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GROWTH OF THE IMC AT THE INTERFACE OF SnAgCuBi (Bi = 0,5; 1,0) SOLDER JOINTS WITH Cu SUBSTRATE

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Original scientific paper

The effects of Bi addition on the intermetallic phase formation in the lead-free solder joints of Sn-Ag-0.5Cu0.5Bi (SAC0,5B) and Sn-Ag-0.5Cu-1.0Bi (SAC1,0B), composition given in weight (measured in %), with copper substrate are studied. The soldering of the copper plate was conducted at 255 °C for 5 s. The joints were subsequently aged at temperatures of 100 °C, 130 °C and 160 °C for 1, 3, 7, 15 days in a convection oven. The aged interfaces were analysed by the optical microscopy and energy dispersive x-ray spectrometry (EDX, JEOL-JXA-840A) microanalysis. Two intermetallic layers are observed at the interface – Cu_3Sn and Cu_6Sn_5. Cu_6Sn_5 is formed during soldering. Cu_3Sn is formed during solid state ageing. Bi decreases the growth rate of Cu_3Sn since it can possibly inhibit Sn diffusion along the grain boundaries. The mechanism of the Cu_6Sn_5 layer growth is discussed and the conclusions for the optimal solder chemical composition are presented.

Keywords: *lead-free solder, intermetallic compound, annealing*

Pojava IMC na granici lemljenih spojeva od SnAgCuBi (Bi = 0,5; 1,0) na Cu podlozi

Izvorni znanstveni članak

Ovdje se analizira utjecaj dodavanja Bi na stvaranje intermetalne faze u bezolovno lemljenim spojevima od Sn-Ag-0.5Cu0.5Bi (SAC0,5B) i Sn-Ag-0.5Cu-1.0Bi (SAC1,0B), sastav dan u težinskim %, na bakrenoj podlozi. Lemljenje bakrene ploče je provedeno na 255 °C u trajanju od 5 s. Spojevi su zatim ostavljeni na temperaturi od 100 °C, 130 °C i 160 °C u trajanju od 1, 3, 7, 15 dana u konvekcijskoj peći. Međupovršine su tada analizirane optičkim mikroskopom i energetskom disperzivnom rendgenskom spektrometrijskom mikroanalizom (EDX, JEOL-JXA-840A). Dva intermetalna sloja su zapažena na međupovršini - Cu_3Sn i Cu_6Sn_5. Sloj Cu_6Sn_5 je nastao tijekom lemljenja. Sloj Cu_3Sn je nastao tijekom sazrijevanja u čvrstom stanju. Dodavanjem Bi smanjuje se nastanak Cu_3Sn jer se tako sprječava širenje Sn duž granica zrna. U članku se dalje raspravlja mehanizam nastanka sloja Cu_6Sn_5 i daju se zaključci za optimalni kemijski sastav lemila.

Ključne riječi: *bezolovno lemilo, intermetalna smjesa, žarenje*

1
Introduction

The unhealthy effects of lead to the environment and human health accelerate the research and development of solder so as to completely eliminate lead. The lead-free solders beside the higher melting temperature, worse wettability (from this different temperature profile, different flux...) are different from the lead containing solders also in different electrical and mechanical properties.

Most of lead-free solder alloys are set up mainly from the addition of a small amount of third and fourth alloy to the binary alloy to increase their properties. Bismuth is added to the solder alloys in order to decrease the melting point, advance mechanical properties and increase creep resistance. Bismuth also advances the wettability, which can play the role in the use of lower soldering temperature [1, 4].

The alloy systems with the Bi addition are used by the Japanese producers of electronics. They use the alloys with a high amount of Sn, mainly SnAgBi, SnAgCuBi.

Typical compositions are tested by the Japanese project NEDO (New Energy and Industrial Technology Development Organization) – SnBi3.0Ag2.0Cu0.5 and after it by project IMS (Intelligent Manufacturing Systems) – SnAg3.0Bi2.0Cu0.5. Only low amount of Bi is preferred in the reduction of melting temperature and gaining better wettability. The addition of higher amount of Bi, approximately 5-20 %, decreases the melting point of the temperature of eutectic SnPb solders. However, they lose the good conditions of SnAgCu alloy system [6].

2
The influence of intermetallic compounds to the joint reliability

The most widespread questions in lead-free solders reliability are the growth of intermetallic compounds, which are localized to the interface between solder and substrate. All known basic materials and coatings in electronic products together with the melted solder with active element (Sn) create the intermetallic compounds (IMC) at the interface solder – substrate. Their existence at the contact area indicates a good metallurgical joint was created [2].

Unwillingly, the excessive IMC growth is mainly indicated by joint heating in working process (changes of atmosphere temperature or temperature changes by heat abstraction from the cover); in case of IMC growth to the heavy thickness and the interface solder – IMC takes place at the source of crack creation and extension.

The growth begins at the room temperature and continues to the area of working temperature of electronics. The growth of layers and the cracks bring together the degradation of mechanical and electrical properties, which causes the decrease of electrical conductivity of joint. More cracks in the layer and also higher transfer resistance cause the higher heat strain of joint. These layers and cracks are further expanded. This process leads to the joint degradation and gradually to the non-functional joint [3, 7].

The excessive growth also consumes the basic metal and thereby causes the gradual reduction of soldered joint. This can lead into the adhesion loss of the substrate, which is not wetted by solder, or it can create the crack due to the strain in intermetallic compound, because of excessive thickness [3, 5].

3
Experimental part

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 ground, polished by diamond paste (1 µm finish) and cleaned by the ultrasonic cleaner. The soldering of the copper plate was conducted at 255 °C for 5 s. After the soldering, the samples were quenched to the room temperature. The joints were subsequently aged at temperatures of 100 °C, 130 °C and 160 °C for 15 days in a convection oven. The samples were gradually taken from the furnace after 1, 3, 7, 11 and 15 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 measured by the energy dispersive x-ray spectrometry (EDX, JEOL-JXA-840A) microanalysis. The results are presented in the following section.

Table 1 Chemical composition (in weight %) of the investigated solder

Acronym	Sn	Ag	Cu	Bi
SAC0.5B	98	1	0,5	0,5
SAC1.0B	97,5	1	0,5	1

4
Results
4.1
Macroscopic and chemical analysis

Cu - SnAg1.0Cu0.5Bi0.5

The microstructure of the interface of soldering joint Cu - SnAg1.0Cu0.5Bi0.5 after soldering process and then soldering heat affected is shown in Fig. 1a, b. After soldering (Fig. 1a) the structure of solder SnAgCuBi0.5 consists of predominantly fine-grained structure. The phases Cu_6Sn_5 and Ag_3Sn which after the heat affection change their shape and size are dispersed in the volume of solder. These phases are formed from Ag and Cu, which are contained in the composition of solders.

Given that the use of soldering materials based on Cu and Sn can be observed at the interface of Cu-substrate/solder creation of IMC Cu_6Sn_5. The size of IMC layer does not get over 1 µm. The further reaction layer at the interface of substrate of the phase Cu_6Sn_5 is created after aging and it is documented as Cu_3Sn (Fig. 1b).

Growth of Cu_3Sn phase can be explained by the fact that the great thickness of Cu_6Sn_5 phase leads to diffusion of Cu at the interface and due to the lack of Sn at the interface of solder joint the phase rich in Cu (Cu_3Sn) is created. Morphology of the IMC is significantly different from each other. IMC Cu_6Sn_5 is initially characterized by its high inequalities in comparison with laminated Cu_3Sn phase. Over time, however serrated shape of Cu_6Sn_5 phase takes laminated shape with a unique layered scallop. During the time of 360 h of annealing there was a relatively continuous layer of the two phases with an average thickness of 22 µm.

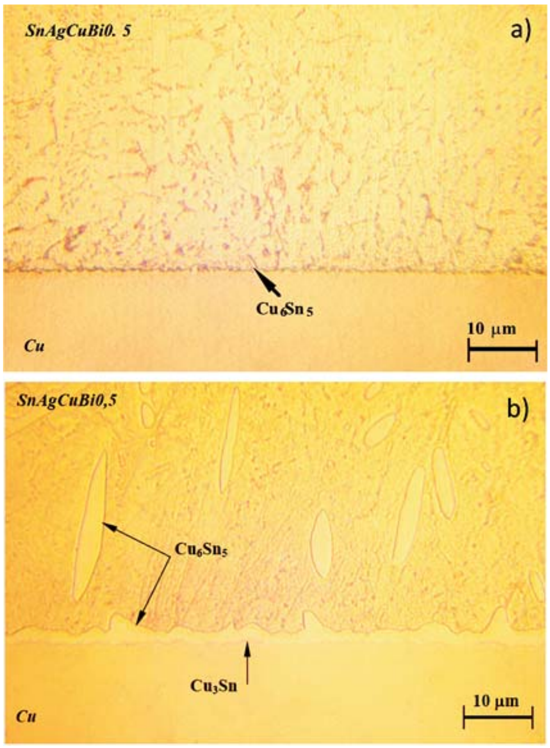

Figure 1 Microstructure evolution of the interfacial area of Cu-SnAg1.0Cu0.5Bi0.5 solder joint a) after soldering *T* = 255 °C, *t* = 5 s, b) aged at 130 °C for 360 h

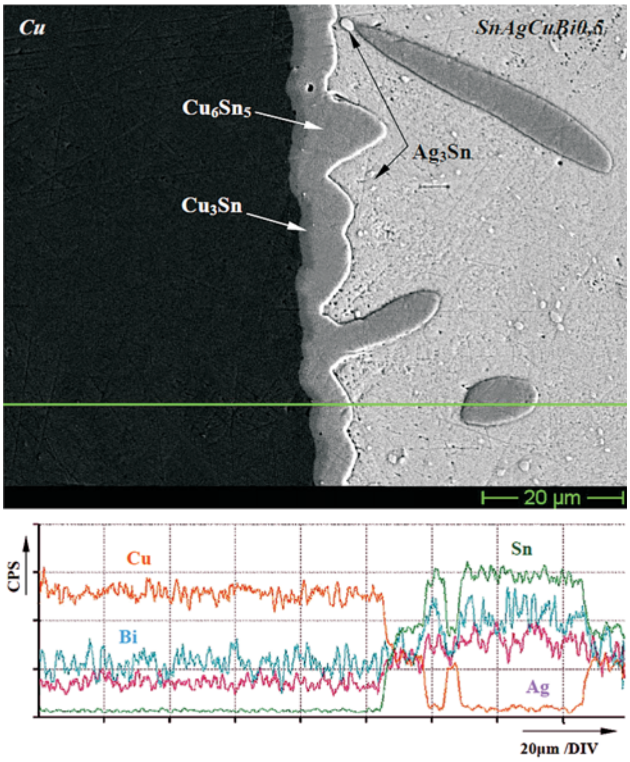

Figure 2 Linear EDX microanalysis of Cu – SnAg1.0Cu0.5Bi0.5 solder joint interface aged at 130 °C for 360 h

In Fig. 2 linear EDX microanalysis the structure of heat affected soldering joint together with the individual increased phases can be observed. The line analysis confirms the presence of phases Ag_3Sn and Cu_6Sn_5 near the interface. Generally, however, larger particles tend to Cu_6Sn_5 phase and smaller particles to Ag_3Sn phase.

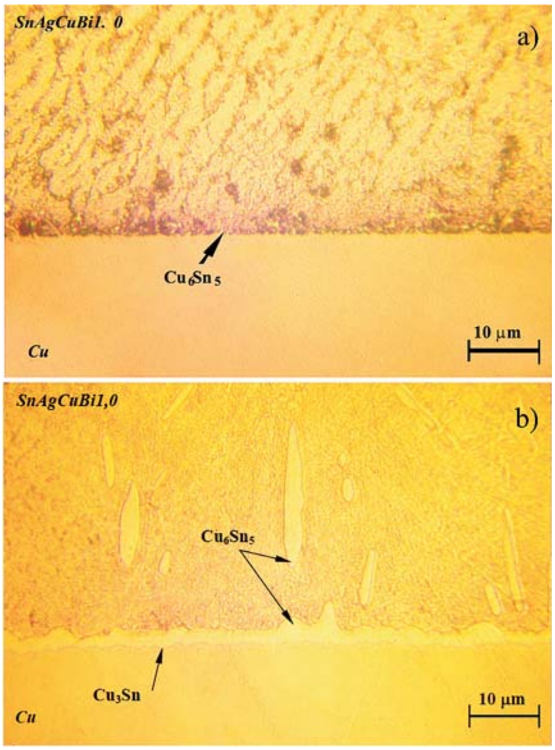

Figure 3 Microstructure evolution of the interfacial area of Cu-SnAg1.0Cu0.5Bi1.0 solder joint a) after soldering $T = 255$ °C, $t = 5$ s, b) aged at 130 °C for 360 h

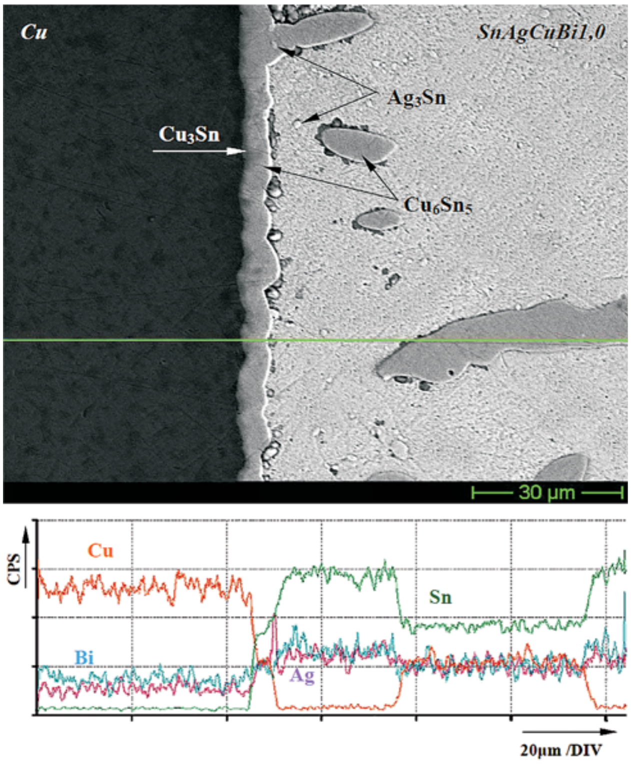

Figure 4 Linear EDX microanalysis of Cu – SnAg1.0Cu0.5Bi1.0 solder joint interface aged at 130 °C for 360 h

SnAg1.0Cu0.5Bi1.0

Structure of solder SnAg1.0Cu0.5Bi1.0 after the soldering shows granular structure (Fig. 3a). Apart from scattered Ag_3Sn phase of various shapes and dimensions the creation of Cu_6Sn_5 was observed in the volume of solder. During the annealing of solder joints there is a change to the growth and change in shape of IMC.

The sequence of creation at the IMC is the same as in SnAnCuBi0.5 solder, ie, as the first Cu_6Sn_5 phase is created and the second phase Cu_3Sn is created after the heat affection (Fig. 3b).

Compared with the solder containing less Bi the thickness of IMC decreased at the interface. Solder SnAgCuBi1.0 also varies in the thickness of phases (Ag_3Sn and Cu_6Sn_5) located in the volume and quantity of solders projecting long-scallop skewer (Cu_6Sn_5 phase) of the interface to solders. These changes, microstructure refinement, can be attributed to a greater number of particles Bi contained in Sn-rich areas.

The linear EDX microanalysis (Fig. 4) of joint Cu - SnAgCuBi1.0 confirms the close interface, which is made from phases Cu_3Sn and Cu_6Sn_5. This was confirmed by the unique occurrence of phases Ag_3Sn in gross IMC Cu_6Sn_5. As for the solder SnAgCuBi0.5 the presence of Bi precipitates in Sn-rich areas of the EDX microanalysis failed.

4.2
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 compared to Cu_3Sn. The layer growth follows the parabolic rate law

$$x = k_{\mathrm{p}} \sqrt{t} + x_0 . \tag{1}$$

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).

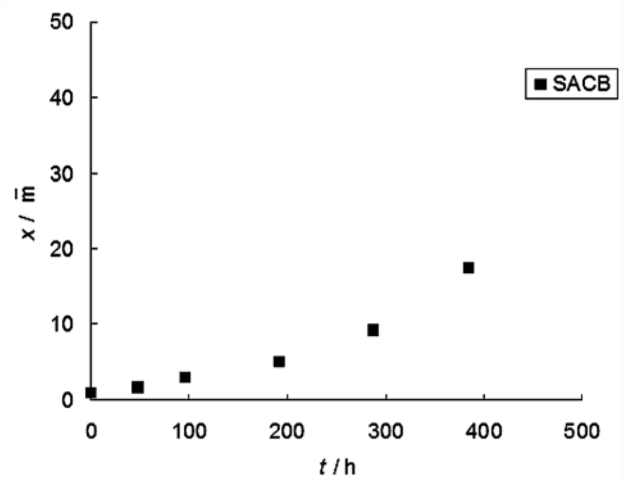

Figure 5 Thickness of the Cu_6Sn_5 layer versus ageing time for solder system SAC1.0B

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

$$\log k_{\mathrm{p}} = \log A - 2{,}303 \cdot \frac{E_{\mathrm{a}}}{R \cdot T} . \tag{2}$$

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. Bismuth decreases the rate of Cu_3Sn layer formation.

5
Conclusion

The effect of bismuth in SnAgCu 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.

From the results of the study of interface of the lead-free soldering joints it is clear that during the annealing (aging) services there are significant structural changes. Adding 1 % Bi to the system of alloy SnAgCu leads to the refinement of grain size of intermetallic phases in the volume of solders. It also suppresses the growth of layers of intermetallic phases at the interface of soldering joints and thus improves the reliability of joints. Due to the low content (0,5 % and 1,0 %) of Bi alloys in the systems of SnAgCuBi the presence of Bi precipitates was confirmed. Future research will be addressed to investigation in lead-free solders based on SnAgCu containing under 0,5 % and 1 % Bi, studying their physical, mechanical and soldering properties.

Acknowledgements

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