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Crystallographic characterization of Cu–In alloys in the 30–37 at% In region

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ABSTRACT

The Cu–In–Sn system is one of the Pb-free options to replace conventional Pb–Sn alloys in electronic industry. However, controversies still exist regarding some regions of the equilibrium phase diagram of the Cu–In–Sn ternary and also of the Cu–In and Cu–Sn binary systems. One of the most controversial fields of the Cu–In binary phase diagram lies between ~33 and 38 at% In and temperatures ranging from 100 up to 500 °C. In this work, binary Cu–In alloys, with 30–37 at% In nominal compositions and annealed at two different temperatures (i.e. 300 °C and 500 °C) for a long period (i.e. 7 months) were characterized by scanning electron microscopy (SEM), wavelength dispersive spectroscopy (WDS) and X-ray diffraction (XRD). Three phases exist over the 33–38 at% In composition range, namely the phase A at high temperatures and the B and C phases at low temperatures. These three phases can be described as superstructures of the hexagonal phase *h* (Cu_2In) and differ, although slightly, from those previously reported in the literature. In addition, it has been demonstrated that even conventional XRD allows to unequivocally distinguishing between these phases despite their similar crystal structure.

1. Introduction

n last decades, an increasing number of new regulations were issued all over the world with the aim of preserving the environment. In particular, one of the current goals of electronic industry is to decrease or even eliminate the use of Pb in solders [1,2]. Sn–In alloys are attractive as Pb-free solders since they exhibit low melting temperatures [1–3]. In addition, these alloys are suitable to joint Cu substrates (which are usually employed in electronic industry) by transient liquid phase bonding (TLPB) [4,5]. This method involves the melting of the Sn–In interlayer and the formation of solid phases by interdiffusion or reaction diffusion. The resultant intermetallic phases have a melting and maximum operation temperature that can be several hundred Celsius degrees higher than the processing temperature.

It has been previously reported that η-$Cu_6(Sn,In)_5$, ζ-$Cu_{10}(Sn,In)_3$, η-$Cu_2(In,Sn)$, δ-$Cu_7(In,Sn)_3$ phases are formed at the interconnection zone in the Cu/In–48Sn/Cu system [6,7]. These intermetallic compounds correspond to binary phases capable of including small quantities of a third element (i.e. In either Sn) in their crystal structure. Nevertheless, several discrepancies still remain concerning not only the Cu–In–Sn ternary phase diagram but also the Cu–In, Cu–Sn and In–Sn binary diagrams [2]. In particular, η-Cu_2In phase belongs to one of the most controversial fields of the Cu–In binary phase diagram which lies between ~33 and 38 at% In and temperatures ranging from 100 up to 500 °C (see Fig. 1a). Therefore, the further study of this region is needed for the practical application of Sn–In soldering alloys in the electronic industry.

Fig. 1a shows the Cu–In phase diagram proposed by Subramanian and Laughlin [8]. The η field in this diagram is based in several previous researches, but mainly in the work by Jain et al. [9]. These authors reported five different phases named as *h*, A and A′ for high temperature, and B and C for low temperature in the 33–38 at% In range. The crystal structure of the phase *h* is full known [10] and can be described with a hexagonal cell. Phases A (PDF 00-026-0523 card) and A′ (PDF 00-026-0522 card) have been assigned orthorhombic cells with a volume ten times and sixteen times larger than the parent hexagonal cell, respectively. No crystallographic cells for B and C phases were proposed in that work.

The results of further investigations carried by Bolcavage and others led to the phase diagram shown in Fig. 1b [11,12]. This diagram indicates that only two phases occur in the 33–38 at% In composition/temperature range, namely η and η', at low and high temperatures, respectively. The η+η′ field seems to be widely

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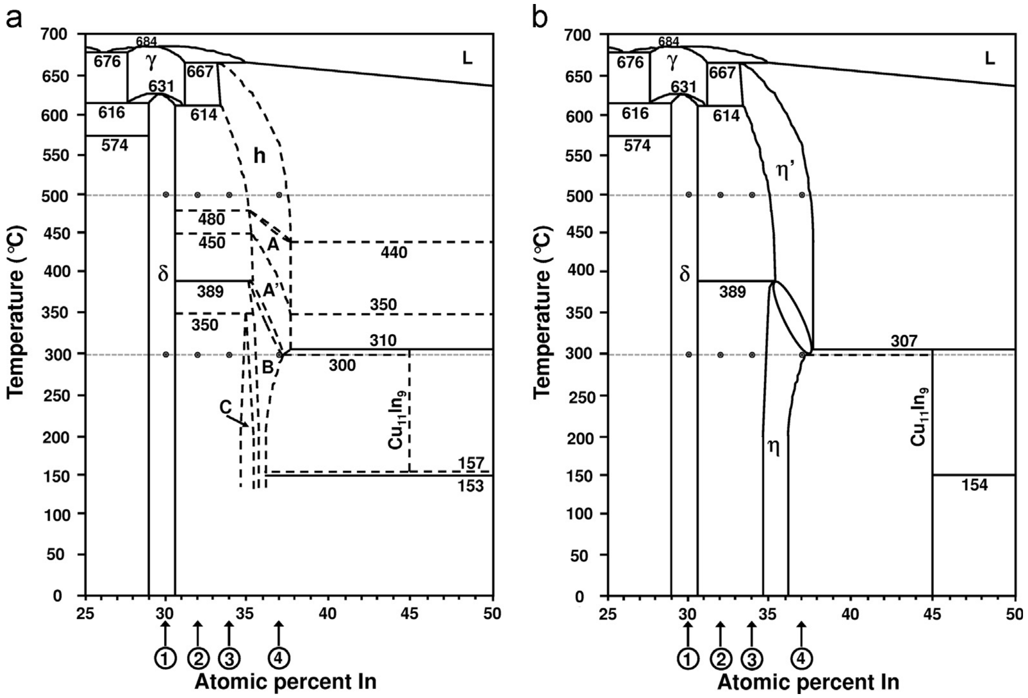

Fig. 1. Cu–In phase diagram according to (a) P. R. Subramanian, D.E. Laughlin [8] and (b) Bolcavage et al. [11]. Nominal composition and annealing temperature of samples studied in this work are also indicated.

accepted as it was incorporated in the subsequent updated Cu–In phase diagrams reported by Okamoto [13,14]. η′ phase presents the same crystal structure of phase h [8,10]. Some X-ray diffraction (XRD) data for phases η and η′ were reported by Bolcavage [11] although they seemed inconsistent.

On the other hand, Elding-Pontén et al. [15] proposed that the η+η′ field is composed of three distinct phases, namely A at high temperatures and B and C at low temperatures. These author described phase A and B as a 10a × 10b × 1c supercell of the hexagonal cell related to phase h whereas phase C was described with an orthorhombic cell. These phases would transform one to another with the continuous rotation of the sub-motif in the electron diffraction pattern. The phase A′ reported by Jain et al. [9] have not been detected by Elding-Pontén et al. [15] and it would be incorporated in the A phase.

As a result, electron and X-Ray diffraction data reported in literature for different phases within the 33–38 at% In region tend to be puzzling. In general, all these phases can be described as NiAs–Ni_2In-type superstructures [8,15,16]. The principal reflections of the related diffraction patterns can be indexed with an hexagonal cell, whereas the remaining reflections present low intensity and are related to domain twining [15,16]. Accordingly, the accurate identification of crystal structure is very difficult. Moreover, in most of the works found in literature, the peak intensity of powder diffraction patterns is visually estimated and hence data comparison can be quite cumbersome.

Further research combining several characterization techniques is required in order to elucidate the controversies mentioned above. This work aims at characterizing binary Cu–In alloys, with 30–37 at% In nominal compositions and annealed at two different temperatures (i.e. 300 °C and 500 °C) for 7 months. These annealing times, which are far longer that those usually reported in the literature, were specially chosen in order to ensure a good phase homogenization. Composition determination and phase identification were performed by wavelength dispersive spectroscopy (WDS) and scanning electron microscopy. In addition, the crystallographic features of these alloys were investigated by X-ray powder diffraction (XRD).

Table 1
Nominal composition, annealing temperature and phase contents in the different samples studied in this work.

Sample name	Nominal composition		Annealing temperature (°C)	Present phases
	at% In[a]	at% Cu		
S1-500	30	70	500	Phase δ (Cu_7In_3) [17]
S2-500	32	68	500	Phase δ (Cu_7In_3) [17]+ Phase A [this work, 15]
S3-500	34	66	500	Phase δ (Cu_7In_3) [17]+ Phase A [this work, 15]
S4-500	37	63	500	Phase A [this work, 15]
S1-300	30	70	300	Phase δ (Cu_7In_3) [17]
S2-300	32	68	300	Phase δ (Cu_7In_3) [17]+ Phase C [15]
S3-300	34	66	300	Phase δ (Cu_7In_3) [17]+ Phase C [15]
S4-300	37	63	300	Phase B [this work, 15]

[a] The experimental error in the sample composition (i.e. the difference between the nominal and the actual composition of the sample) is up to ± 1 at% In.

2. Experimental

Eight samples with nominal composition within 30–37 at% In range were prepared. 99.999% Cu and 99.999% In ingots were melted together under Ar atmosphere and then the melt was cooled down to room temperature. Four samples were subsequently annealed during 7 months at 300 °C under Ar atmosphere and then quenched down to room temperature. The same procedure was applied to the remaining samples but in this case at 500 °C. Nominal composition and annealing temperature of all studied samples are indicated in Fig. 1 and listed in Table 1.

The morphology of the samples was analyzed by using a Philips 515 SEM. Images were acquired with backscattered electrons in order to maximize atomic number contrast.

Lineal composition profiles with 1–4 μm steps were determined by using the WDS technique employing a Cameca SX50