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Influence of Sb and Cu in Sn-Sb-Cu alloys on wetting of Cu and Cu-solder-Cu joint strength

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Abstract

The influence of Sb (5, 10 and 20 at.%) and copper (0, 1.8, 3.4 and 3.7 at.%) in lead-free Sn-Sb-Cu solder on wetting of copper substrate at the temperature 623 K (350 °C) in air using flux and in N_2+10H_2 gas until 1800 s was studied by the sessile drop method. Wetting angle in air increases with the increase of Sb and Cu concentration in the solder whereas wetting in N_2+10H_2 practically does not depend on the Sb concentration. The influence of antimony and copper in Sn-Sb-Cu solder on the strength of Cu-solder-Cu joints prepared at the same conditions as wetting was also studied. Shear strength of the joints produced in air and in the gas mildly decreases with increasing amount of antimony and copper in both cases with the production of the joint in air as well as in the gas.

The solidus and liquidus temperatures as well as heats of melting of all solders in ribbon and bulk shape were determined by differential scanning calorimetry (DSC) method.

Key words: lead-free solder, antimony, wetting, Cu-solder-Cu strength

1. Introduction

With the implementation of the restriction of use of certain hazardous substances (RoHS) and the regulations of the waste of electrical and electronic equipment (WEEE) the research on lead-free solder alloys has received much widespread attention. Most of these solders are tin containing binary and ternary alloys. SnAgCu (SAC) solder has been proposed as the most promising substitute for lead-containing solder (Sn-Pb). Addition of certain elements even improved wetting of copper substrates by this alloy [1, 2]. Restriction of certain hazardous substances does not refer to the lead-containing solder for higher temperatures – Sn95Pb. In 2007, the European Union funded the COST MP 602 Action to find suitable lead-free substitutes for high temperature solders. One of the possibilities is represented by Sn-Sb and Sn-Sb-Cu based alloys as potential replacements of high-Pb solders [3, 4].

Jang et al. [5] report soldering behaviour of lead-free SnSb alloys on Cu foils and phased-in Cu-Cr thin film. With the increase of Sb content from 5 to 15 wt.% wetting angle decreased from 50 to 20 degrees on Cu foils. Solders showed much lower wetting angles on Cu-Cr thin film than on Cu foils. Mahidhara et al. [3] indicate wetting angle of copper substrate by Sn-5%Sb to be equal to 43 degrees. El-Bahay et al. [6] measured contact angle of Sn-5wt.% solder at temperature 573 K after 60 s on different substrates inter alia Cu and CuZn with wetting angles 40 and 41 degrees, respectively. Plevachuk et al. [7] measured surface tension and density of binary Sn-Sb and ternary Sn-Sb-Cu liquid alloys. Surface tension decreases with the increase of the Sb content for binary $Sn_{90}Sb_{10}$ and $Sn_{80}Sb_{20}$ alloy. The results also showed that wetting angle increases with increasing amount of antimony (from 28 degree for Sn-5at.%Sb to 43 degree for 20 at.% Sb in Sn) [7].

The aim of this contribution is to prepare Sn-Sb alloys with various concentrations of Sb and to investigate their properties as the ground for development of high-temperature lead-free solders as well as the influence of copper in the solder (Sn-Sb-Cu) on

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Table 1. Composition of Sn-Sb-Cu solders (in at.%)

Solder	Sn	Sb	Cu
S1	95	5	
S2	90	10	
S3	80	20	
S4	90.8	7.4	1.8
S5	86	10.6	3.4
S6	76.1	20.2	3.7

its properties. Wetting characteristics of copper substrates by studied solders in air with flux as well as in deoxidising gas and details of copper-solder-copper joints preparation and their shear strength are given.

2. Experimental

Lead-free solders based on Sn were prepared by melting the appropriate amounts of relevant metals of the purity 99.99 and better. Melting was done in induction furnace under argon atmosphere. Part of each solder was produced in form of ribbon 5 mm wide and ~ 0.05 mm thick by rapid quenching, the rest was in bulk form. Six different solders were prepared; their compositions are given in Table 1.

The differential scanning calorimetry (DSC) was used to study the melting and solidification phenomena, especially to determine the solidus, T_{xm} (the onset temperature of the first melting peak during the heating) and the liquidus T_{xs} (the onset temperature of the first solidification peak during the cooling) of each solder. Perkin-Elmer DSC 7 instrument, heating and cooling rates of $\pm$ 10 K min^{-1} and flowing argon atmosphere were used. The precision of the DSC data is $\pm$ 0.5 K and $\pm$ 2 J g^{-1}.

The bulk form of solders was used for wetting experiments (cube of the solder with the edge length ~ 4 mm); the solder in ribbon form was used for joint preparation. The wetting of copper substrate was studied by sessile drop method in air atmosphere and in deoxidising gas (N_2+10H_2). Deoxidising gas was chosen to prohibit the presence of oxygen in the furnace and to eliminate possible oxide layer on the substrate or on the solder specimen. The stated gas composition is considered to be sufficient and is used commonly for soldering in industrial conditions. Copper substrate was mechanically polished and cleaned in alcohol followed by etching in 10 % sulphuric acid in methanol. Substrate roughness was not measured but it is generally known that if metal wets smooth-faced surface then the surface with higher roughness is wetted with smaller wetting angle. Substrate as well as the cube of solder prior to the insertion into the furnace was daubed by rosin moderately activated flux. For experiments using deoxidising gas the flux was not used. The drops of solder on horizontal substrate were photographed by digital camera at the temperature of 623 K up to 1800 s and wetting angles were measured by personal computer. Precision of the wetting angle measurement is ± 1 degree. Copper substrates for making joint were treated by the same way as for wetting.

Prior to placing the solders in ribbon form into metallic holder they were daubed for joining in air by rosin moderately activated flux. Joining in deoxidising gas flux was not used. Holder was placed into the furnace and the joints were prepared at the temperature 623 K and time 1800 s. For each set of joints four specimens were prepared. Three of them were used for shear strength measurement by Zwick testing machine using the push-off method, one was used for the microstructure study.

3. Results and discussion

3.1. *DSC of the solders*

The continuous-heating DSC curves exhibit only the sharp and massive melting endothermic effect above 506 K, or eventually the reciprocal solidification exothermic effect below 520 K for all solders. In the case of $Sn_{95}Sb_5$ (the solder denoted as S1), these DSC peaks are narrow and their width well reflects the difference between the solidus and liquidus of the corresponding phase Sn(Sb) in the Sn-Sb phase diagram [8]. With increasing content of Sb and Cu in the alloy, both melting and solidification effects become wider, presenting a secondary shallow peak (shoulder) always at the high temperature side of the sharp main peak. The typical details of the DSC curves measured on the solder S5 are shown in Fig. 1.

The temperatures of solidus and liquidus and the heats of melting for the as-prepared ribbon and bulk shape binary and ternary alloys are summarised in Table 2. For the majority of electronic components the maximum exposure temperature limits the temperature to 533 K. It follows that the used solder must have the liquidus temperature sufficiently low in order not to damage the component during soldering. Simultaneously, the used solder must have solidus temperature sufficiently high not to allow the solder joints to loose their mechanical strength. Solders S1, S2 and S4 meet these requirements. Solders S3, S5 and S6 could be used for higher temperatures.

3.2. *Wetting*

Figure 2a shows the time dependence of the wetting angle of copper substrate by three Sn-Sb solders with various Sb concentrations during 1800 s at 623 K

Table 2. Solidus, liquidus and melting enthalpies of both ribbon-shape (R) and bulk-shape (B) Sn-Sb and Sn-Sb-Cu alloys as measured in DSC at 10 K min^{-1}

Sample	T_{xm} (K)	T_{xs} (K)	H_{total} (J g^{-1})	Sample	T_{xm} (K)	T_{xs} (K)	H_{total} (J g^{-1})
$Sn_{95}Sb_5$/R	513.8	503.5	57.9	$Sn_{90.8}Sb_{7.4}Cu_{1.8}$/R	510.6	511.8	59.0
$Sn_{95}Sb_5$/B	510.2	506.2	58.8	$Sn_{90.8}Sb_{7.4}Cu_{1.8}$/B	508.7	512.0	60.6
$Sn_{90}Sb_{10}$/R	520.5	533.2	58.9	$Sn_{86}Sb_{10.6}Cu_{3.4}$	513.3	547.2	61.9
$Sn_{90}Sb_{10}$/B	526.1	533.3	62.4	$Sn_{90.8}Sb_{10.6}Cu_{3.4}$	506.8	557.2	67.0
$Sn_{80}Sb_{20}$/R	519.3	592.6	68.3	$Sn_{76.1}Sb_{20.2}Cu_{3.7}$	511.4	586.6	74.3
$Sn_{80}Sb_{20}$/B	514.6	573.3	67.4	$Sn_{76.1}Sb_{20.2}Cu_{3.7}$	510.3	591.1	79.6

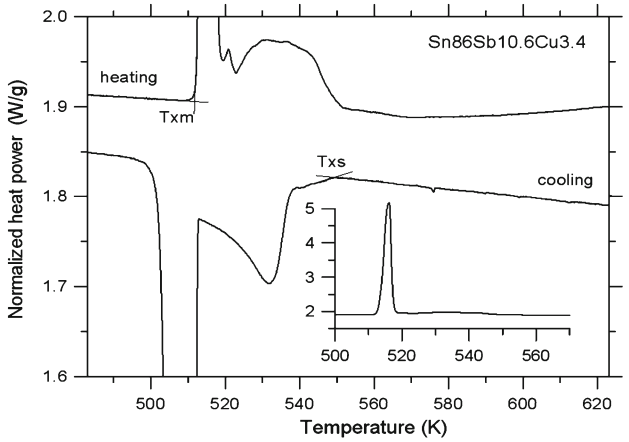

Fig. 1. Details of the heating and cooling DSC curves at ± 10 K min^{-1} of the as-prepared ribbon-shape solder S5. Complete melting peak is in the inset.

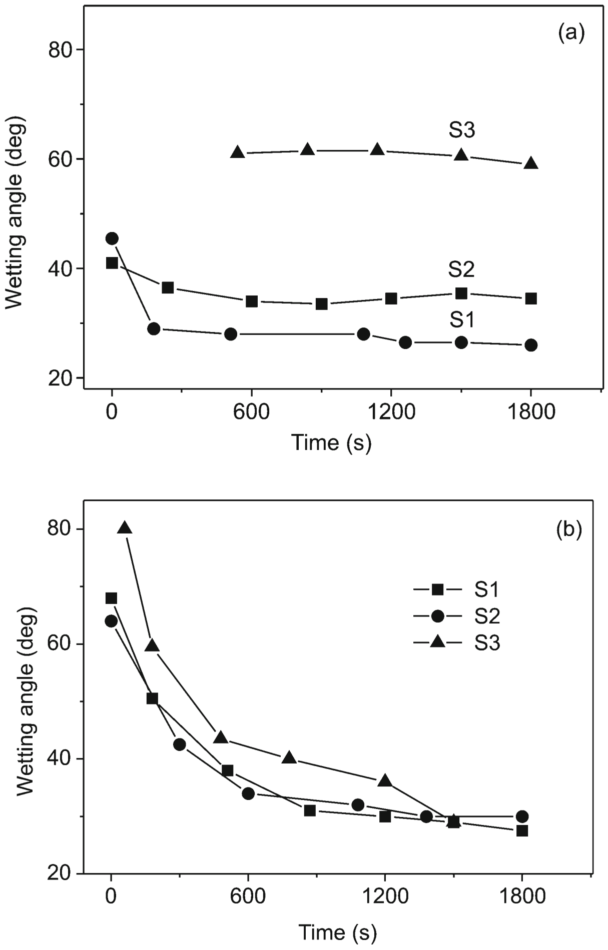

Fig. 2. Time dependences of the wetting angle of copper substrate by Sn-Sb solders with various Sb (S1, S2, S3) concentration during 1800 s at 623 K in air using flux (a) and in N_2+10H_2 gas (b).

in air using flux. Wetting angle increases with the increase of Sb concentration in the solder. Figure 2b shows similar dependence of wetting angle but the wetting was done in the deoxidising gas (N_2+10H_2). Wetting angles for all three solders are practically equal – around 30°. The comparison of these two figures reveals that during heating of the solder (wetting) oxidation starts due to higher concentration of antimony in the solder. Figure 3a shows time dependence of the wetting angle of copper substrate by three Sn-Sb-Cu solders with various Sb and Cu concentration (see Table 1) during 1800 s at 623 K in air using flux. Figure 3b shows similar dependence of wetting angle when wetting was in N_2+10H_2 gas. Comparing Figs. 3a,b one can see that oxidation of antimony as well as of copper substrate (even with using the flux) plays negative role in the wetting. The comparison also reveals stronger effect of copper (in solder) than that of antimony. Wetting in gas practically does not depend on the copper concentration in solder (wetting angles for all concentrations are the same). Wetting angles measured in air and in deoxidising gas after wetting at 623 K for 1800 s are given in Table 3. Wetting angles of pure tin are also given for comparison. Influence of temperature on wetting angle of copper by Sn-Sb solders is shown for temperatures 553, 573 and 623 K and S1 solder on Fig. 4.

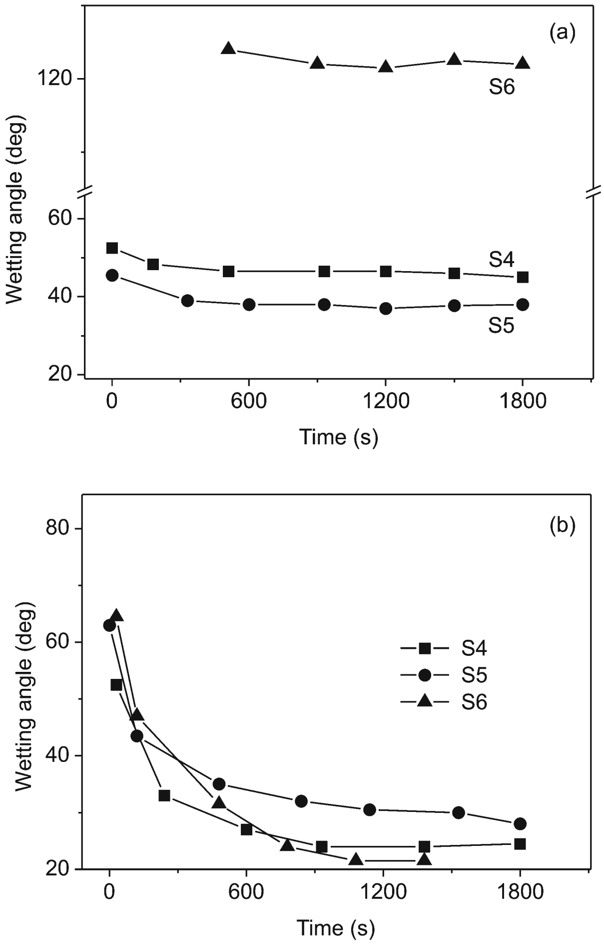

Fig. 3. Time dependences of the wetting angle of copper substrate by three Sn-Sb-Cu solders with various Sb and Cu (S4, S5, S6) concentration during 1800 s at 623 K in air using flux (a) and in N_2+$10H_2$ gas (b).

Table 3. Comparison of wetting angle Θ in air and in deoxidising gas

Solder	S1	S2	S3	S4	S5	S6	Sn
Air	26	34.5	59	45	38	122	32
N_2+$10H_2$	27.5	30	27	24.5	28	21.5	28

Wetting angle decreases with increasing wetting temperature.

For wetting of copper in air by Sn-Sb solders with flux the wetting angles are close to the ones mentioned in literature (see Introduction). Wetting angles increase with increasing antimony concentration in solder. For wetting in deoxidising gas the wetting angles are lower than in the case of wetting in air and practically do not depend on the antimony concentration in solder.

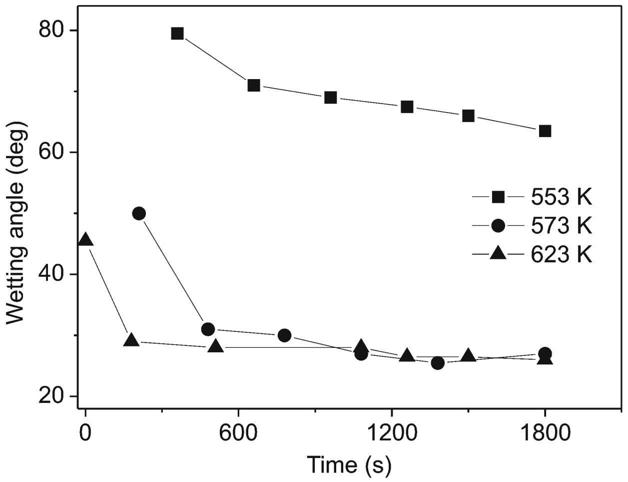

Fig. 4. Time dependences of the wetting angle of copper substrate by S1 solder for temperatures 553, 573 and 623 K in air.

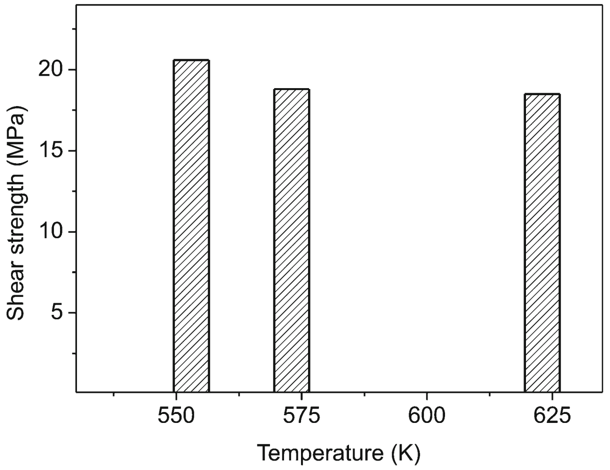

Fig. 5. Shear strength of Cu-Cu joints produced with S1 solder for temperatures 553, 573 and 623 K after 1800 s in air atmosphere.

3.3. Shear strength of Cu-Cu joints

Figure 5 shows shear strength of Cu-Cu joints produced with S1 solder for temperatures 553, 573 and 623 K after 1800 s in air atmosphere. Shear strength mildly decreases with temperature. Figure 6 shows shear strength of Cu-Cu joints produced with Sn-Sb (S1-S3) (a) and Sn-Sb-Cu (S4-S6) (b) solders in air and in the deoxidising gas at the temperature 623 K after 1800 s. Shear strength of the joints prepared in air with S1-S3 solders mildly decreases with increasing Sb concentration in the solder. At the same time shear strength of the joints produced with S1-S3 solders in gas also decreases with increasing Sb concentration. Shear strength of the joints produced with S1-S3 in

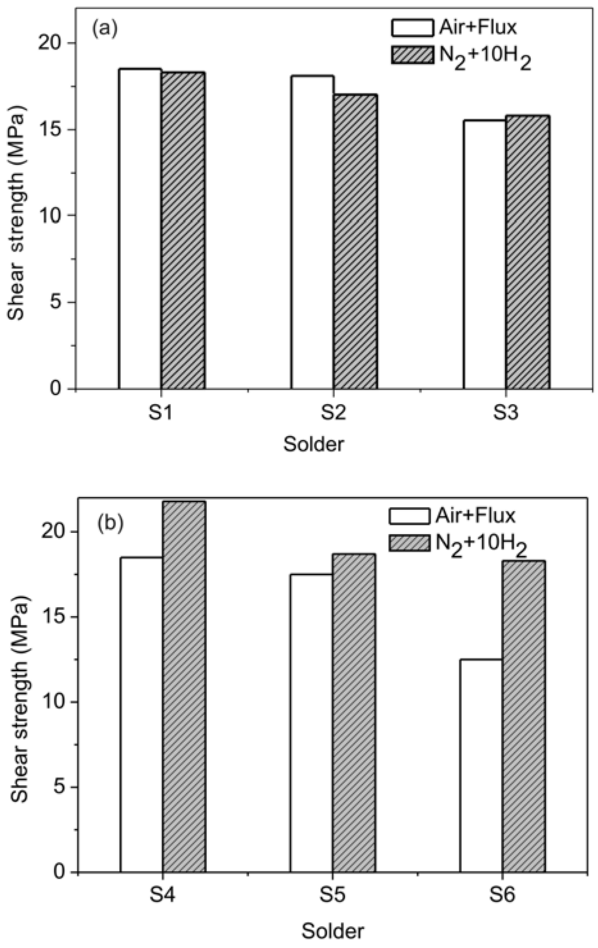

Fig. 6. Shear strength of Cu-Cu joints produced in air and in the deoxidising gas at the temperature 623 K after 1800 s with S1-S3 (a) and S4-S6 (b) solders.

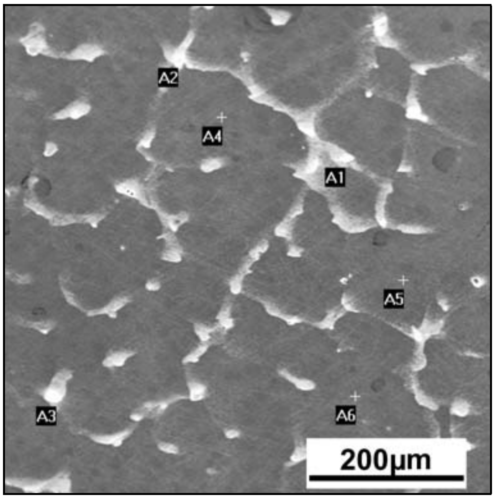

Fig. 7. Microstructure of as prepared S1 solder.

air and in N_2+10H_2 gas is practically the same for given Sb concentration. Situation with the joints made with S4-S6 (containing also copper) solders is a little bit different. Shear strength of the joints made with the solders containing copper also decreases with increasing amount of copper in both cases with the production of the joint in air as well as in the gas. The decrease of the strength of the joint made in air for the highest Cu concentration is very pronounced. It can be due to oxidation of copper. Solder S6 does not wet the copper substrate in air. The decrease of the strength of the joints qualitatively follows the decrease of wetting angle of the copper substrate. In the case of the joint prepared in gas the regress of strength is qualitatively similar as for the solders without copper. However, the strength of the joints made in gas is higher for all Cu concentrations than the strength of the joints made in air. The course of the strength change due to the Cu concentration is similar as in the case of the joints prepared in air.

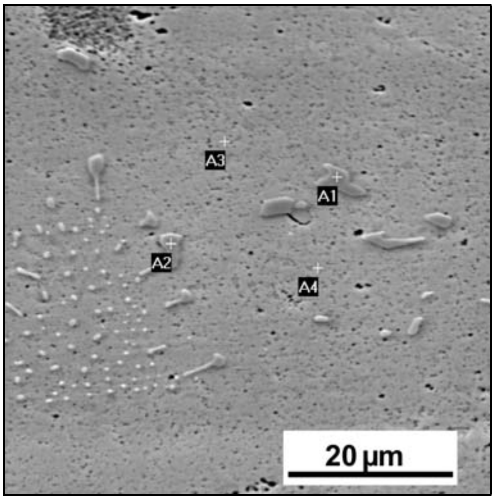

Fig. 8. Microstructure of as prepared S4 solder.

Table 4. Concentration (in at.%) of Cu, Sn and Sb in A_i points

Point	Sn	Sb
A1	91.8	8.2
A2	91.8	8.2
A3	91.7	8.3
A4	90.8	9.2
A5	91.9	8.1
A6	90.7	9.3

3.4. Microstructure of as-prepared solders

As an example, Figs. 7 and 8 show the microstructure of as-prepared $Sn_{95}Sb_5$ (S1) and $Sn_{90.8}Sb_{7.4}Cu_{1.8}$ (S4) solders, respectively. Tables 4 and 5 give composi-

Table 5. Concentration (in at.%) of Cu, Sn and Sb in A_i points

Point	Cu	Sn	Sb
A1	49.7	45.2	5.1
A2	59.8	36.9	3.3
A3	0.7	88.2	11.1
A4	0.5	89.6	9.9

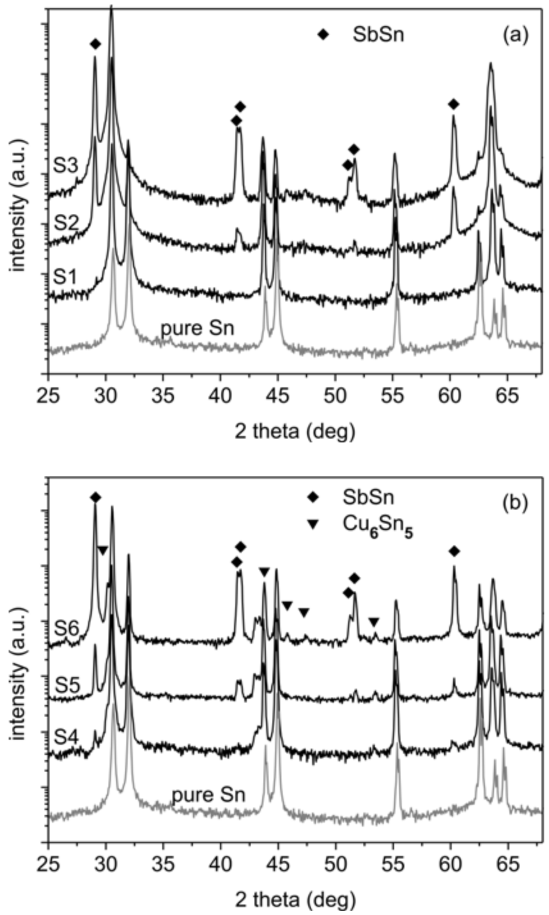

Fig. 9. X-ray profiles taken from as-prepared Sn-Sb (a) and Sn-Sb-Cu (b) solders.

tion in the indicated points. The results show the presence of solid solution of antimony in tin in S1 solder. S4 solder consists of solid solution of Sb in Sn and phases SbSn and Cu_6Sn_5. Figures 9a,b show X-ray profiles taken from all Sn-Sb solders (a) and from all Sn-Sb-Cu solders (b). As-prepared copper-free solders consist of solid solution of Sb in Sn (S1) and solid solution of Sb in Sn and SbSn phase (S2, S3). Solders containing copper consist of solid solution of Sb in Sn, SbSn phase and Cu_6Sn_5 phase. The higher is the amount of antimony and copper in the solder the higher is the amount of SbSn and Cu_6Sn_5 phases. The measured diffraction pattern of pure tin is also shown on both figures for convenience.

4. Conclusions

The obtained results can be summarised as follows:

1. Solidus and liquidus temperatures as well as heats of melting of Sn-Sb and Sn-Sb-Cu solders were determined. Three solders (S1, S2, S4) meet the requirements to be used for electronic components.
2. Antimony and copper in Sn-Sb-Cu solder increase wetting angle of copper substrate when wetting is done in air (with flux).
3. Antimony and copper in Sn-Sb-Cu solder practically do not affect the wetting angle of copper substrate when wetting is done in deoxidising gas (N_2+$10H_2$).
4. Shear strength of the joints Cu-solder-Cu produced in air (with flux) as well as in deoxidising gas decreases with increasing Sb and Cu concentration. For given Sb content the shear strength is practically the same, independent of the production method.
5. Copper in the solder affects the shear strength of the joints more than antimony.

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