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# Grain Boundary Wetting Phase Transitions in the Al-Sn and Al-Sn-Pb Systems

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**Abstract.** The temperature dependencies of the contact angle $\theta$ at the intersection of a grain boundary in Al bicrystals with the solid/liquid interface has been measured for a symmetric tilt <011>{001} grain boundary with a tilt angle $\phi$ of 38.5°. The contacts with liquid Sn and two Sn–Pb alloys (containing 27 and 60 wt.% Pb) were studied. The temperature dependencies $\theta(T)$ present the evidence of the grain boundary wetting phase transition at $T_w$. The addition of Pb diminishes $T_w$ and increases the discontinuity in the temperature derivative of the grain boundary energy.

## 1. Introduction

Since their prediction by Cahn [1] the study of wetting phase transitions has been of great experimental and theoretical interest, primarily for planar solid substrates and fluid mixtures [2–4]. Particularly, it was experimentally shown that the wetting transition is of first order. The discontinuity of the surface energy was measured, and the hysteresis of the wetting behaviour was observed [5,6]. The experimental data about wetting phenomena on solid/solid interfaces, for example on grain boundaries (**GB**s), are less studied [7]. The important difference is that in the case of GB wetting only two phases coexist, namely a liquid phase and a solid one containing the boundary between the misoriented grains (Fig.1). Therefore, the contact angle $\theta$ also depends only on two different surface energies (the GB energy $\sigma_{GB}$ and the energy of the solid/liquid interphase boundary $\sigma_{SL}$) instead of three ones in the usual experiments (Fig. 1(c)):

$$\sigma_{GB} = 2\,\sigma_{SL}\cos(\theta/2). \qquad (1)$$

If $\sigma_{GB} < 2\sigma_{SL}$, the GB is incompletely wetted and the contact angle $\theta>0$ (Fig.1(c)). At the temperature $T_w$ of the *GB wetting phase transition* $\sigma_{GB} = 2\sigma_{SL}$. At $T \geq T_w$ the GB is completely wetted by the liquid phase and $\theta=0$ (Fig. 1(d)). If two GBs have different energies the temperatures of their GB wetting transitions will also differ: the lower $\sigma_{GB}$, the higher $T_w$ (Fig. 1(e)). If the GB wetting phase transition is of first order, there is a discontinuity in the temperature derivative of the GB energy at $T_w$ which is equal to $[\partial\sigma_{GB}/\partial T - \partial(2\sigma_{SL})/\partial T]$ [1,6]. If the GB wetting phase transition is of second order $\partial\sigma_{GB}/\partial T = \partial(2\sigma_{SL})/\partial T$ at $T_w$. Recently, the temperature dependencies of $\theta$ for GBs in Al bicrystals in contact with a Sn–Al melt were investigated. The temperatures $T_w$ were measured for GBs with different energies and the tie lines of the GB wetting phase transition were determined in the bulk phase diagram [8]. The goal of this work was to investigate the influence of Pb additions to a Sn-rich melt on the temperature of the GB wetting phase transition. In the present work, the temperature dependencies of $\theta$ for GBs in Al bicrystals in contact with liquid Sn and Sn–Pb alloys were investigated. It is interesting to study the influence of Pb concentration in the Sn-rich melt on the temperature of the GB wetting phase transition because the influence of the third component on $T_w$ was never investigated (at least on bicrystals). The system Sn–Pb is important because Sn and Pb have a simple eutectic phase diagram and serve as a base for many solders [9,10].

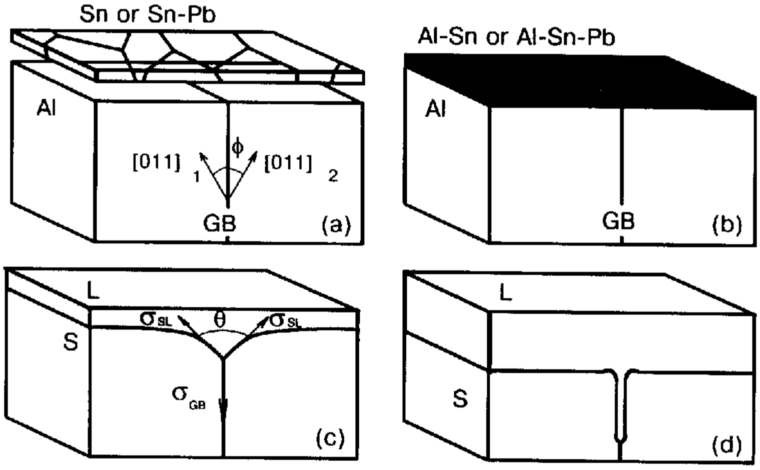

Fig.1. (**a**) The Al bicrystal and a Sn or Sn–Pb polycrystal before the formation of the contact. (**b**) The Al bicrystal with a melted Al–Sn or Al–Sn–Pb layer on the top after the formation of the contact at about 240°C. (**c**) The bicrystal in contact with the liquid phase. The GB is incompletely wetted. The contact angle $\theta>0$. (**d**) The GB is completely wetted at $T>T_w$ : $\theta=0$.

## 2. Experimental

A symmetrical tilt 38.5°<011>{001} GB was chosen for the measurements having a misorientation angle near the $\Sigma9$ coincidence misorientation ($\Sigma$ being the reciprocal density of coincidence sites). The bicrystals were produced from Al of 99.999 wt.% purity using a modified Bridgman technique. At intermediate stages of the bicrystal production the monocrystalline seeds, etched for 1–5 min in a solution of 10 ml HF, 50 ml $HNO_3$ and 50 ml HCl, were oriented by laser optics directly on the spark erosion machine used for cutting. Finally, the orientation parameters of the bicrystals were controlled using Laue back reflection. For the wetting experiments the samples were covered with a layer of Sn or Sn–Pb alloys with Pb concentrations of 27 and 60 wt.% (Fig.1 (a) and (b)). For this purpose the Al bicrystals were etched for 40–60 s with the solution mentioned above and brought in contact with liquid Sn or Sn–Pb alloy of 99.9999 wt.% purity at about 240°C in an atmosphere of pure argon without overpressure. The surface layer at the end of the bicrystal dissolves in the liquid Sn or Sn–Pb alloy and saturates the melt up to the liquidus concentration. The contact between the melt and the Al bicrystal forms within a few seconds. The annealed samples were 2–3 mm long. The thickness of the Sn layers was 0.2–0.4 mm. All individual samples were cut from the same bicrystal. The bicrystalline samples coated with a Sn-rich layer were placed together with an oxygen getter (a piece of a Ta foil) in evacuated silica capsules with a residual pressure of $4\times10^{-4}$ Pa. Each sample was annealed at a prescribed temperature maintained constant within ±0.2°C for 20 min and subsequently quenched in water with a cooling rate of $10^2$ K/s. After quenching the samples were embedded in a holder and then mechanically ground and polished to make a polished surface parallel to the {011} surface of the Al bicrystal and perpendicular to the GB and solid/liquid interface. The polished surface was etched for a few seconds in a 5% aqueous solution of HF. The contact area between the GB and the interphase boundary was photographed in an optical microscope, and the contact angle $\theta$ was measured with an accuracy about 0.5°.

## 3. Results and discussion

The temperature dependencies of the contact angles for Al–Sn, Al–(Sn–27wt.%Pb) and Al–(Sn–60 wt.% Pb) are shown in Fig. 2. All $\theta(T)$ dependencies are convex in the broad temperature interval below $T_w$. At temperatures between 500°C and $T_{wSn}$ the additions of Pb to the melt diminish the contact angles $\theta$. The energy $\sigma_{SL}$ of the solid/liquid interface decreases with the addition of Pb, because the GB energy $\sigma_{GB}$ is the same at the given temperature. Below 500°C the influence of Pb on $\theta$ (and, therefore, on $\sigma_{SL}$) is negligible. The temperatures of the GB wetting phase transition in the Al–Sn, Al–(Sn–27 wt.% Pb) and Al–(Sn–60 wt.% Pb) systems are $T_{wSn} = 617\pm1$°C, $T_{w27} = 580\pm5$°C and $T_{w60} = 600\pm5$°C, respectively. The accuracy of $T_w$ is defined by the temperature interval between the experimental points. Therefore, the influence of the Pb concentration is not monotonous.

The Pb–Sn and Sn–Al bulk phase diagrams are shown in Fig. 3. The tie line of the GB wetting phase transition is shown (dashed line) in the (Al)+L field of the Al–Sn diagram. In the upper part of the Pb–Sn diagram the points are shown for the temperatures $T_{wSn}$, $T_{w27}$ and $T_{w60}$. It can be clearly seen that a correlation exists between the liquidus temperature in the Pb–Sn system and the temperatures of the GB wetting phase transition in the ternary Al–(Sn–Pb) system.

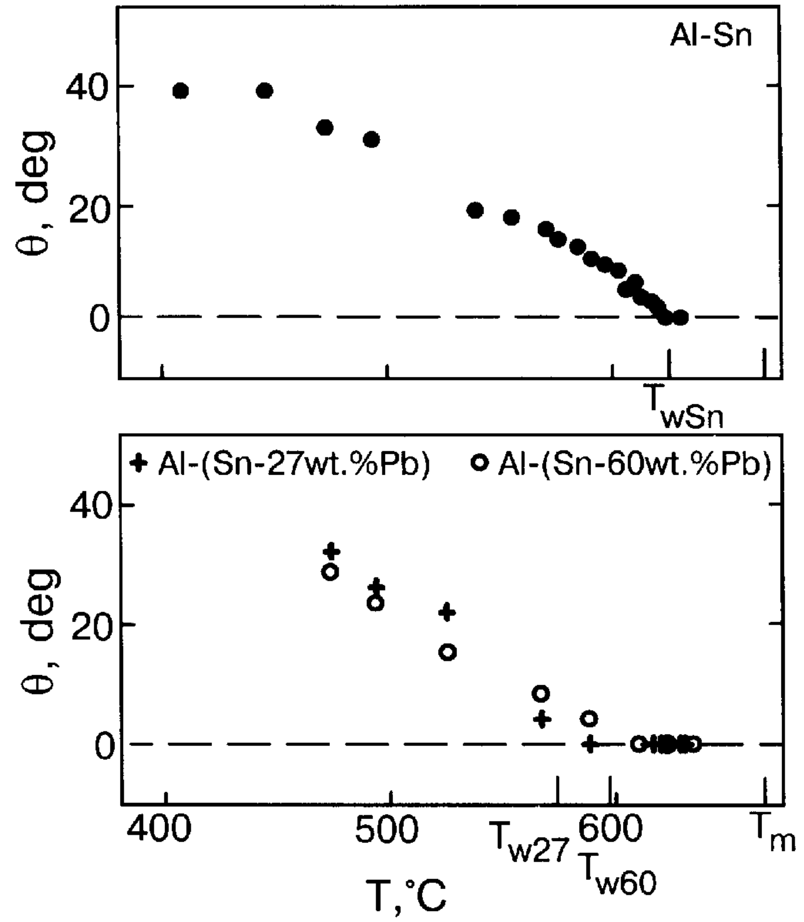

Fig. 2. The temperature dependencies of the contact angle θ for a 38.5°<011> {001} GB in the Al-Sn, Al-(Sn-27 wt.% Pb) and Al-(Sn-60 wt.% Pb) systems. The wetting temperatures are $T_{wSn}$ = 617±1°C, $T_{w27}$ = 580±5°C and $T_{w60}$ = 600±5°C, respectively. $T_m$ = 660°C (melting temperature of Al).

If the energies $\sigma_{GB}$ and $\sigma_{SL}$ depend linearly on the temperature, the phenomenological theory [1] predicts for a wetting phase transition of first order—analogously to fluids on a solid substrate—that the temperature derivative of the macroscopic GB energy has a discontinuity Δ at $T_w$ given by

$$\partial(2\sigma_{SL})/\,\partial T - \partial\sigma_{GB}\,/\partial T = -2\sigma_{SL}\,\partial(\cos\theta)/\,\partial T \qquad (2)$$

This equation is obtained by differentiating the law of cosines for the triangle built by $\sigma_{SL}$, $\sigma_{GB}$ and $\sigma_{SL}$ (Fig. 1 (c)) at $T_w$ where cos θ = 1. The θ(T) dependencies measured close to $T_w$ permit us to estimate the values of $\partial(\cos\theta)/\,\partial T$ in the temperature interval where the θ(T) dependencies can be treated as linear (from $T_w$ to about $T_w$-100 K). We can estimate the right-hand part of Eq.(2) knowing that $2\sigma_{SL} = \sigma_{GB}$ at $T_w$ and using the value $\sigma_{GB}$ = 350 mJ/m$^2$ for Al near the melting temperature $T_m$ [11] because in our case $T_w$ is close to $T_m$ (660°C). For the Al-Sn system $\partial(\cos\theta)/\partial T$ = 160/mK and the discontinuity is equal to -5.6±0.1 mJ/m$^2$K. For the Al-(Sn-27 wt.% Pb) system $\partial(\cos\theta)/\partial T$ = 200/mK and Δ = -7±1 mJ/m$^2$K.. For the Al-(Sn-60 wt.% Pb) system $\partial(\cos\theta)/\partial T$ = 200/mK and Δ = -15±0.3 mJ/m$^2$K. Therefore, Δ increases monotonously with the Pb content in the Sn-Pb melt.

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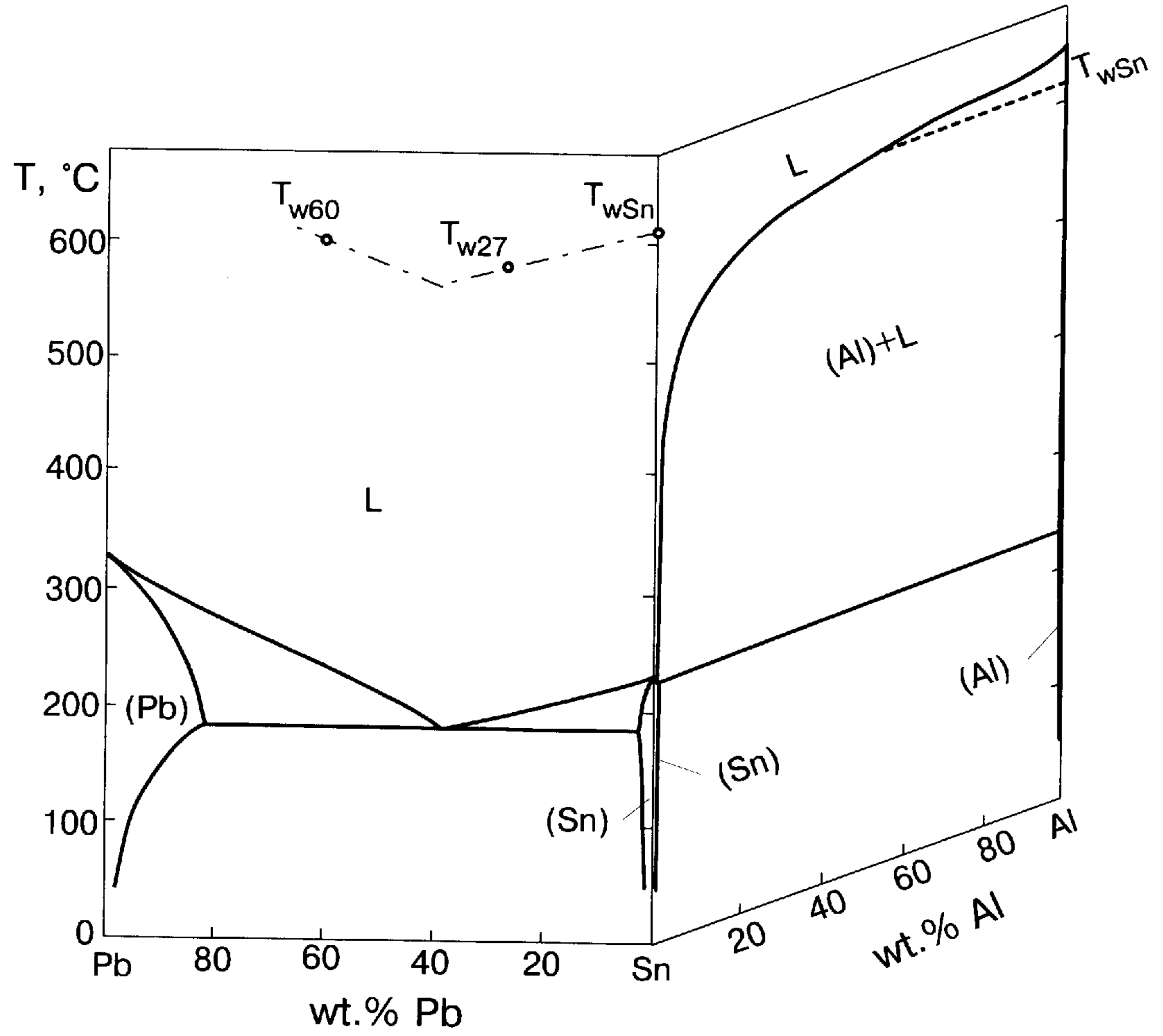

Fig. 3. The phase diagrams Pb–Sn and Sn–Al. The tie line at $T_{wSn}$ for the GB wetting phase transition in the Al–Sn system (dashed line) is shown. The points are the wetting temperatures $T_{wSn}$, $T_{w27}$ and $T_{w60}$ in the Al–Sn, Al–(Sn–27 wt.% Pb) and Al–(Sn–60 wt.% Pb) systems, respectively.

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