

# EFFECT OF In ADDITION ON Sn-Ag SOLDER, ITS WETTING AND SHEAR STRENGTH OF COPPER JOINTS

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Received 21 January 2005, accepted 29 April 2005

Effect of indium addition on microstructure of the solders, their enthalpy changes, wetting of copper substrate, strength and structure of the copper joints were studied. Lead-free solders near to eutectic binary Sn-3.5Ag alloy containing 0, 6.5 and 9 wt.% of indium were prepared in induction furnace in Ar atmosphere followed by planar flow casting into the form of ribbon. Indium decreases the onset temperature for melting and freezing to 206 and 181 °C for 9 wt.% indium, respectively. Enthalpy change of the melting as well as of the freezing also decreases with increase the amount of indium. Wetting of Cu substrate by the solders was investigated by sessile drop method at the temperatures 250, 280 and 320 °C. Indium decreases the contact angle down to 36° for 9 % In, 320 °C and 1800 s. Copper joints were made with solders at the temperatures 250, 280 and 320 °C for 1800 s in air. Cu plates prior to joining were daubed by flux based on rosin. Shear strength moderately decreases with amount of indium and with joining temperature from 23.6 MPa for indium free solder at 250 °C to 17.6 MPa for highest amount of indium at 320 °C.

**Key words:** lead-free solder, wetting, copper joints, shear strength

## 1. Introduction

The soldering material widely used is Sn-Pb alloy [1], which has low melting point and good electrical and strength properties. The use of lead has gained attention because the waste of assembled boards may cause environmental problems due to their toxicity. Several alloys are considered representative of viable candidates for replacing eutectic Sn-Pb system. Many of the systems are based on adding small quantity of third or fourth elements to binary alloy system in order to lower the melting point and increase the wetting and reliability.

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Two eutectic solder systems, Sn-Ag and Sn-Zn, are the basic alloys that provide a melting temperature range similar to that of the Sn-Pb eutectic at 173 °C. Melting temperature of Sn-3.5Ag (221 °C) is higher than that of eutectic Sn-37Pb and the wetting property is worse. To improve these properties additional elements such as Bi, Cu, In and Zn are added. These additional elements lower the liquidus temperature and improve the tensile strength [2]. Choi et al. [3] investigated the effect of addition of In (up to 11.5 wt.% of In) to the Sn-3.5Ag eutectic solder on its structure. The addition of about 9 % In lowered the liquidus temperature below 210 °C and resulted in a change of the microstructures and secondary phases. After ageing the solders at 150 °C for 500 hours coarsening of the secondary phases was observed.

The aim of this paper is to characterize the effect of indium addition in lead-free Sn-3.5Ag solder on some of its thermal properties, on the wetting of copper and on the structure and strength of copper joints.

## 2. Experimental procedure

Lead-free solders based on Sn-3.5Ag eutectic alloys were prepared by melting appropriate amount of Sn (99.99) and Ag (99.99) and desired amount (6.5 and 9 wt.%) of In (99.999) was added. Melting was done in induction furnace under argon atmosphere. The solders were prepared by planar flow casting in the form of ribbon 5 mm wide and 0.05 mm thick.

The microstructure of the solders was investigated with scanning electron microscope (SEM) equipped with the energy dispersion X-ray analyser. The wetting properties of the solders over the substrate are regarded as important factors. The Cu substrates were polished with 1  $\mu\text{m}$  diamond paste and cleaned in acetone followed by etching in 10% sulphuric acid in methanol. After washing and drying the substrates were daubed by rosin moderately activated flux. Contact angle was measured by sessile drop method. Piece of solder ( $\sim 0.4$  g) after melting in the furnace (air atmosphere) was photographed during 30 minutes in regular time intervals at the temperature 250, 280 and 320 °C. Perkin-Elmer DSC 7 was used for differential scanning calorimetry to determine the melting and phase transition temperatures at a heating rate 10 K/min in argon atmosphere.

Mechanical strength and microstructure of copper-solder-copper joint prepared by direct bonding were also studied. Shear strength was considered as a main indicator of mechanical properties of such joints. The reliability of the solder joint is strongly affected by the type and extent of the interfacial reaction between solders and plates. Accordingly the interaction between solder and plate is important and a deeper understanding of the internal reaction between these two components and the influence of this reaction on the shear strength of the joint is necessary.

Joints were formed by placing the solder ribbon between the Cu plates which were daubed by the flux and maintaining in the furnace for 30 minutes at the

temperatures 250, 280 and 320 °C with load of  $\sim 2$  g in air atmosphere. For given set of parameters, four specimens were prepared, one was used for a structural study with the analysis of interface between the components (Cu-solder-Cu) and three of them were used for shear strength measurements. Shear strength of the joints was measured by Zwick testing machine.

### 3. Results and discussion

#### 3.1 Differential scanning calorimetry

The results obtained by differential scanning calorimetry are summarized in Table 1, where  $T_{xm}$  and  $T_{xf}$  are onset temperatures of melting and freezing, respectively,  $\Delta H_m$  and  $\Delta H_f$  are enthalpy changes of melting and freezing, respectively.

Indium decreases the melting and freezing temperature in comparison with indium free solder by 19° (melting) and 11° (freezing) for 9 wt.% of indium. Enthalpy change of the melting as well as of the freezing also decrease with increasing amount of indium ( $\sim 10.5$  % and 6–7 %, respectively).

Table 1. Enthalpy change, onset temperatures of melting and freezing of relevant solder

Solder	Sn-3.5Ag	Sn-3.5Ag-6.5In	Sn-3.5Ag-9In
$T_{xm}$ [°C]	225	209	206
$\Delta H_m$ [J/g]	67	60	61
$T_{xf}$ [°C]	192	182	181
$\Delta H_f$ [J/g]	–64	–60	–59
$T_{xm} - T_{xf}$ [°C]	33	27	25

#### 3.2 Wetting

Figure 1 (a,b,c) shows the time dependence of the contact angle of the solders with 0, 6.5 and 9 wt.% of indium on the Cu substrate. The pictures show the mild decrease of contact angle with time for given temperature as well as the decrease of contact angle with temperature for given solder. These angles are constant after about 10 minutes. At the interface between the liquid solder and solid copper the interaction is relatively fast and the microstructure of the interface is stable. For the solder not containing In the interaction is even faster. Figure 2 shows the contact angle of the studied solder for the temperatures of 250, 280 and 320 °C in dependence on the amount of indium. Indium decreases the contact angle on Cu substrate down to about 36° for 320 °C and 30 minutes for 9 % of In in sample. Lin and Lin [4] measured influence of surface roughness of Cu plating on Si substrate on the wetting angle of Sn-Pb and various lead-free solders and the influence of various fluxes. Contact angle between solder and substrate mildly decreases with

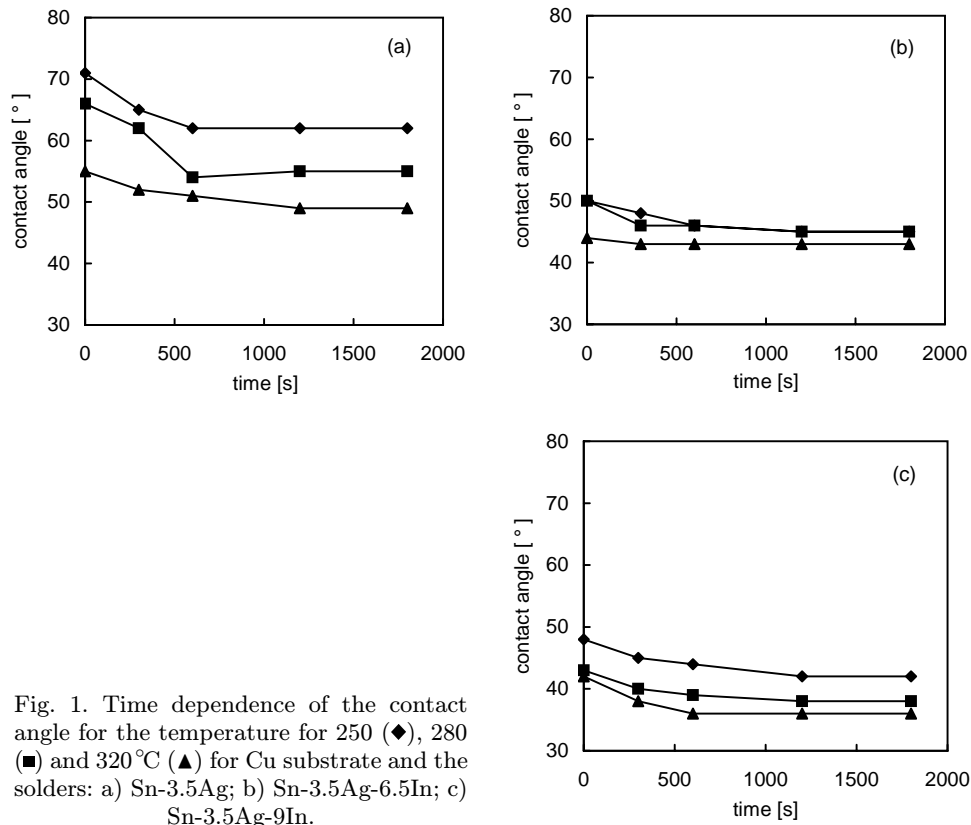


Fig. 1. Time dependence of the contact angle for the temperature for 250 (◆), 280 (■) and 320°C (▲) for Cu substrate and the solders: a) Sn-3.5Ag; b) Sn-3.5Ag-6.5In; c) Sn-3.5Ag-9In.

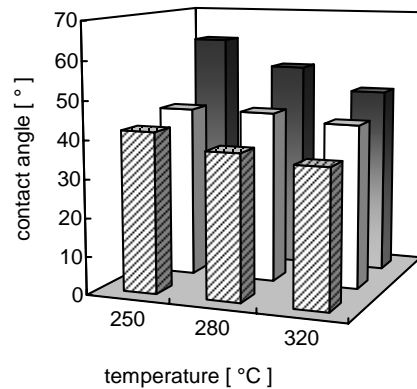


Fig. 2. Contact angle between the solders and Cu substrate for temperatures 250, 280 and 320°C in dependence on the amount [wt.%] of indium: 0 (■), 6.5 (□) and 9 (▨).

the increase of surface roughness of Cu plating. Except the roughness, bigger effect on the contact angle has a type of the flux. For Sn-3.5Ag solder and 280°C the wetting angle is in the interval 30°–40° depending on the type of flux [4].

### 3.3 Microstructure of the solders and soldered joints

Figure 3 shows the section of the Sn-3.5Ag solder on copper substrate after wetting at 250 °C for 1800 s. At the boundary a  $\eta'$  [5] phase arises and copper diffuses deeper into the solder and the particles of the same phase are arising. Increase of the wetting temperature results in coarsening of the phase at the interface and in solder (Fig. 4). Adding indium into the Sn-3.5Ag solder gives rise to a new phase containing indium (Fig. 5, points A4, A6) with composition close to  $\text{Ag}_3\text{In}$  (Table 2). The structure of the joints is similar to that of the drop of solder on copper substrate. Figure 6 shows the structure of the joint prepared with Sn-3.5Ag

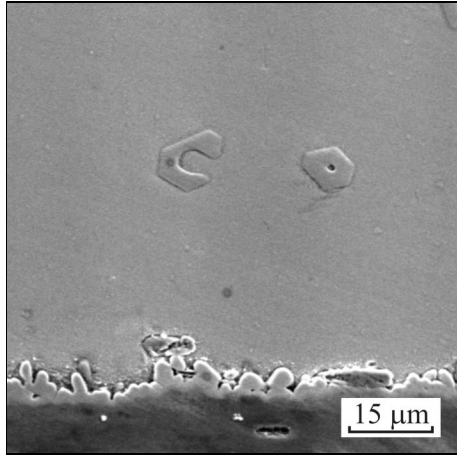


Fig. 3. Structure of Sn-3.5Ag on Cu substrate after 1800 s at 250 °C.

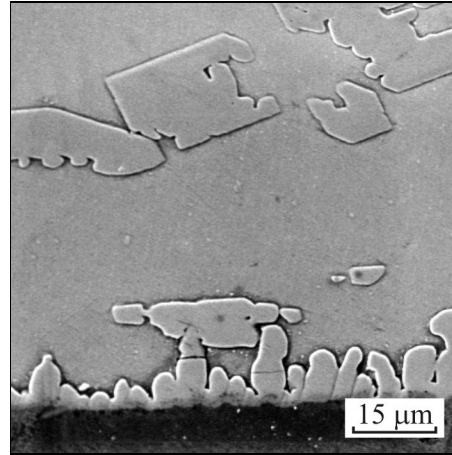


Fig. 4. Structure of Sn-3.5Ag on Cu substrate after 1800 s at 320 °C.

Table 2. Composition at the boundary between Cu and Sn-3.5Ag-9In solder after wetting for 1800 s at 250 °C (see Fig. 5)

Point	Cu [at.%]	Ag [at.%]	In [at.%]	Sn [at.%]
A1	63.7	0.1	0.2	35.9
A2	62.7	0.8	0	36.6
A3	0.9	88.3	7.9	2.9
A4	2.8	75.9	18.6	2.8
A5	3.0	67.7	5.9	23.4
A6	2.4	76.1	16.8	4.6

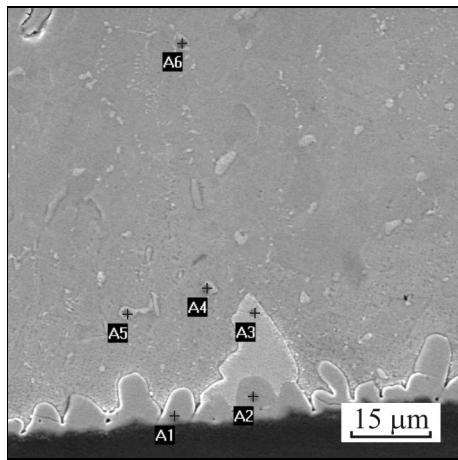


Fig. 5. Structure of Sn-3.5Ag-9In on Cu substrate after 1800 s at 250°C.

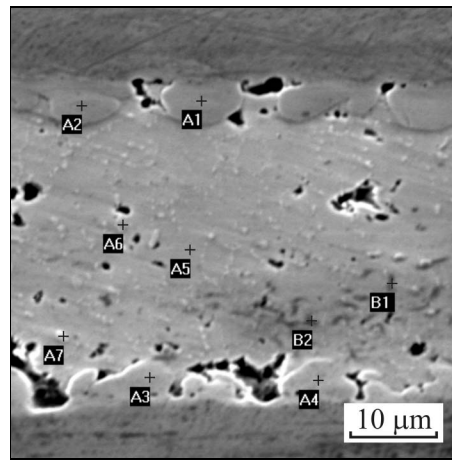


Fig. 6. Structure of the joint prepared with Sn-3.5Ag solder at 320°C and 1800 s.

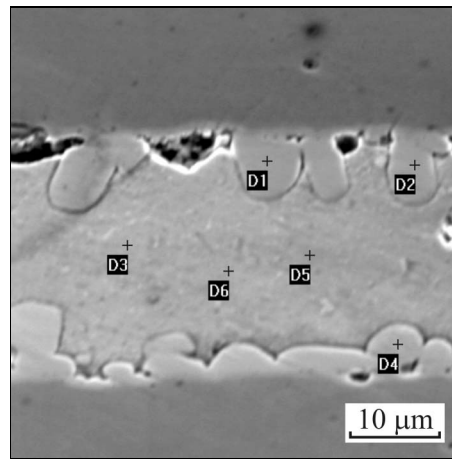


Fig. 7. Structure of the joint prepared with Sn-3.5Ag-9In solder at 320°C and 1800 s.

solder at 320°C and 1800 s. Structure contains several pores, which can be due to the residue of the flux. Structure of the joints containing indium shows less pores (Fig. 7). This can be due to improved capillarity of the solder containing indium.

### 3.4 Joint strength

Figure 8 shows the shear strength of the joints made from various solders in between Cu plates at the temperatures of 250, 280 and 320°C. Shear

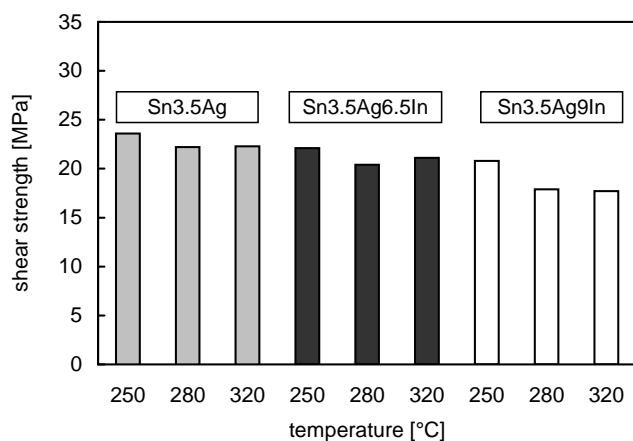


Fig. 8. Shear strength of the joints made of Cu-solder-Cu for various solders and temperatures of joining and amount of indium. Joining time 1800 s.

strength of the joints mildly (6–14 %) decreases with the temperature of joining for all solders. Similarly the shear strength decreases with increasing amount of indium. At the same time the difference in shear strength for higher temperatures is lower than for the temperatures 250 and 280 °C. From these results it can be seen that  $\eta'$  phase containing  $\sim 44$  at.% Sn which originates at the boundary between the solder and copper substrate is responsible for the decrease of the joint strength.

#### 4. Summary

1. Effects of indium (up to 9 wt.%) in Sn-3.5Ag lead-free solder on its thermal properties, wetting of copper substrate and structure and strength of copper joints were studied.

2. Indium decreases the onset temperatures of melting and freezing from 225 and 192 °C for 0 % In to 206 and 181 °C for 9 wt.% of In, respectively. The solder thus fulfils one of the requirements for new lead-free solders: significantly decreases melting temperature.

3. Indium decreases the enthalpy change of melting and freezing from 67 and  $-64$  J/g for indium free solder to 61 and  $-59$  J/g for 9 wt.% In, respectively.

4. Wetting angle between copper substrate and Sn-Ag-In solder decreases with increasing amount of indium and wetting temperature and time which results in improving of spreading. Joint strength moderately decreases with increasing joining temperature and the amount of indium.

5. The decrease of joint strength is probably due to the coarsening of the phase located at the substrate – solder boundary.

6. Presented conclusion results in improved solder containing indium in comparison with the Sn-3.5Ag one (lower melting temperature, lower contact angle, mild decrease of shear strength).

#### Acknowledgements

We would like to dedicate this paper to Prof. RNDr. Pavel Lukáč, DrSc., Dr.h.c. from the Department of Metal Physics of Mathematical and Physical Faculty of Charles University in Prague on the occasion of his 70<sup>th</sup> birthday. Authors are grateful to Drs. Janíčkovič and Illeková from the Institute of Physics SAS for preparing of solders and experiments with calorimetry and Dr. Zemánková from the Institute of Materials and Machine Mechanics SAS for electron microscopy. This paper gives the results obtained in the frame of COST 531 program: Lead-free solder materials.

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