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The influence of silver content on structure and properties of Sn–Bi–Ag solder and Cu/solder/Cu joints

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ABSTRACT

The effect of silver content on structure and properties of $Sn_{100-x}Bi_{10}Ag_x$ ($x=3$–10 at%) lead-free solder and Cu–solder–Cu joints was investigated. The microstructure of the solder in both bulk and rapidly solidified ribbon forms was analyzed by scanning electron microscopy (SEM) and X-ray diffraction. The peculiarities in melting kinetic, studied by differential scanning calorimetry (DSC), and silver influence on it are described and discussed. The wetting of a copper substrate was examined by the sessile drop method in the temperature range of 553–673 K in air and deoxidizing gas ($N_2+10\%H_2$) at atmospheric pressure. Cu–solder–Cu joints were also prepared in both atmospheres, and their shear strength was measured by the push-off method. The produced solders consisted of tin, bismuth and Ag_3Sn phases. The product of the interaction between the solder and the copper substrate consists of two phases: Cu_3Sn, which is adjacent to the substrate, and a Cu_6Sn_5 phase. The wetting angle in air increased slightly as the silver concentration in the solder increased. Wetting of the copper substrate in N_2+10H_2 gas shows the opposite tendency: the wetting angle slightly decreased as the silver content in the solder increased. The shear strength of the joints prepared in air (using flux) tends to decrease with increasing production temperature and increasing silver content in the solder. The equivalent decrease in the shear strength of the joints prepared in N_2+10H_2 is more apparent.

1. Introduction

Sn–Pb solders were the most used joining materials in the electronic industry for many years because of their low cost and superior properties. Recently, the regulation of certain hazardous substances (RoHS) and waste electrical and electronic equipment (WEEE) has resulted in extensive research on lead-free solders. Nowadays SnAgCu (SAC) alloys are considered to be the best substitution for lead containing solders with Pb content up to ~85 wt% [1,2]. However, for high melting ($t_l>503$ K) solders, no proper equivalent is available at the moment. There are many potential candidates. Majority of these systems were studied in the frame of COST MP0602 Action. Many of the studied alloys were based on Sn (Sn–Sb, Sn–Au, Sn–Zn–Ni), ternary alloys e.g. Al–Zn–X (X=Ga, Ge, Mg, Ni, Sb and Sn), Al–Sb–Zn, Ag–Sb–Sn and many others. One potential candidate is also Sn–Bi–Ag system in tin rich corner.

The phase diagram for ternary Sn–Bi–Ag alloys was comprehensively investigated both experimentally and numerically in [3–5]. DSC curves for Sn–Bi–Ag solders obtained at heating show endothermal peak in the interval 409–413 K. Some authors associate this with melting of Sn/Bi eutectic, others—with $Sn+Bi+Ag_3Sn\rightarrow L+Ag_3Sn$ reaction [3–5]. As a rule, the fraction of liquid phase at $t>413$ K is rather low (not exceeding 1% for 8 wt% of Bi content [5]). This phenomenon, however, causes some restrictions in usage of Sn–Bi–Ag alloys in the step soldering technology, in which soldering occurs more than once during the manufacturing process but for soldering of wires and printed circuit boards it is acceptable.

The microstructure of Sn–Bi–Ag solder was found to consist of Ag_3Sn particles, Sn-rich and Bi-rich phases in different combinations, depending on the cooling rate after reflow [6]. After aging, Bi in SAC–Bi and SnAg–Bi alloys was found as precipitates at grain boundaries and grain interiors [7]. The solid solubility limit of Bi in the Sn–Ag-based alloy is about 4 wt% at room temperature

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[3–5], and with increased Bi addition, the supersaturated Bi would precipitate in the form of pure Bi phase from the Sn matrix. Additions of Bi tend to suppress the formation of large Ag_3Sn particles from the solder matrix [8]. No ternary compounds were found in this system [3]. In the Sn–Bi–Ag/Cu solder systems Cu reacts only with Sn, not with Ag or Bi [9]. Because of the formation of the Cu_6Sn_5 intermetallic compound (IMC), Ag and Bi are expelled from the reaction front into the molten solder between the IMC scallops. The existence of Bi and Ag in the gaps prevents the Cu–Sn grains from joining together and forming a continuous layer. The higher the Bi and Ag concentration in the solder, the more Bi and Ag is formed in the gaps. Bi and Ag additions affect the total thickness of interfacial reaction layers [9].

Several authors have examined wetting and mechanical properties of SnBiAg solders and joints with various concentrations of bismuth. Vianco and Rejent [10] showed that additions of 1–10 wt% Bi into the Sn–3.5 wt% Ag solder improve its wetting performance on Cu. Increasing the Bi content in the solder raised the Cu–solder–Cu joint shear strength to 81 MPa, as determined by the ring-and-plug test [10]. The microhardness reached maximum values of 30 (Knoop, 50 g) and 110 (Knoop, 5 g) for Bi contents greater than ~4–5 wt%. He and Acoff [9] investigated the effect of reflow and the thermal aging process on microhardness of Sn–3.7 wt% Ag solder with 0, 1, 2, 3, and 4 wt% Bi. They proved that the microhardness increases with increasing Bi in the solder, regardless of reflow or thermal aging process. Huang and Wang showed that bismuth additions linearly increase the ultimate tensile strength of Sn–Ag lead-free solders [8]. The mechanical properties and the microstructure for the Sn–3 wt% Ag solders with 0, 3, and 6 wt% of Bi, connecting two Cu substrates, were experimentally examined in [9]. It was stated that for the solder between the Cu substrates, the strength increases from 90 to 140 MPa with increasing concentration of Bi from 0 to 6 wt%. The mechanical properties of bulk Pb-free solder alloys containing Bi have been characterized for the as-cast and aged samples in [7,11,12]. Room and elevated-temperature tensile testing showed that the addition of Bi greatly reduced the loss in strength due to aging that occurs in the Sn–Ag–Cu ternary alloys. In SnAg–Bi the tensile strength increased after aging. Hence, it is a common place in all the works that bismuth additions into Sn–Ag or SAC solders improve its mechanical properties and wetting ability on Cu substrate.

It is a well known fact that by adding silver to tin one improves its reliability and wetting ability; however, nobody studied precisely the influence of silver content on the structure and properties of Sn–Bi–Ag solder itself and its interaction with substrates. Thus the aim of this work is to determine the effect of silver on (a) melting kinetics, (b) wetting properties and (c) shear strength of $Sn_{100-x}Bi_{10}Ag_x$ alloys and Cu/solder/Cu joints as well as to connect these properties with its microstructure.

2. Experimental

A series of lead-free $Sn_{100-x}Bi_{10}Ag_x$ solders with different Ag content (Table 1) was prepared by melting appropriate amounts of the relevant metals, with purity 99.99% and higher, in an induction furnace in an overpressure of argon at approximately 870 K. Their chemical composition was determined using an atomic emission spectrometer Spectrum Flame Modula S. Solders were prepared in two forms: bulk and ribbon. The bulk solder was used for DSC and for wetting experiments. Solders in ribbon form were prepared by rapid quenching of the melt and used for the preparation of copper–solder–copper joints and DSC measurements. The microstructure of the solder in both forms was investigated by SEM equipped with an energy dispersive analyzer. SEM used was JEOL 7600F with a Schottky FEG emitter and EDX from Oxford Instruments X-max with a 50 mm^2 detector. Software used for control of EDX acquisition and semiquantitative analysis was Oxford Instruments INCA version 4.15.

Table 1
Composition of $Sn_{100-x}Bi_{10}Ag_x$ solders (at%).

Solder	Sn	Bi	Ag
B1	86.7	10.0	3.3
B2	85.3	10.0	4.7
B3	83.3	10.0	6.7
B4	81.7	10.0	8.3
B5	80.0	10.0	10.0

The Perkin–Elmer DSC7 differential scanning calorimeter was calibrated for a heating rate of ± 10 K/min. The same aluminum sample pan was always loosely covered with the lid. A reference pan containing no sample and a flowing (20 ml/min) argon atmosphere were used. The sample mass was ~10 mg.

Two independent samples were always used; thus, the reproducibility of each effect has been proven and the accuracy of measurement of each quantity has been calculated to be ± 0.5 K for temperature and ± 2 J/g for the enthalpy. The instrument was calibrated for the heating regime; therefore, each temperature determined during the cooling should be corrected by the addition of +0.578 K. Each sample was measured in three subsequent heating and cooling cycles in order to test the reversibility and reproducibility of the effects. Each exothermal or endothermal effect (peak) was characterized by its onset (T_x) and endset (T_e) temperature and the transformation enthalpy (ΔH). Each deduced effect was assigned a call number, which increased following the heating and is written as a subscript of the effect of numerical value, e.g., $T_{xm,1}$, $T_{em,1}$, and ΔH_{m1} in the case of the first melting effect and $T_{xs,1}$, $T_{es,1}$ ΔH_{s1} in the case of the last cooling effect. The connection between the effects at heating to those at cooling is a natural choice for the cyclic nature of the DSC measurement.

The wetting of the copper substrate was studied by the sessile drop method. A cube of solder with the edge length of ~4 mm and the substrate were mechanically polished and cleaned in alcohol, followed by etching in 10 vol% sulfuric acid in methanol. The solder was placed on the substrate, which was then introduced into the furnace. Both the substrate and the solder were covered with flux (solution of colophony and diethylammonium dichloride in isopropyl alcohol) prior to insertion into the furnace. An additional wetting of the copper substrate was performed in deoxidizing $N_2+10\%H_2$ gas. The measurements in both atmospheres were done at 553, 573, 623, 653 and 673 K for 1800 s at atmospheric pressure. The drop of the solder was photographed by a digital camera (Olympus 550 with telephoto lens), and the wetting angle was measured using a personal computer.

The samples after the wetting experiments were cut (by Buhler diamond saw) to reveal the cross-section. After the metallographic treatment (carborundum paper, diamond paste+emulsion), the microstructure of the interface was studied by scanning electron microscopy using an energy-dispersive X-ray analyzer (EDX) and X-ray diffraction (XRD). For X-ray diffraction analysis, most of the Cu (substrate) and solder was removed from the specimen in order to maximize the interface area. Two X-ray diffractometers were used. One was a conventional horizontal diffractometer HZG-4 with Cu K_α radiation in the Bragg–Brentano configuration with a graphite monochromator in the diffracted beam. The second one was a Bruker D8 Discover Super Speed Solution diffractometer equipped with an 18 kW Cu rotating anode and a TXS generator operating at 12 kW.