhibit Cu_6Sn_5. However, at longer soldering times, or higher soldering temperatures they found that Cu_3Sn can be transformed to Cu_6Sn_5 by dissolution, or it could also react with Sn atoms and form Cu_6Sn_5.

This assertion is in contradiction with results of Park and Arroyave [17] who carefully investigated formation and growth of these two IMC compounds during the early stages of soldering. They claim that the Cu_6Sn_5 layer formed much faster than the Cu_3Sn layer due to its larger driving force for precipitation at the metastable substrate/liquid interface. The scallop morphology of the Cu_6Sn_5 grains can be observed before the nucleation of the Cu_3Sn IMC, induced by fast grain boundary diffusion coupled with the widening of the grain boundary grooves within the Cu_6Sn_5 layer. Published thickness of IMC layers after soldering (10 sec) was 0.9 and 0.1 μm for Cu_6Sn_5 and Cu_3Sn IMC respectively [17]. These findings are in very good agreement with our results (see first data points of IMC thickness in Fig. 2)

According to our expectations and reviewed literature [18-20] the IMC layer thickness increases with increasing ageing time. With increasing ageing time, the layers became gradually thicker and more segmented with significant nodulations, showing the typical scallops [12]. The thickness of the Cu_3Sn phase is uniform and follows the surface of Cu. Separate forms of the Cu_6Sn_5 and Ag_3Sn IMC phases were observed in the solder volume. Evolution of IMC thickness [9] of Cu_3Sn and Cu_6Sn_5 dependence on the square root of time are showed in Fig. 2. Measured data points were fitted by linear function in order to demonstrate that interfacial IMC layers increase linearly with the square root of the aging time according the equation [19, 20].

$$X = X_0 + k.t^{1/2} \qquad (1)$$

Where X is the thickness of the IMC layer, X_0 is the thickness of IMC layer at t = 0 s, t is the ageing time and k is the growth rate constant. This $t^{1/2}$ dependence indicates that the rate controlling mechanism for the growth of the layers is volume diffusion process [18].

The increase of the IMC Cu_6Sn_5 thicknesses is almost identical for the both solders which indicates that both IMC phases are growing at a similar rate [8].

On the other hand, the formation of Cu_3Sn is much slower because it is affected by two phenomena. First, it is the phase stability of Cu_6Sn_5 according to the reaction [18, 20]:

$$Cu_6Sn_5 + 9Cu \rightarrow 5Cu_3Sn \qquad (2)$$

and second, is the diffusion of Sn atoms through Cu_6Sn_5 layer and diffusion of Cu atoms through Cu_3Sn layer and subsequent grow of the Cu_3Sn IMC layer according to the reaction [18]:

$$3Cu + Sn = Cu_3Sn \qquad (3)$$

The IMC thickness increases with increasing temperature and time and can reach the critical thickness (about 5 μm or more) when numerous of cracks appear resulting in a total loss of the joint reliability.

Mechanical testing of the soldered joints (before and after annealing) focused at the measurement of shear strength [21]. The results shown in Fig. 3 indicate that solder joints formed by eutectic SAC reached the highest values of shear strength. The shear strength after ageing of eutectic SAC is equal to the shear strength of eutectic SnCu0.7 solder before annealing. The lowest value of shear strength is found in the soldered joints after annealing formed by the binary eutectic SnCu0.7 solder; also the scatter of measured values is the highest. The main reason of this effect is the coarsening of IMC particles within bulk solders [20]. These IMC particles are much bigger and irregularly distributed in the bulk solder than in as-soldered specimens.

During the shear test, the solder joint will fracture along the weak points, which indicates the failure mode of the solder joint. Yoon and Jung published that the fracture occurred inside the bulk solder for samples aged at 150 °C up to 250 h while the joint failed partially at the solder/Cu_6Sn_5 interface for samples aged 500 h or longer [18]. This transition can be directly linked to the formation of thick Cu–Sn IMC layer.

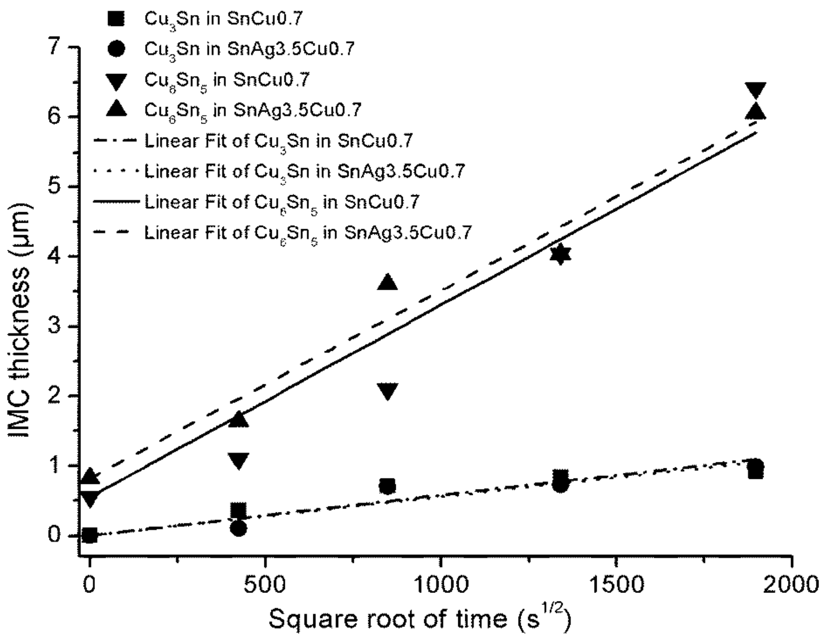

Fig. 2. Intermetallic thickness dependence of the square root of ageing time at 150 °C.

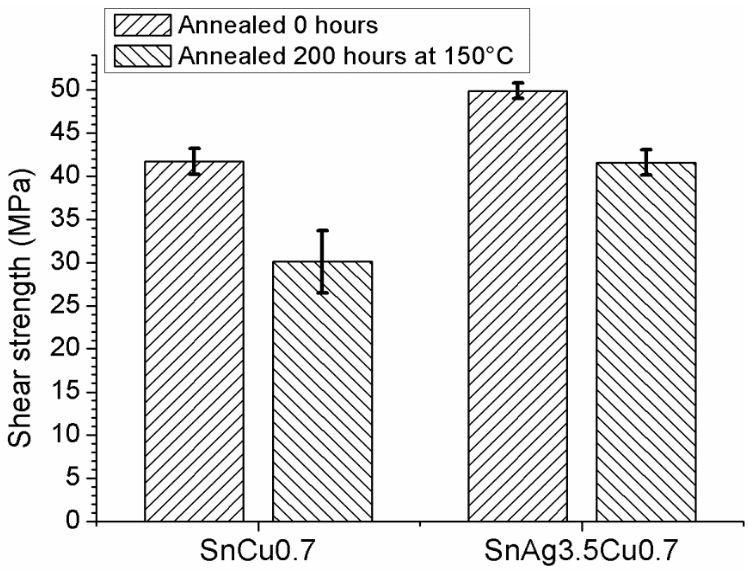

Fig. 3. Shear strength of soldered joints before and after heat treatment [15].

These results suggest that the interface between the solder and the Cu_6Sn_5 IMC is brittle and that the failure mode of the solder joint changed to the interface-related one as the Cu_6Sn_5 IMC layer became thick [18].

According to Lee [19], thermal aging leads also to a coarsening of the solder microstructure. Therefore, the reduction in shear strength can reasonably be attributed not only to the increased thickness of the brittle intermetallic layer, but also to the agglomeration of IMC, or to the coarsening of the Cu_6Sn_5 and/or Ag_3Sn particles in microstructure [19].

4. Conclusions

In this work two eutectic lead-free solders SnCu0.7 and SnAg3.5Cu0.7 were investigated. The microstructures of soldered joints before and after heat treatment at various times were analysed. For the longer ageing times, the Cu_3Sn IMC layers were observed. This IMC layer grows faster up to 200 hours of ageing time. At longer exposition times the additional growth of this phase is minimal. On the other hand with the further increase of time, the layers of Cu_6Sn_5 IMC phases became gradually thicker and more segmented with significant nodulations, showing the typical scallops.

The soldered joints with the ternary eutectic solder SnAg3.5Cu0.7 showed higher value of shear strength than joints formed with binary eutectic SnCu0.7 solder. After heat treatment both soldered joints exhibit decrease in shear strength. Moreover, the scatter in measured shear strength increases after ageing of the SnCu0.7 soldered joints.

The growth of IMC layers after heat treatment is related with decrease of shear strength. Already after 200 hours of exposition at higher temperature the shear strength of soldered joints significantly decreases. Due to additional growth of the IMC layer with longer exposition times the additional decrease of shear strength is expected. Such a degradation of joining properties can be serious issue in electronic devices exposed to higher temperatures, as well as in other products that are working at elevated temperatures.

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