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FORMATION OF IMC THE INTERFACE OF SNAGCU1,0BI SOLDER WITH CU SUBSTRATE

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Abstract: *The effects of Bi addition on the intermetallic phase formation in the lead-free solder joints of SnAgCu1,0Bi (composition given in weight %) with copper substrate are studied. The aged interfaces were analysed by the optical microscopy and energy dispersive x-ray spectroscopy (EDX) microanalysis. The mechanism of the* Cu_6Sn_5 *layer growth is discussed and the conclusions for the optimal solder chemical composition are presented.*

Key words: *lead-free solder, intermetallic compound, formation, growth, annealing*

1. INTRODUCTION

Increasing environmental and health concerns about the lead toxicity limit of traditional Sn-Pb alloys in soldering technology and stimulate the development of alternative, lead-free solder alloys for electronic applications (Suganuma, 2004; Viňáš et al., 2010). Among the currently considered compositions, ternary eutectic Sn-Ag-Cu alloys have received a lot of attention due to their reasonable melting temperature (217 °C), increased strength and a lower wetting angle comparing to binary Sn-Ag eutectic alloys (Madeni et al., 2006; Viňáš et al., 2010). Ag and Cu elements are used in low concentrations and thus, they are not considered to be an environmental hazard. Nevertheless, challenges remain with respect to the relatively high melting point of these alloys. The melting point of a traditional Sn-Pb solder is only 183 °C. In order to decrease the melting point of Sn-Ag-Cu alloys, additional elements in low concentrations are needed. Bismuth is potential candidate that may significantly lower the melting of the Sn-Ag-Cu eutectic. Furthermore, this element is able to increase the solder's mechanical strength and improve the wettability (***, 2007; ***, 2004).

2. EXPERIMENT

The lead free solder samples were prepared by melting the pure metals (Sn, Ag, Cu, Bi), in the respective concentrations, in alumina crucibles. The used metals were of 99.99% purity. The chemical compositions of the samples, measured by the energy dispersive x-ray spectrometry (EDX, JEOL-JXA-840A), are given in Table 1. The technical copper plate (99.99 %) was used as the substrate material. The copper surface was grinded, polished by diamond paste (1 µm finish) and cleaned by the ultrasonic cleaner.

The soldering of the copper plate was conducted at 250 °C for 5 s. After the soldering, the samples were quenched to the room temperature. The joints were subsequently aged at temperatures of 130 – 170 °C for 2-16 days in a convection oven. The samples were gradually taken from the furnace after 2, 4, 8, 12 and 16 days. The samples were mounted in the epoxy resin and the cross sections were made. Prior to the analysis, the interface was polished with the diamond paste and finally etched in a nitric acid solution (5% HNO3 + 2% HCl + 93% methanol) for 2-4 s. The microstructure of the soldered joints and the morphology of intermetallic phases were investigated by the optical microscope. The chemical composition of the phases was investigated by the EDX microanalysis (JEOL-JXA-840A).

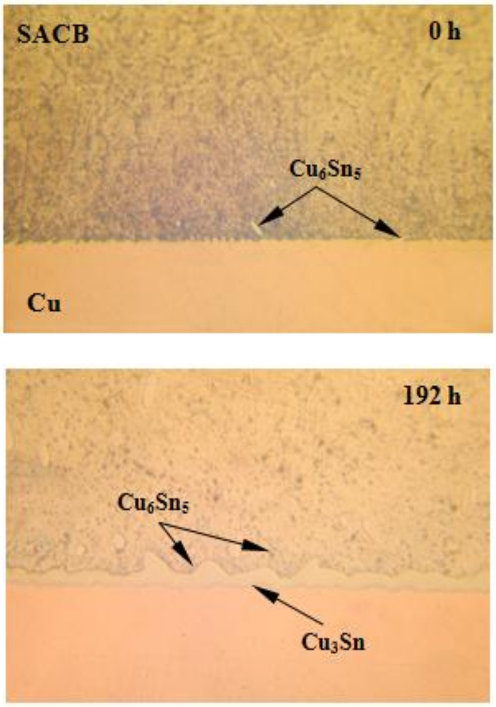
Acronym	Sn	Ag	Cu	Bi
SACB	97,5	1	0,5	1

Tab. 1. Chemical composition (in weight %) of the investigate solder

3. RESULTS

3.1 Macroscopic analysis

The microstructure of the SACB-Cu solder joint is presented in Figure 1. Similarly to the previous case, the interface layer between the materials immediately after the soldering consisted only of a scallop-shaped Cu_6Sn_5. The average thickness of Cu_6Sn_5 was 0.85 µm. During the subsequent solid-state ageing, this layer continued to grow. Cu_6Sn_5 layer is formed by nucleation during soldering between the solid copper substrate and liquid Sn-based lead free solder. At early stages, the layer is expected to grow in the horizontal direction until the grains start impinging one another. The scallop-like shape of this phase is probably a result of the grain coarsening. The scallop-like shape disappears at later stages of ageing which suggests a change in the growth mechanism to the steady growth in the perpendicular direction to the interface.



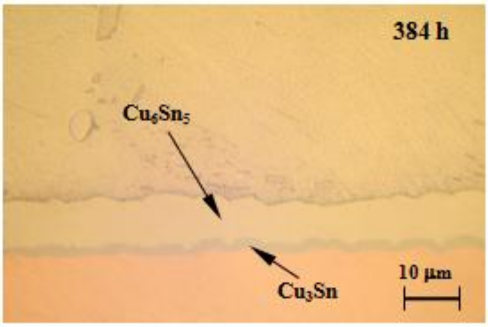


Fig. 1. Microstructure evolution of the Cu/SACB interface after soldering and solid state ageing at 150°C for 0, 192, 384 hours

3.2 Chemical analysis

The chemical composition of the cross section is presented in Figure 2. Bismuth does not significantly influence the chemical composition of intermetallic phases. This is probably due to the low concentration. The element is located mostly in the solder bulk. Nevertheless, bismuth seems to suppress the formation of the second layer, Cu_3Sn. The thickness is smaller comparing to the Cu_3Sn layer formed at the Cu-SAC interface.

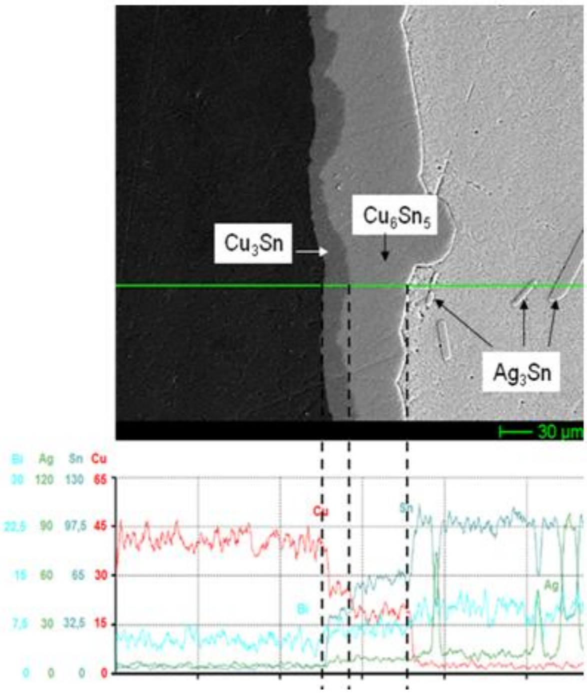


Fig. 2 Element distribution across the Cu/SACB interface, measured by EDX, after solid state ageing for 384 h

3.3 Growth kinetics of intermetallic phases

The time evolution of the Cu_6Sn_5 layer thickness is given in Fig. 3. The Cu_6Sn_5 layer grows with a significantly higher rate comparing to Cu_3Sn. The layer growth follows the parabolic rate law

$$x = k_p \sqrt{t} + x_0 \qquad (1)$$

In this equation x is the layer thickness, t is the ageing time, k_p is the parabolic rate constant and x_0 is the layer thickness before ageing (at t = 0 h).

The growth kinetics is thermally activated. The parabolic rate constants obey the Arrhenius equation

$$\log k_p = \log A - 2.303 \frac{E_A}{RT} \qquad (2)$$

In this equation, A is the pre-exponential factor, E_A is the activation energy, R is the molar gas constant and T is the ageing temperature. The apparent activation energy for the Cu_6Sn_5 layer formation is 71 kJ mol^{-1}. Bismuth decreases the rate of Cu_3Sn layer formation.

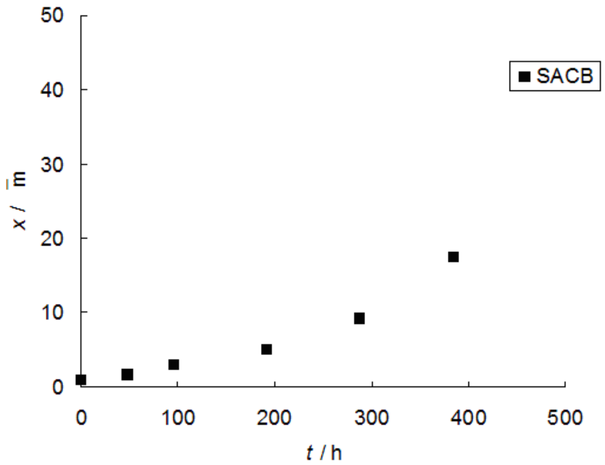


Fig. 3. Thickness of the Cu_6Sn_5 layer versus ageing time for solder system SACB

4. CONCLUSION

The effect of bismuth in Sn-Ag-Cu solders on the kinetics of intermetallic phase formation at the solder-copper interfaces was investigated. The interface layer consisted of two parallel layers - Cu_3Sn and Cu_6Sn_5. Cu_6Sn_5 was formed during soldering and grew parabolically during subsequent solid state ageing. Cu_3Sn was formed during solid state ageing and its growth rate was decreased by Bi additions in the lead-free solder. It is suggested that Cu_3Sn grows by Sn diffusion. Bismuth can substitute Sn in intermetallic compounds, $Cu_3(Sn,Bi)$ compounds form at Cu_3Sn grain boundaries where they inhibit Sn diffusion.

Future research will address to investigation in lead-free solders based on SnAgCu containing under 1% Bi and In, studying their physical, mechanical and soldering properties.

5. ACKNOWLEDGEMENTS

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