The Influence of Quenching Baths on Grain Boundary Wetting Transition in Sn–25 at% In alloy

C. -H. Yeh^{1,a}, L.-S. Chang^{1,b} and B. Straumal^{2,c}

¹Department of Materials Engineering, National Chung Hsing University, 40227 Taichung, Taiwan/R.O.C. ²Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, 142432 Russia

^achyeh@dragon.nchu.edu.tw, ^blschang@dragon.nchu.edu.tw, ^cstraumal@issp.ac.ru

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Abstract. The wetting behavior of grain boundaries is affected by temperature, pressure and misorientation of grain boundaries. However, the influence of quenching baths on liquid state grain boundary wetting is rarely reported. In this work, this effect in the Sn–25 at% In alloy was investigated. The Sn–In alloy was prepared by smelting of In and Sn at 300°C for 6 hr in Ar atmosphere. Samples were annealed at temperature between 130 and 165°C and quenched in two kinds of baths: -10° C salt-saturated water and liquid nitrogen. The results from X-ray diffraction show a difference in preferential orientations between samples quenched in these two baths. Metallographic analysis reveals that the percentage of grain boundaries fully wetted in samples quenched in -10° C salt-saturated water is lower than that quenched in liquid nitrogen. It is pointed out that a proper quenching bath is necessary for preserving the initial microstructure of grain boundary wetting.

Introduction

Grain boundary (GB) wetting phenomena influence many properties of polycrystalline materials, such as brittleness [1-6], plasticity [7], sintering rate, electrical performance [8], etc. The so-called GB wetting transition is the transition from an incomplete GB wetting into a complete one. In this case, GB is wetted by a second phase which is liquid in the solid-liquid (S+L) region of the respective phase diagram. When this transition occurs, the liquid phase penetrates along GBs. For a complete wetting a continuous layer covers a whole GB; if such a layer appears to be interrupted, the GB is regarded as an incompletely wetted GB. The thermodynamic criterion for a GB which is completely wetted is known as the Gibbs-Smith condition [9] in which the GB energy, σ_{GB} should be higher than the energy of two solid-liquid interfaces energy, $2\sigma_{SL}$,

$$\sigma_{\rm GB} > 2\sigma_{\rm SL}.$$
 (1)

GB wetting phenomena have been studied and published in several papers and books. The wetting behavior of GBs is affected by temperature, pressure and misorientation [10-12]. Straumal *et al.* have studied the GB wetting by liquid Sn in Zn bi-crystals [10]. They noted that the temperature of the wetting transition for high-energy GBs is lower than that for low-energy GBs. Meanwhile, the degree of GB wetting depends on the annealing temperature, and the dihedral angle decreases with increasing temperature. Lojkowski *et al.* studied the pressure effect in Fe–Si bi-crystals on the GB wetting transition by liquid Zn [11]. They concluded that high pressure causes a dewetting of liquid Zn at GBs in Fe–6 at% Si bicrystals. The pressure of the dewetting transition is higher for a special GB than that for a general GB. It was also revealed that in this case the liquid phase film between two solid-liquid interfaces is not fully disordered.

Among many binary alloy systems, In-Sn alloys are widely used in developing cutting edge

microelectronic devices. The GB wetting in these alloys plays an important role in their performance, e.g. the electrical resistance of solders. However, a detailed investigation on this subject is still lacking. The main reason for this deficiency is the low melting temperature of this group of alloys whose microstructure evolves at temperatures not much above ambient temperature and, therefore, depends strongly on the quenching duration after annealing. This paper aims to report the first observation of the phase structure and microstructure variation of the GB wetting in Sn–25 at % In alloys quenched in two different kinds of bath after annealing and the understanding of the influence of quenching baths on the GB wetting transition.

Experimental

The Sn-25 at.-% In alloy noted as Sn75In25 was prepared by smelting of In (99.9995%) and Sn (99.999%) at 300°C for 6 hr in an Ar atmosphere. The smelted ingots were homogenized at 100°C for 24 hr. The ingots were sliced into several samples. They were encapsulated and annealed in argon atmosphere between 130°C and 170°C for 10 hr. Thereafter, they were quenched in two different ways. One part of them was directly quenched in a -10°C salt-saturated ice water bath. Another part was quenched in a liquid nitrogen bath following quenching in a 5°C water bath. Finally, all samples were ground, polished and etched in 10% HCl ethyl alcohol solution for 10 s.

The microstructure of the etched Sn75In25 samples was observed with a Neophot-32 light microscope equipped with 8 Mpix Canon Digital Rebel XT camera, and numbers of GBs completely and incompletely wetted were counted and the portion of the GBs completely wetted was calculated with a computer aid. Over 200 GBs in each sample were analyzed. The quantification of the GBs wetting in this analysis was performed in adopting the following criteria. First, every GB is considered to be completely wetted only when a continuous layer does cover the whole (visible part of the) GB. And, if such a layer appears to be interrupted, the GB is regarded as a GB incompletely wetted. Simultaneously, a MAC MXP3 TXJ-9006 X-ray diffractometer (XRD) was used to identify phases of the samples. The XRD parameters were acquired in the diffraction angle interval 200 with a sampling width of 0.01° and scanning speed of 1°.

Results and discussion

Phase Analysis. The XRD patterns of as-prepared and annealed samples after quenching in the -10° C salt-saturated ice water bath and liquid nitrogen bath are shown in both wide and narrow angle ranges in Figure 1. The XRD patterns show that directly after homogenization, the starting Sn75In25 alloy is a non-stoichiometric γ compound. A liquid phase forms in the γ -matrix during annealing in the region of the solid-liquid phases coexistence. The liquid phase undergoes a eutectic transformation and transforms into the γ - and β -phases during quenching. This is revealed from the XRD patterns showing that all annealed samples contain a small amount of β -phase around $2\theta = 33^{\circ}$. However, two different tendencies of peak height change with changing annealing temperature can be distinguished. For the samples quenched in the salt-saturated ice water bath (Fig. 1a), the peak intensity of β -phase reaches its maximum as the annealing temperature is 142°, while that for the samples quenched in liquid nitrogen keeps increasing as the annealing temperature increases from 133 to 164°C.

Three factors influence the final amount of β -phase in the annealed and quenched samples: (1) the amount of liquid in isothermally annealed samples, (2) the indium content in the liquid and (3) the cooling duration of the liquid phase. According to the In–Sn phase diagram, the narrowest solubility range of In in the γ phase is 13-28 at. %. A liquid phase with a concentration within this range will completely transform into the γ -phase as long as it is quenched rapidly enough. If the In content in liquid is in excess of the upper solubility limit of the γ -phase, the liquid will pass across the eutectic line during quenching and the β -phase will form. Generally, two statements about the quenching of the Sn75In25 alloy can be made: (1) if it takes a sample longer to cool down from a



Figure 1 The XRD patterns in wide and narrow ranges of diffraction angle 2θ for the Sn₇₅In₂₅ samples as prepared and after annealing and quenching in the (a) salt-saturated ice water bath and (b) liquid nitrogen bath.

certain annealing temperature within the S+L region, less β -phase forms due to a longer precipitation time of the γ -phase. (2) the higher the annealing temperature, the more β -phase forms due to a higher liquid portion existing originally.

Using these concepts mentioned above, the XRD results shown in Figure 1 can be better understood. In Figure 1a, at high temperatures more liquid is able to transform into the γ -phase and the β -phase peak reduced. However, in Figure 1b, the peak intensity of β -phase increases with increasing annealing temperature. These phenomena result from the difference in cooling ability between the two kinds of quenching baths. Apparently, the cooling rate of quenching in the salt-saturated ice water bath is slower than that in the nitrogen bath.



Figure 2 Optical micrographs of the Sn75In25 samples after annealing: (a) blank (b) 135°C (c) 142°C (d) 152°C (e) 164°C for quenching in a salt-saturated ice water bath and (f) 133°C (g) 142°C (h) 152°C (i) 161°C for quenching in a liquid nitrogen bath.



Figure 3 The dependence of the percentage of fully wetted GBs on the annealing temperature for Sn75In25 alloy for quenching in salt-saturated ice water (-10°C) and liquid nitrogen baths.

Microstructure Analysis. A shift of wetting phase transition temperature has been observed. It follows from the optical micrographs of annealed Sn75In25 samples quenched in a salt-saturated ice water bath in comparison with those quenched in a liquid nitrogen bath (Figure 2). Figure 2 shows the micrographs of the Sn75In25 samples annealed at various temperatures and quenched in the two kinds of baths. The microstructure of as-prepared sample is a fine lamellar structure (Figure 2a). The microstructure of samples annealed for 10 h differs from the initial one. The micrographs of the annealed samples (Figures 2b to 2i) show that the fine lamellar structure transforms into a coarse granular structure. The dark grains and the light areas around them are respectively the γ -phase and a mixture of the β - and γ -phases which solidifies from liquid during quenching. These light areas are usually supposed to represent the location of liquid phase during the annealing.

Some GBs are fully wetted by the liquid phase (the light areas) in samples annealed at temperatures below 160°C, probably because these GBs have a higher energy than that of other GBs making the wetting transition at them occur at lower temperatures. All GBs in Sn₇₅In₂₅ alloys are completely wetted, and some liquid phase boundaries become coarser gradually at the annealing temperatures above 160°C (Figures 2e and 2i). Figure 3 shows the results of quantification analysis done on the micrographs. The percentages of GBs fully wetted in the Sn75In25 alloys quenched in a salt-saturated ice water and liquid nitrogen baths are presented in relating to the annealing temperature. It can be seen that the percentages increase with increasing annealing temperature. Besides, it is also shown in Figure 3 that the extent of GB wetting in samples quenched in a salt-saturated ice water bath is in general lower than that for samples quenched in a liquid nitrogen bath.

It has been mentioned in the previous section that a sample cooled down more slowly contains less β -phase. It is easy to understand that the portion of GBs completely wetted diminishes if a sample is cooled down more slowly. A high cooling rate retains the microstructure of the GB wetting phase transition rapidly. Therefore, for ensuring an accurate study on the GB wetting phase transition in the In–Sn system, quenching in a liquid nitrogen bath following a 5°C water quenching

is more proper than quenching in salt-saturated ice water.

Conclusions

The grain boundary wetting behavior of the Sn–25 at.-% In alloy quenched in different baths was investigated. The major phase structure of annealed samples is γ -InSn₄ phase and contain a small amount of β -In₃Sn phase after quenching. The phase evolution and shift of wetting phase transition temperature were observed by means of X-ray diffraction and optical microscopy. The percentage of GBs fully wetted increases with increasing annealing temperature. The extent of GB wetting phase transition of samples quenched in salt-saturated ice water is lower than that quenched in liquid nitrogen. This reveals that the quenching in a liquid nitrogen bath following a 5°C water quenching is more proper for an accurate study on the GB wetting phase transition in the In–Sn system. The same conclusion can also be made from the results of phase analysis.

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