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# The Grain Boundary Wetting in the Sn– 25 at% In Alloys

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**Abstract.** The grain boundary (GB) wetting was investigated in the Sn – 25 at.% In alloy. It was found that the portion of GBs wetted by the melt depends on the annealing temperature. No GB completely wetted by melt was observed at 140°C, while all GBs were fully wetted after annealing at 180°C. Between 140°C and 180°C the portion of wetted GBs increases with increasing temperature. The tie-lines of GB wetting phase transition were constructed in the Sn–In bulk phase diagram.

## Introduction

The grain boundary (GB) phase transitions play of an important role in determining many properties of polycrystalline materials, such as brittleness [1-6], plasticity [7], electrical conductivity, sintering rate, mechanical properties, etc. One important kind of the GB phase transitions is the wetting transition [8]. The GB wetting may happen if a GB is in equilibrium contact with a liquid phase (see Fig. 1). If the GB energy, $\sigma_{GB}$, is lower than the energy of two solid-liquid interfaces, $2\sigma_{SL}$, the GB is not completely wetted, and the dihedral angle $\theta>0$. If $\sigma_{GB} \geq 2\sigma_{SL}$, the GB is completely wetted by the liquid phase, and $\theta = 0$. With increasing temperature, the $\sigma_{GB}$ and $2\sigma_{SL}$ decrease simultaneously (Fig. 2). However, $2\sigma_{SL}$ is influenced by the temperature stronger than $\sigma_{GB}$ due to the higher disorder of the solid-liquid interface. If both curves intersect at the temperature $T_w$ below a melting temperature $T_m$, the complete GB wetting occurs between $T_w$ and $T_m$. The wetting temperature $T_w$ is a constant for a certain GB in the (S+L) two-phase region of the phase diagram, since the compositions of solid and liquid phases do not change macroscopically. Therefore, a tie-line of a GB wetting phase transition appears at $T_w$ for a GB with a certain $\sigma_{GB}$. $T_w$ is different for GBs with different values of $\sigma_{GB}$. Minimal $T_w$ corresponds to the GBs with maximal $\sigma_{GB}$.

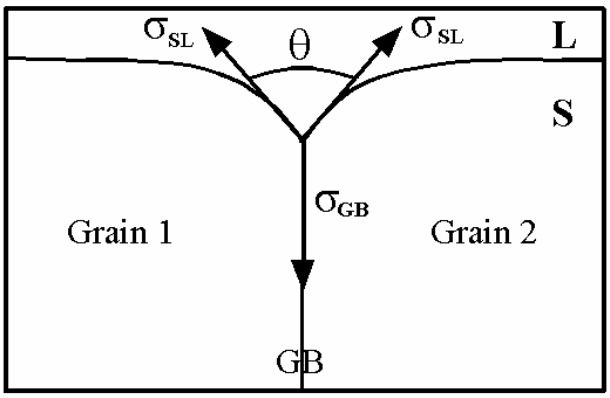



Figure 1 A grain boundary (GB) and two adjacent grains in equilibrium contact with a liquid phase L and the dihedral angle θ. $\theta > 0$ because $2\sigma_{SL} \geq \sigma_{GB}$

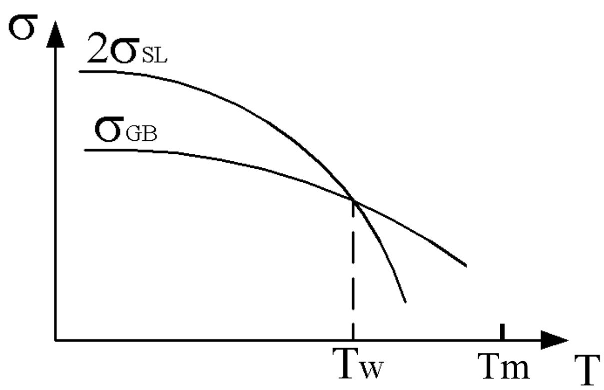



Figure 2 GB energy $\sigma_{GB}$ and interphase boundary energy $\sigma_{SL}$ decrease with increasing temperature. The intersection of two curves $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ is the temperature of GB wetting transition, $T_W$. $T_m$ is the melting temperature.

The GB wetting phenomena were studied in several polycrystalline metals, alloys and ceramics. For example, Straumal *et al.* investigated the GB wetting of annealed Zn-Al and Zn-Sn alloys [9, 10]. They concluded that the GB wetting depends on the temperature, and the dihedral angle decreases with increasing temperature. Majumder *et al.* discussed the influence of an external applied shear stress on the GB wetting phenomenon and indicated that the extent of the GB wetting of favorably oriented GBs depends on the fluid mobility β, which is defined as the ratio of the rate of stress relaxation by the GB wetting to the rate of stress relaxation by the GB diffusion [11].

Due to the urgent demand of lead-free solders in electronic industries now, it is important to understand the knowledge of GB wetting transitions of the In–Sn alloy which is the main part of the most potential materials for lead-free solders. The goal of this research was to investigate the influence of annealing temperature on the GB wetting phenomenon and consequently to find the temperature limits of the GB wetting transition of the In–Sn phase diagram.

## Experimental

The Sn–25 at% In alloy which is indicated as Sn75In25 was prepared by smelting of In (99.9995%) and Sn (99.999%) at 300°C for 6 hr in Ar atmosphere. The smelted ingots were homogenized at 100°C for 24 hr. The ingots were sliced into several specimens. They were annealed in furnace in argon atmosphere between 140°C and 180°C for 10 hr (Fig. 3[12]). Thereafter, they were quenched in liquid nitrogen, then ground, polished and finally etched in 10 % HCl alcohol solution for 10 to 15s.

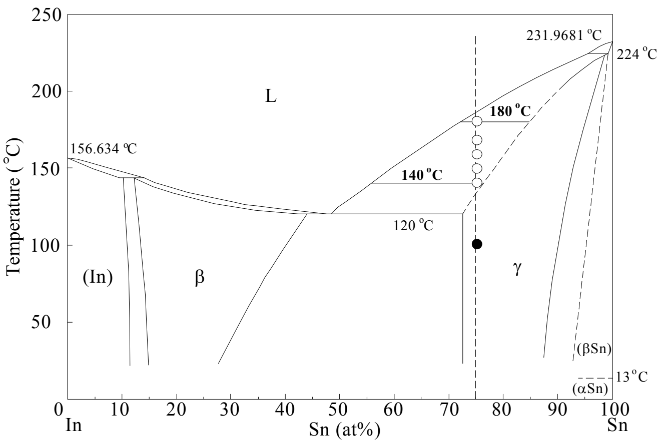



Figure 3 The In–Sn bulk phase diagram [12]. Vertical dotted line shows the Sn–25 at% In alloy in this study. Open circles denote the annealed samples. Full circle marks homogenized sample. The tie-lines at $T_{W(low)} \approx 140$°C and $T_{W(high)} \approx 180$ °C represent the lower and higher temperatures limits of GB wetting by liquid phase, respectively.

Etched Sn75In25 samples were photographed using light microscope Neophot 2 equipped with a digital 6.5 Mpix Canon EOS 300D camera and ImageExpert™ software for image processing. The portion of completely wetted GBs was counted using software for quantitative metallography. The quantification of the wetted GBs by light microscopical analysis was performed adopting the following criterion: every GB was considered to be wetted only when a continuous layer had covered the whole (visible part of the) GB; if such a layer appeared to be interrupted, the GB was regarded as a non-wetted GB. Over thousand GBs were analyzed at each annealing temperature. An MXP3 X-ray diffractometer (XRD) produced by MAC Science was used to identify the phases of the specimens. The XRD parameters were acquired in the diffraction angle interval 2ϕ between 20 and 80° with a sampling width of 0.01° and scanning speed of 1°. The composition of the GBs was analyzed by means of electron probe microanalysis (EPMA) using the JEOL JXA-8200SX instrument. The measurements were performed in the line scan mode at an accelerating voltage of 15.0 kV.

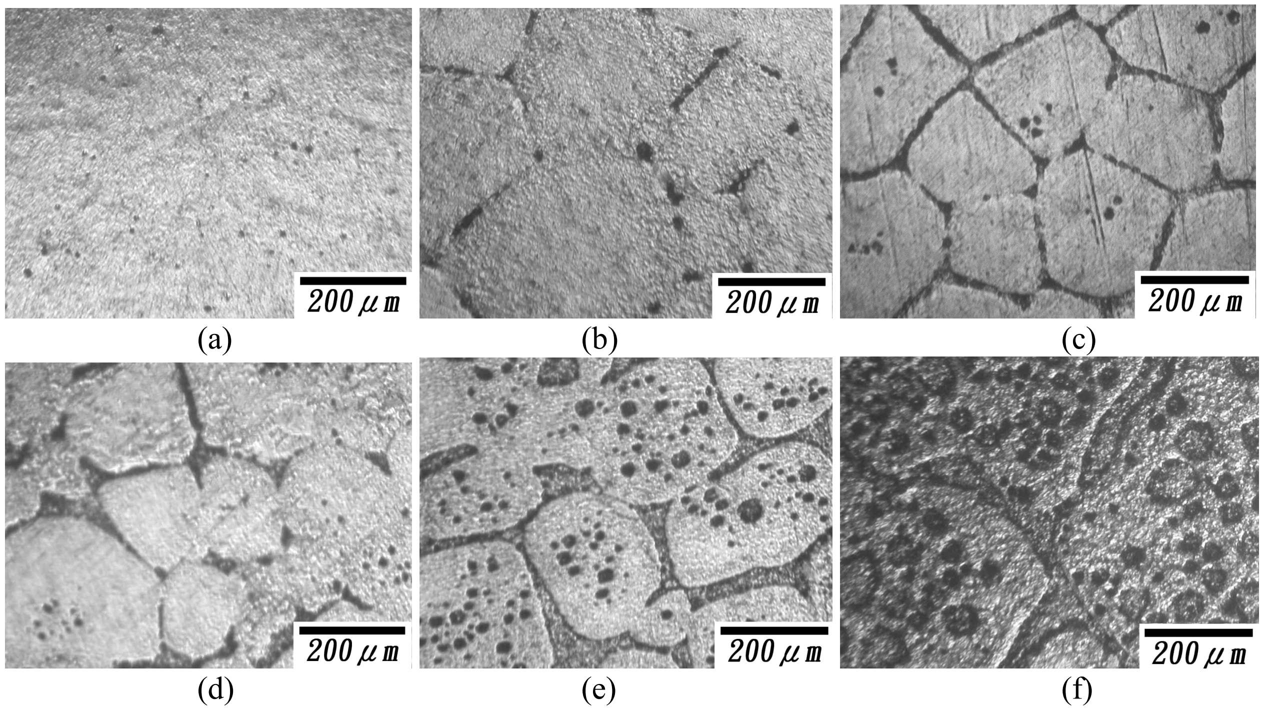



Figure 4 Light micrographs of the Sn75In25 specimens (a) as-prepared and after annealing at (b) 140, (c) 150, (d) 160, (e) 170 and (f) 180°C.

## Results and discussion

The light micrographs of Sn75In25 alloy as-prepared and annealed are shown in Fig. 4. No In-enriched GBs can be observed in the as-prepared one (Fig. 4a) even after chemical etching. Figure 4b to 4f are the micrographs of the Sn75In25 specimens annealed at 140, 150, 160, 170 and 180°C and quenched, respectively. The grain size of these specimens was approximately 200 μm. During the annealing between 140 and 180°C the liquid phase with liquidus concentration $C_L$ (Fig. 3) was present in the samples. During quenching the liquid phase underwent the eutectic transformation at $T_e$ = 120°C, became fine-crystalline and appears gray after etching in the light micrographs (Figs. 4b to 4f). Similar etching does not reveal any In-rich areas in the sample homogenized at 100°C (Fig. 4a). XRD reveals in the homogenized sample only the $InSn_4$ (γ) phase (bottom spectrum in Figure 5). XRD reveals also that the samples annealed between 140 and 180°C, i.e. in the two-phase S+L area of the Sn–In phase diagram (Fig. 3) contain after quenching a small amount of $In_3Sn$ (β) phase (weak peaks at 2ϕ = 32.2°, Fig. 5). This β–phase is confined in the areas which were liquid during the annealing and underwent the eutectic transformation during quenching.

The amount of the liquid phase in the sample increased with increasing annealing temperature, according to the level rule (see the phase diagram in Fig. 3). It can be easily seen by comparing Figures 4b to 4f.

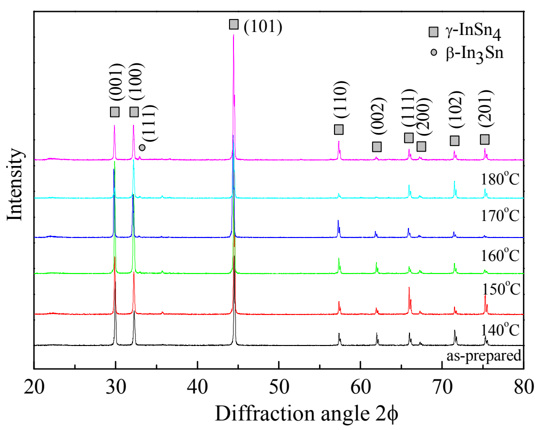
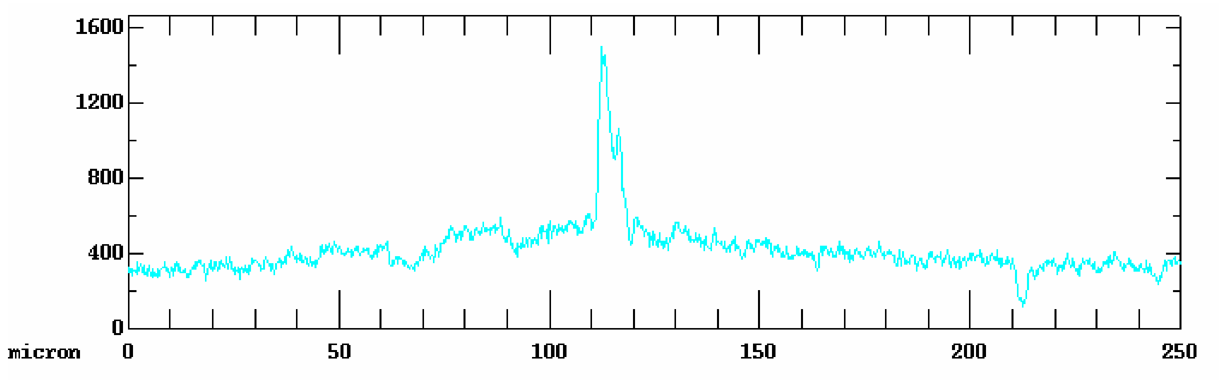
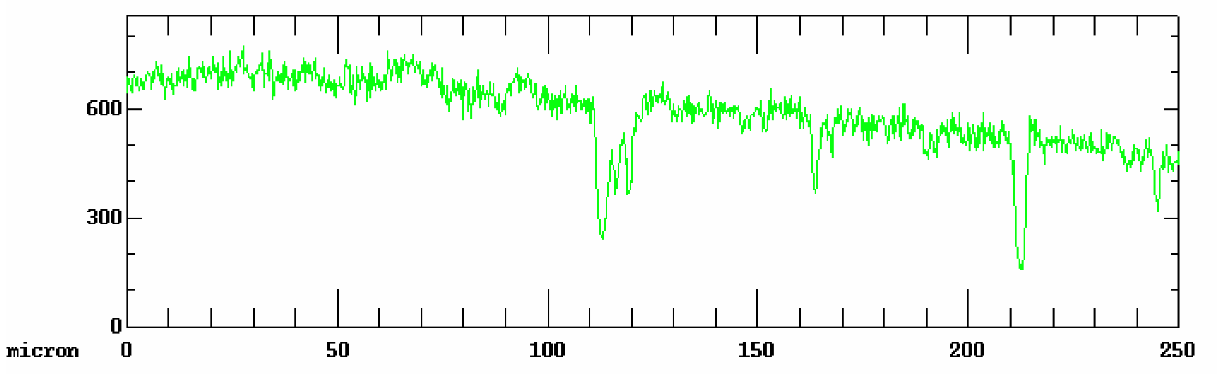


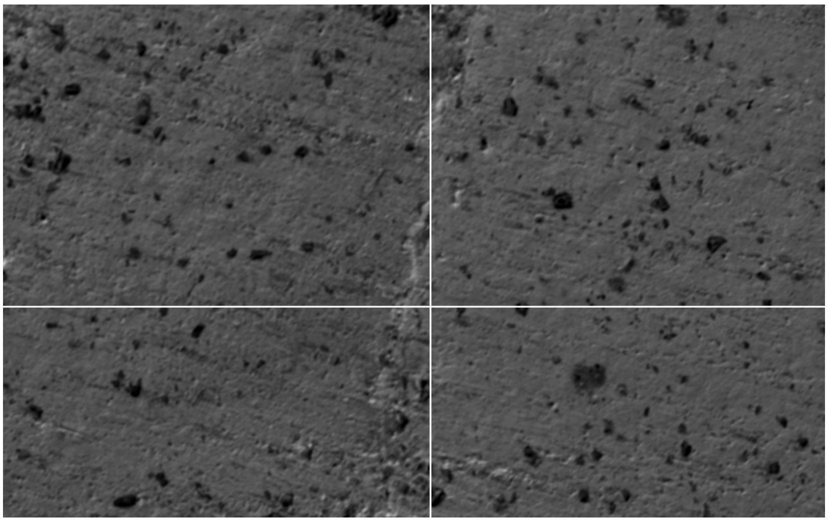

Figure 5 XRD patterns of the Sn75In25 specimens as-prepared and annealed at various temperatures. The diffraction peaks for the $\gamma$-$InSn_4$ and $\beta$-$In_3Sn$ phases are marked by squares and circles, respectively




(a)




(b)



(c)

Figure 6 (a) In and (b) Sn concentration profiles measured by EMPA for the Sn75In25 specimen annealed at 150°C and (c) the corresponding micrograph in which the scan line and the GB region are indicated

Consequently, XRD reveals that the content of β–phase in quenched samples (though been very low) increases with increasing annealing temperature (Fig. 5). EPMA also reveals the increased In concentration in the areas appeared gray in the light micrographs (Fig. 6). If the In atoms in grains of 25% In reveal about 400 counts (Fig. 6a), the average number of 800 counts in the GB region corresponds to the equalmolar of Sn and In in GBs. The mean In concentration is close to the respective liquidus concentrations at the annealing temperatures (Fig. 3).

Therefore, we can conclude that the configuration of gray areas in Figs. 4b to 4f (after quenching) represents well the morphology and distribution of a liquid phase at the annealing temperature. At 140, 150 and 160°C (Figs. 4b, 4c and 4d) the amount of the liquid phase was low, and it was mainly confined between solid grains of the γ-phase. Only few liquid particles were observed in the bulk. At 170 and 180°C (Figs. 4e and 4f) the amount of a liquid phase was high, and it was present also in the bulk of the γ-grains as spherical droplets.

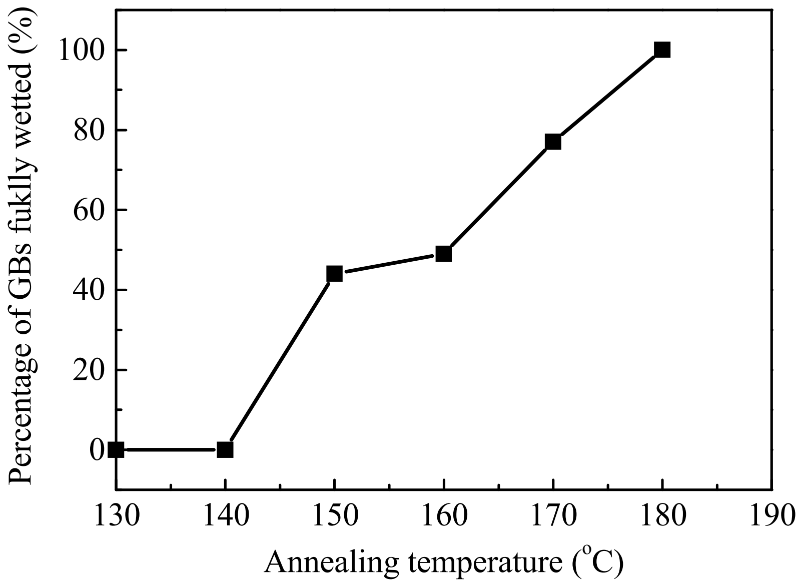



Figure 7 Percentage of the GBs fully wetted related to the annealing temperature for Sn75In25 alloy

After annealing at 140°C for 10 hr the liquid phase became visible in GBs (Fig. 4b). However, only few GBs were completely wetted. The majority of GBs revealed the dihedral contact angle larger than zero. In the specimens annealed at 150, 160 and 170°C (Figs. 4c, 4d, and 4e) an amount of completely wetted GBs increased, i.e. the dihedral angle decreased to zero with increasing annealing temperature. This phenomenon is owing to the anisotropy of GB energy at various GBs in polycrystalline materials [13]. The coarsening of grains divided by wetted GBs is more pronounced at higher temperatures (Figs. 4e and 4f).

The percentage of GBs completely wetted by a liquid phase in the Sn75In25 alloy at various annealing temperatures was calculated. The result is plotted in Fig. 7. Clearly, the percentage of completely wetted GBs increased with increasing annealing temperature. Below 140°C, no GBs were completely wetted. Above 140°C, few GBs underwent the wetting transition. One can say accordingly that the lower temperature limit of a GB wetting by liquid phase, $T_{W(low)}$, is nearly 140°C for the Sn75In25 alloy. The percentage of completely wetted GBs reaches 100% at 180°C. This reveals that the higher temperature limit of GB wetting, $T_{W(high)}$, lies close to 180°C. These temperature limits of the GB wetting of Sn75In25 alloy were indicated as tie-lines in the region of solid-liquid two phase equilibrium on the Sn-rich side of the In–Sn phase diagram (Fig. 3).

## Conclusions

The GB wetting by a liquid phase in the In–Sn alloy containing 25 at% In was investigated. The phases, composition, and percentage of completely wetted GBs in these alloys annealed between 140 and 180°C and quenched into a liquid nitrogen were analyzed by means of light microscopy, XRD and EPMA. It was found that the extent of GB wetting transition in this alloy depended on the annealing temperature. The lower and higher temperature limits of the GB wetting transition are 140 and 180 °C, respectively. These limits were indicated as tie-lines in the Sn-rich side of the In–Sn phase diagram.

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