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Effect of indium on the microstructure of the interface between Sn3.13Ag0.74CuIn solder and Cu substrate

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ABSTRACT

Influence of indium in Sn3.13Ag0.74Cu solder containing 4, 15, 30, 50 and 75 at.% In on the microstructure at the solder/Cu interface after wetting at 523 K for 1800 s was studied. The scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX), standard and spatially resolved X-ray diffraction (XRD) techniques were used to determine the phases present at the solder/Cu interface. It was found that for In concentration up to 30 at.% the interface is formed by Cu_6Sn_5 phase. For higher In content (50 and 75 at.% In) interface consists of copper rich $Cu_{41}Sn_{11}$ phase.

1. Introduction

The paper [1] of most of the authors of the present manuscript was dedicated to the measurements of density and surface tension of the Sn3.13Ag0.74Cu + In liquid alloys at In concentration 2–75 at.%. For the same alloys wetting conditions of copper substrate were studied in the temperature interval 523–593 K up to 1800 s. Sessile drop method of contact angle measurement was used. Wetting angle decreases from ∼37° to ∼22° with temperature of wetting and also with increasing indium concentration in solder. Similar results were obtained studying the wetting of copper substrate by copper-free (Sn3.5AgIn) solder [2], the angles ranging, however, from ∼60° to ∼35° for 0 to 9% In.

This contribution is a continuation of Part I [1] and it is directed to the use of the same alloys (solders) to study the interfacial phenomena between the copper substrate and relevant solder after wetting the copper at 523 K and 1800 s.

In the past several years a number of studies have been published on various aspects of the reactions between Sn–Ag, Sn–Cu and Sn–Ag–Cu alloys and various substrates, eg. Ref. [3]. Reaction between Sn in these molten solders and Cu substrate at the Cu/solder interface results in the formation of η (Cu_6Sn_5) layer. For longer solder time between η and Cu substrate a thin layer of ε (Cu_3Sn) is observed to form. Thickness of both layers and grain size of scalloped η phase increased with increasing solder time for all three solders [4], but the fastest growth was for the SnAgCu solder and the lowest one for the SnAg.

The present paper shows the influence of indium (4–75 at.%) addition to the Sn–3.13Ag–0.74Cu (in at.%) solder on the microstructure of the interface between the solder and copper substrate after reaction the substrate at 523 K and 1800 s. The aim of this contribution is to find the relation between the wettability increase observed in Ref. [1] and In content as well as the microstructure at the solder/Cu interface.

2. Experimental

Lead-free solder alloys based on close to eutectic Sn–3.13Ag–0.74Cu (in at.%) alloys containing 2, 3, 4, 15, 30, 50 and 75 at.% indium were prepared in the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences. They were used for study of wetting conditions (sessile drop method) of copper substrate [1] as well as for study of interaction product(s) originated during wetting process (in this paper). Copper substrate was square form with edge length of 25 mm and thickness of 1.5 mm. Prior the experiment substrates were mechanically polished and cleaned in alcohol followed by etching in 10% sulphuric acid in metanol. Specimens of solder were of cube form with edge length of ∼4 mm. Prior to experiment they were grinded and cleaned in alcohol. Before placing the assembled specimen into the furnace (cold zone) both parts (substrate and solder) were daubed by rosin moderately activated flux and the furnace was heated up. After reaching the required temperature speci-

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men was placed into the thermally stabilized furnace zone (air atmosphere). Photos of drops were taken with digital camera up to 1800 s after melting (reached after ~30 s) at given temperatures (523, 553 and 593 K) and contact angles were measured by computer. The wetting angles decreased with temperatures and increasing indium concentrations in the solders from ~37° for the solder without indium at 523 K down to ~22° for the solder with 75 at.% indium at 593 K [1].

Specimens after wetting the copper by solders containing indium in the interval 4–75 at.% at 523 K and 1800 s were used for study of interaction phenomena at the boundary between copper plates and solder.

These specimens with solidified drop were cut perpendicularly to the substrate plane. Cross-sections of the specimen were metallographically prepared by grinding, polished by 1 μm diamond paste and etched in solution of picric and hydrochloric acids in alcohol.

Microstructure of the interface between the solder and copper substrate as well as microstructure of the solder itself were studied by scanning electron microscopy (SEM) JEOL JSM 53-10. An energy-dispersive X-ray spectrometer (EDX) KEVEX DELTA 4 was used to measure the chemical composition of the interface between the solder and substrate as well as bulk solder. After SEM investigation most of the copper substrate was cut away to increase relatively the volume of solder and the interface between the substrate and the solder. After such modification the specimens were exposed to X-ray diffraction.

Two X-ray diffraction methods were used. The first one was standard X-ray diffraction—provided phase analysis from the specimen. The overall microstructure and phase composition of the solder–substrate interface were analyzed in a classical manner by X-ray diffraction (XRD) using conventional HZG-4 diffractometer with Cu-Kα radiation in Bragg–Brentano configuration with graphite monochromator in the diffracted beam (Fig. 6a–e).

The other method, X-ray diffraction (X-scan) was employed to obtain diffraction profile from the phase(s) situated at the interface between the solder and substrate to determine small amount of phase(s) adjacent to the substrate. Two modifications of this method were used. First modification is based on setting the diffraction conditions (θ–2θ) to the strongest X-ray line of given or assumed phase. This is accomplished by scanning across the interface between substrate and solder by moving the specimen. Settings (θ–2θ) are repeated for the strongest line of other phases. X-ray diffraction intensity of the relevant line and position of this maximum gives us the location of the phase in regard to the boundary. This spatially resolved phase analysis in the direction perpendicular to the Cu–solder interface was performed using horizontal X-ray diffractometer equipped with an 18 kW Cu rotating anode. The horizontal beam size was restricted by a primary divergence slit, yielding a beam width of 0.05 mm; vertical size of the beam was limited to 6 mm. The X-scans were performed typically in the range of ±3 mm from the position of the interface with step size of 0.05 mm. Curves in Figs. 7, 8 and 11 are constructed from many points (each 0.05 mm is one value of intensity) and only some points are drawn.

The other modification is based on the measurements of complete 2θ diffraction patterns from e.g. 30° to 90° starting with the position of primary X-ray beam with narrow slits (0.1 mm × 6 mm) partially also on copper substrate and taking several X-ray diffraction patterns, moving the specimen 0.1 mm step by step up to 1 mm length from the origin after each scan. An X-ray mapping in the direction perpendicular to the plane of the Cu–solder interface obtained in this manner allowed to verify the observations from both SEM and classical X-ray scan on the phases existence (Figs. 9 and 10).

3. Results

3.1. Morphology and chemistry of the solder/copper interface by SEM and EDX

Figs. 1–5 show the microstructure of the interface between the SnAgCuIn solder and copper substrate and microstructure of the solders after wetting at 523 K for 1800 s with the content of indium 4,15, 30, 50 and 75%, respectively, obtained by SEM. Reaction layers in all specimens except for specimen with 75 at.% indium have scalloped interface with the solder while the interfaces with copper are relatively flat. The thickness of these layers was calculated from the measured surfaces (by PC Sigma Scan Pro 5) and the length of the layers. The thicknesses of the interface layers (which were identified by X-ray diffraction) are given in Table 1.

The microstructure of the drop after 1800 s wetting of the solder containing 4% In at 523 K (Fig. 1) consists of phases (based on EDX results) Sn, and Cu_6Sn_5 and Cu from the substrate. The results of EDX measurements of the composition in points shown in Fig. 1 are listed in Table 2.

For solder containing 15% In (Fig. 2) the phase with composition corresponding to Ag_3In was detected. The second phase present was Cu_6Sn_5 and Sn (Table 3).

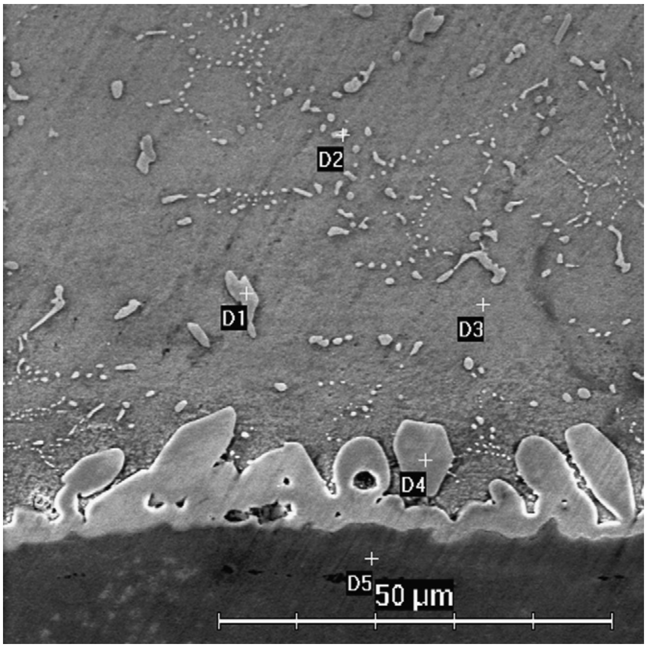

Fig. 1. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–4In after wetting at 523 K, 1800 s.

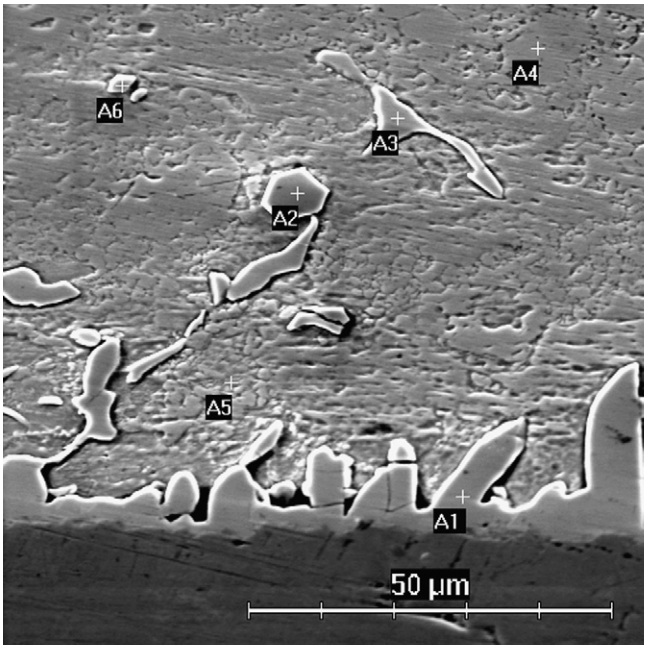

Fig. 2. SEM image of the interface between copper and Sn–3.13Ag–0.71Cu–15In after wetting at 523 K, 1800 s.

Table 1
Average thicknesses of interface layers between the solder and substrate after wetting the substrate at the temperature 523 K and 1800 s.

Amount of In in solder (at.%)	Average thickness (μm)	Interface layer(s)
4	8.2	Cu_6Sn_5
15	9.7	Cu_6Sn_5
30	8.5	$Cu_{41}Sn_{11}$; Cu_6Sn_5
50	7.7	$InSn_4$; $Cu_{41}Sn_{11}$
75	5.5 (2.8)	$Cu_{41}Sn_{11}$; Cu_6Sn_5 (discontinuous)