

Wetting Transition on Grain Boundaries in Al Contacting with a Sn-rich Melt

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Received March 8, 1995

Abstract. The contact angle θ at the intersection of a grain boundary in Al bicrystals with the solid Al/liquid Al–Sn interphase boundary has been measured for two symmetric tilt $\{011\}\{001\}$ grain boundaries with tilt angles ϕ of 32° and 38.5° . The temperature dependencies $\theta(T)$ present the evidence of the grain boundary wetting phase transition at T_w . The observed hysteresis is consistent with the assumption that the wetting transition is of first order. The determined discontinuity in the temperature derivative of the grain boundary energy is $-5.6 \mu\text{J}/\text{m}^2\text{K}$ ($T_{w1} = 617^\circ\text{C}$) for the boundary with a low energy ($\phi = 38.5^\circ$) and $-17 \mu\text{J}/\text{m}^2\text{K}$ ($T_{w2} = 604^\circ\text{C}$) for the grain boundary with a high energy ($\phi = 32^\circ$).

Keywords: grain boundaries, wetting transition, phase diagrams

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, namely the discontinuity of the surface energy was measured and the hysteresis of the wetting behavior was observed [5, 6]. The experimental data about wetting phenomena on solid/solid interfaces, for example on the grain boundaries (GBs), are much more poorer [7]. The important difference is that in case of GB wetting only two phases coexist, namely the liquid (melt) phase and the solid one containing the boundary between the misoriented grains (Fig. 1). Therefore, the contact angle θ also depends only on two different surface energies (the GB energy σ_{GB} and the energy of the solid/liquid interphase boundary σ_{SL}) instead of three ones in the usual experiments (Fig. 1(c)):

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

If $\sigma_{\text{GB}} < 2\sigma_{\text{SL}}$, 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 $\sigma_{\text{GB}} = 2\sigma_{\text{SL}}$, 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 σ_{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 $[\partial\sigma_{\text{GB}}/\partial T - \partial(2\sigma_{\text{SL}})/\partial T]$ [1, 6]. If the GB wetting phase transition is of second order, $\partial\sigma_{\text{GB}}/\partial T = \partial(2\sigma_{\text{SL}})/\partial T$ at T_w . The theory predicts also the form of the temperature dependence $\theta(T)$ at $T \rightarrow T_w$: it must be convex for a first order wetting transition ($\theta \sim \tau^{1/2}$ where $\tau = (T_w - T)/T_w$; upper line in Fig. 1(f)) and concave for a second order wetting transition ($\theta \sim \tau^{3/2}$; lower line in Fig. 1(f)) [2].

Unfortunately, the existing experimental data (for review see [7]) do not allow us to determine whether the GB wetting phase transition is of first or second order. Firstly, in most of these works the temperature intervals between the experimental points are too large for allowing the decision about the actual form of the $\theta(T)$ dependency close to T_w . Secondly, most of these data were obtained on polycrystals and cannot be used for a correct description of the GB wetting transition because the GBs are randomly inclined towards the section plane preventing precise measurements of θ ,

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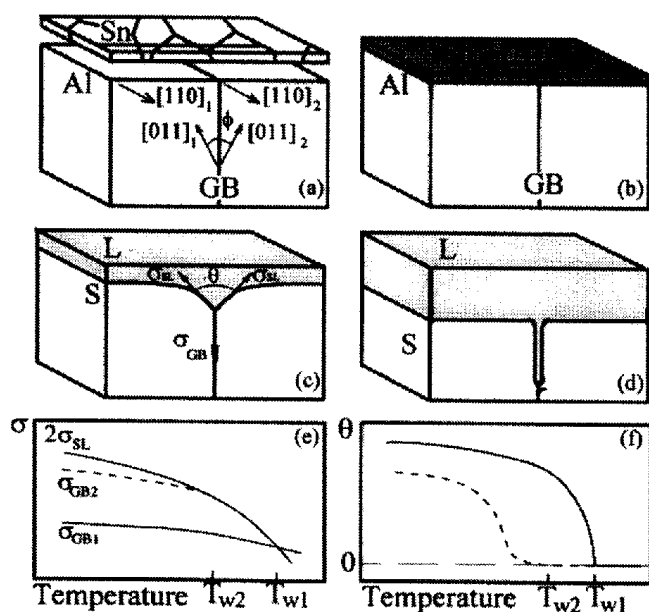


Fig. 1. (a) The Al bicrystal and a Sn polycrystal before the formation of the contact. (b) The Al bicrystal with a (Sn) + (Al) layer on the top after the formation of the contact at about 240°C. (c) The bicrystal in contact with the liquid phase at $T_w > T > 317^\circ\text{C}$. The GB is incompletely wetted. The contact angle $\theta > 0$. (d) The GB is completely wetted, $T > T_w$, $\theta = 0$. (e) Schematic dependencies of $2\sigma_{\text{SL}}(T)$ together with $\sigma_{\text{GB1}}(T)$ and $\sigma_{\text{GB2}}(T)$ for two different GBs. They intersect at the temperatures T_{w1} and T_{w2} of the GB wetting phase transition. At T_{w1} there is a difference between temperature derivatives of $\sigma_{\text{GB1}}(T)$ and $\sigma_{\text{SL}}(T)$ (transition of first order). At T_{w2} the temperature derivatives of $\sigma_{\text{GB2}}(T)$ and of $\sigma_{\text{SL}}(T)$ are equal (transition of second order). (f) Schematic temperature dependencies of the contact angle θ corresponding to the curves drawn in Fig. 1(e).

and only the θ values averaged over many GBs can be obtained. By the averaging of θ important features of the GB wetting transitions are smeared out because the properties of GBs depend strongly on their crystallographic parameters [8]. Therefore, θ should be measured on *individual GBs in oriented bicrystals* [9]. In this case the GB lies perpendicular to the section plane, and the crystallographic parameters of the GB can be predetermined by the bicrystal production.

2 Experimental

In the present work, the *temperature dependencies of θ* for GBs in Al bicrystals in contact with a Sn-rich melt were investigated in the whole temperature interval of the coexistence between the solid Al and Sn-rich melt using minimal temperature steps near T_w . The objectives of this work were to determine experimentally whether the *GB wetting transition is of first or*

second order and to measure T_w for GBs with different energies.

The Al–Sn system was chosen for the measurements because the data for polycrystals show that there is a GB wetting phase transition somewhere between 580 and 620°C [10]. Besides, the solubility of Sn in solid Al is very low (max. 0.25 wt.%) [11]. Therefore, the contact between the Al bicrystal and the Sn-rich melt is very close to the equilibrium at all temperatures studied. In former GB wetting experiments the solubilities of the second component in a material of the bicrystal were high and temperature dependent [10]. Therefore, uncontrollable equilibration processes in the solid phase during the annealing influenced the value of θ and avoided the precision measurements.

At the coincidence misorientation (CM) some sites in the ideal interpenetrating lattices of the two misoriented grains coincide, forming the coincidence site lattice (CSL) characterized by the reciprocal density, Σ , of coincidence sites. In the misorientation angle—temperature plots the localized regions exist near the CMs where the GBs have a “special” structure and “special” properties, surrounded by the regions of the so-called general GBs [8]. At the lines dividing these regions, the GB properties change abruptly [12, 13]. Therefore, a special ($\phi = 38.5 \pm 1^\circ$; near the $\Sigma 9$ CM) and a general ($\phi = 32 \pm 0.5^\circ$) symmetrical tilt $\{011\}\{001\}$ GB were chosen for the measurements. Experimental data and computer modeling of such GBs in Al indicate that the GB with a tilt angle of 38.5° has a low energy and the other GB has a high energy [14].

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. The flat bicrystals, having dimensions $2 \times 8 \times 120$ mm with the flat GB laying parallel to the long axis and perpendicular to the (011) surface, were grown in high-purity graphite crucibles in an atmosphere of high-purity argon (with an oxygen content equivalent to the vacuum of 10^{-5} Pa).

For the wetting experiments the samples were covered with a Sn layer (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 of 99.9999 wt.% purity at about 240°C

in an atmosphere of pure argon. The surface layer at the end of the bicrystal dissolves in the liquid Sn and saturates the melt up to the liquidus concentration. The contact between the molten Sn(Al) and the Al bicrystal forms within a few seconds. Then the apparatus was cooled down and the Sn-coated Al sample was cut by spark erosion. The samples annealed were 2–3 mm long with 0.2–0.4 mm thick Sn layers. All individual samples were cut from the same bicrystal. The annealing temperatures (30 for the bicrystal with $\phi = 32^\circ$ and 23 for the bicrystal with $\phi = 38.5^\circ$) were between 317 and 630.5°C.

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 4×10^{-4} Pa. Each sample was annealed at a prescribed temperature maintained constant within $\pm 0.2^\circ\text{C}$ for 20 min and subsequently quenched in water with a cooling rate of 10^2 K/s. The sample reached the temperature of the furnace after about 4 min, and θ reached its equilibrium value after about 6 min (Fig. 4). The measured θ values begin to differ from the equilibrium value only at cooling rates of about 10^{-2} K/s (Fig. 4).

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 with a magnification of 1000:1, and the contact angle θ was measured. The error bars were defined by subsequent measurements of θ on different distances from the former surface after removing 100–200 μm thick layers. It is very important that all annealing temperatures are higher than the coating temperature and some Al dissolves in the Sn-rich melt according to liquidus line. During this dissolution process the interphase boundary moves at a distance about 100–1000 μm from the former position (Fig. 1(b) to (d)), and the contaminations eventually present on the interphase boundary due to the coating process dissolve in the melt. It is also important that a 200–300 μm thick layer is mechanically removed before the measurements. Therefore, the contact angle is measured deep in the sample where θ is determined only by σ_{GB} and σ_{SL} in equilibrium with the (very clean) bulk Al and Sn–Al melt without an influence of the (eventually contaminated) surface.

3 Results and Discussion

Figure 2 shows optical micrographs of the 38.5° {011}{001} bicrystal for different temperatures. The GB lies perpendicular to the plane of the Al/Sn contact and to the {011} section surface. It can be clearly seen how the contact angle θ decreases with increasing temperatures, tends to zero at $T = T_w$ and remains zero at $T > T_w$.

The temperature dependencies of the contact angles of both GBs studies are shown in Fig. 3. Both $\theta(T)$ dependencies are convex in the broad temperature interval below T_w . At all temperatures below T_{w1} the contact angles for the GB with $\phi = 38.5^\circ$ are smaller than those for the GB with $\phi = 32^\circ$. This means the energy σ_{GB2} is really lower than σ_{GB1} as expected from the selection of the GB misorientation parameters. At the temperature T_w the GB wetting phase transition occurs and for $T > T_w$ the contact angle $\theta = 0^\circ$. The GBs studied have different temperatures for the wetting phase transition: $T_{w1} = 617 \pm 1^\circ\text{C}$ for $\phi = 38.5^\circ$ and $T_{w2} = 604 \pm 1^\circ\text{C}$ for $\phi = 32^\circ$. Figure 4 shows the hysteretic character of this transition. After cooling down from $T_1 > T_w$ to $T_2 > T_w$ the angle θ changes slowly from 0 to the equilibrium value for T_2 .

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

$$\partial(2\sigma_{\text{SL}})/\partial T - \partial\sigma_{\text{GB}}/\partial T = -2\sigma_{\text{SL}}\partial(\cos\theta)/\partial T. \quad (2)$$

This equation is obtained by differentiating the law of cosines for the triangle built by σ_{SL} , σ_{GB} and σ_{SL} (Fig. 1(c)) at T_w where $\cos\theta = 1$. The $\theta(T)$ dependencies measured with small temperature steps close to T_w permit us to estimate the values of $\partial(\cos\theta)/\partial T$ with a high accuracy in the temperature interval where the $\theta(T)$ dependencies can be treated as linear (from T_w to about $T_w - 70$ K). We can estimate the right-hand part of Eq. (2) knowing that $2\sigma_{\text{SL}} = \sigma_{\text{GB}}$ at T_w and using the value $\sigma_{\text{GB}} = 350$ mJ/m² for Al near the melting temperature T_m [14] because in our case T_w is close to T_m (660°C). For the 32° {011}{001} GB $\partial(\cos\theta)/\partial T = 480/\mu\text{K}$ and the discontinuity is equal to -17 $\mu\text{J}/\text{m}^2\text{K}$. For the 38.5° {011}{001} GB $\partial(\cos\theta)/\partial T = 160/\mu\text{K}$ and the discontinuity is equal to -5.6 $\mu\text{J}/\text{m}^2\text{K}$. Therefore, the discontinuity of σ_{GB} is much lower for the special GB ($\phi = 38.5^\circ$, near $\Sigma 9$) than for the

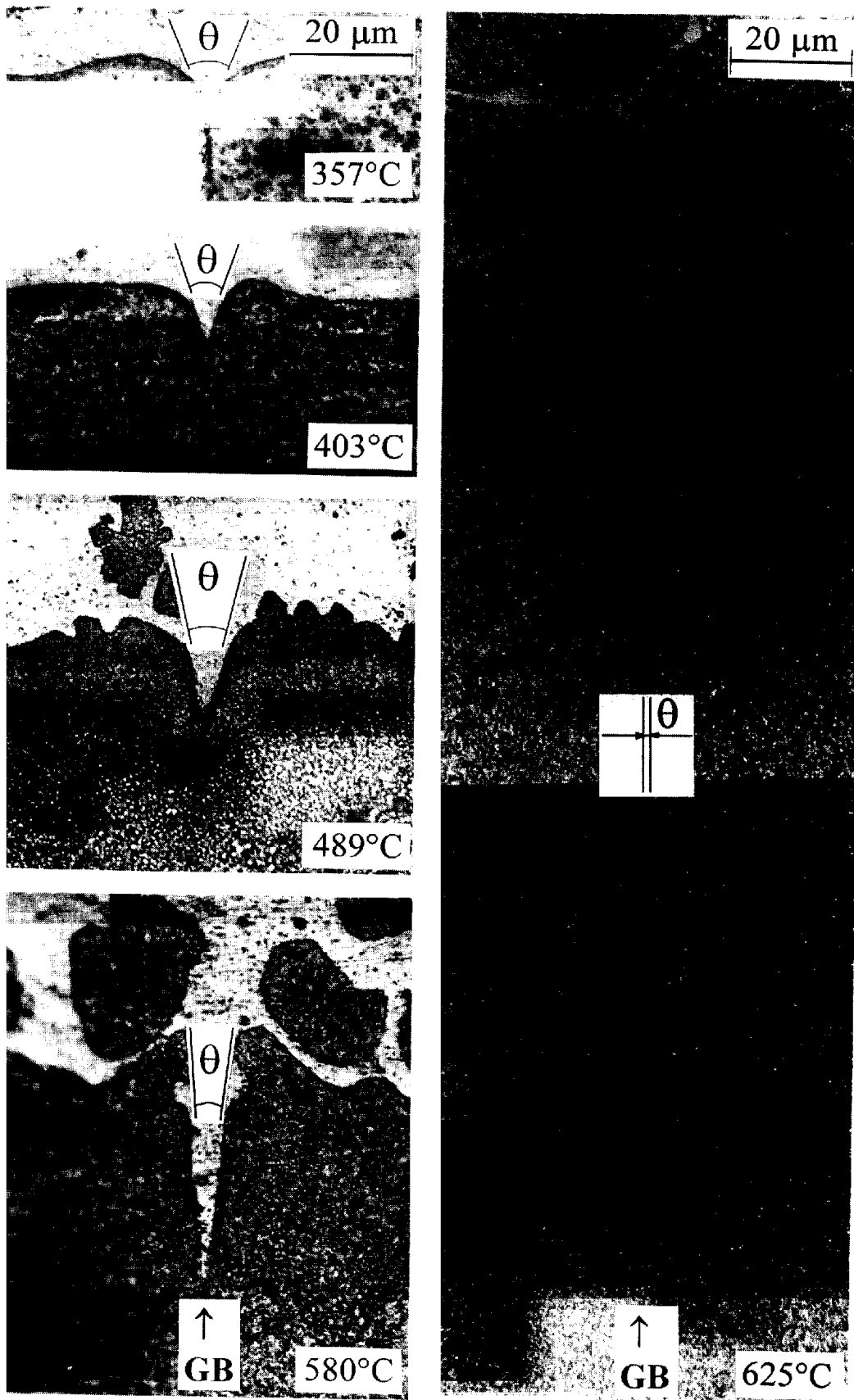


Fig. 2. Optical micrographs of the contact area between the $38.5^\circ\langle 011\rangle\{001\}$ bicrystal (below) and a Sn-rich melt (above) after annealing at different temperatures and subsequent quenching. The section plane is parallel to the $\{011\}$ planes of both grains and perpendicular to the GB, the solid/melt interface and the line of their contact (see Fig. 1).

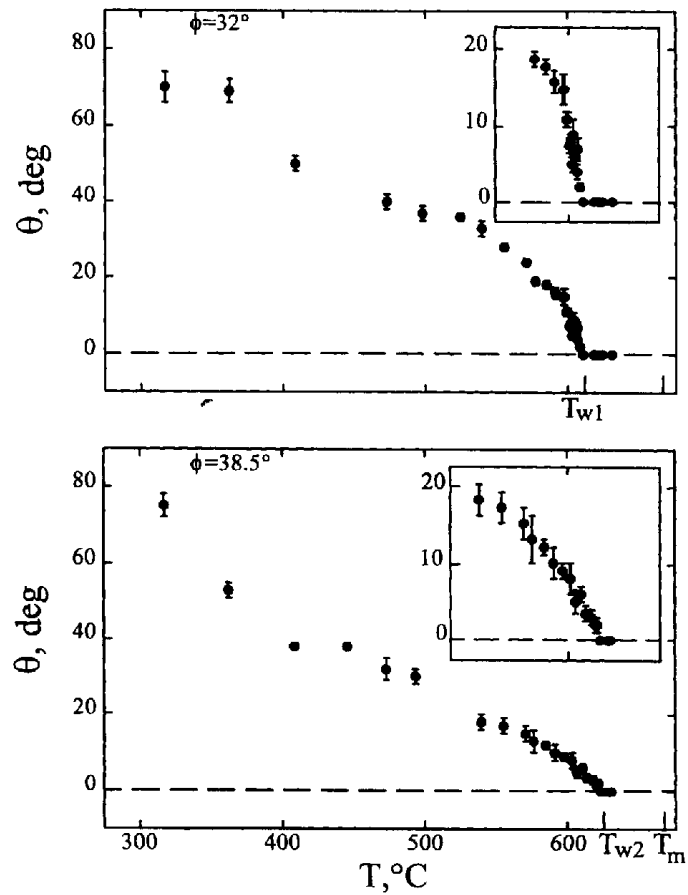


Fig. 3. The temperature dependencies of the contact angle θ for $32^\circ(011)\{001\}$ and $38.5^\circ(011)\{001\}$ GBs. The wetting temperatures, T_{w1} and T_{w2} , are $604 \pm 1^\circ\text{C}$ and $617 \pm 1^\circ\text{C}$, respectively. The insertions show the enlarged $\theta(T)$ curves near T_w .

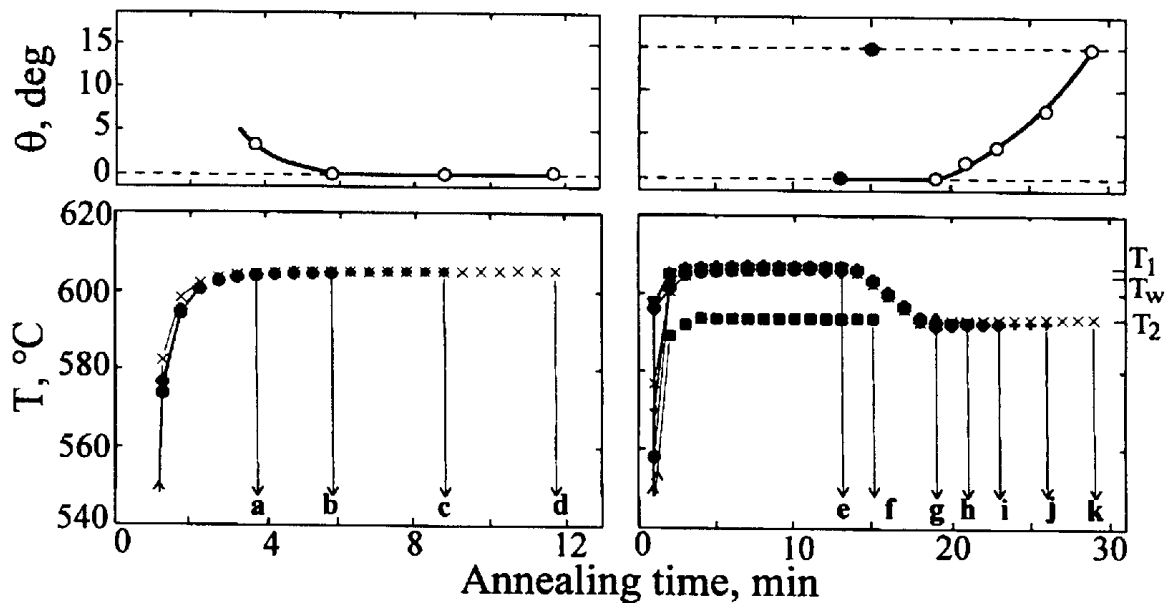


Fig. 4. The contact angle θ after different annealings. (a–e) Heating up to $T_1 > T_w$ and quenching. (f) Heating up to $T_1 < T_w$ and quenching. (g–k) Heating up to $T_1 > T_w$, cooling down to $T_2 < T_w$, and quenching.

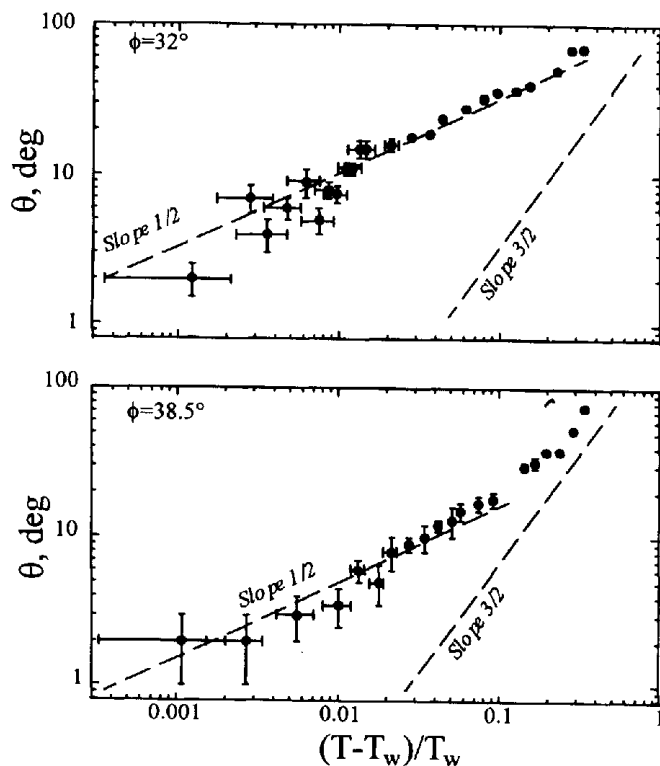


Fig. 5. The dependencies of the contact angle on $(T - T_w)/T_w$. The slopes of 1/2 and 3/2 shown with dashed lines correspond to wetting phase transitions of first and second order, respectively [2].

general GB ($\phi = 32^\circ$). These discontinuity values are higher than the value for fluocarbon-alcohol fluid ($-0.9 \mu\text{J}/\text{m}^2\text{K}$ [6]) due to the high surface energies of metals.

The theory predicts a $\theta \sim \tau^{1/2}$ behavior for a wetting transition of first order and $\theta \sim \tau^{3/2}$ for a transition of second order [2]. The $\theta(\tau)$ dependencies are shown for both GBs studied in Fig. 5. In both cases the experimental points correspond to a slope of 1/2 for temperatures about 200–250 K below T_w . All these

facts show that the GB wetting phase transition in the present study is a first order transition.

Acknowledgments

The authors are grateful to Profs. Brèchet, Gottstein, Shvindlerman and Drs. Chenal and Rabkin for fruitful discussions. This work was partly supported by the INTAS programme under contract 93-1451. One of us (D.A.M.) acknowledges the support from the Alexander von Humboldt Foundation.

References

1. J.W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).
2. S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J.H. Lebowitz (Academic, London, 1988), Vol. 12, p. 2.
3. D. Jasnov, *Rep. Prog. Phys.* **47**, 1059 (1984).
4. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
5. H. Kellay, D. Bonn, and J. Meunier, *Phys. Rev. Lett.* **71**, 2607 (1993).
6. J.W. Schmidt and M.R. Moldover, *J. Chem. Phys.* **79**, 379 (1983).
7. E.I. Rabkin, L.S. Shvindlerman, and B.B. Straumal, *Int. J. Mod. Phys. B* **5**, 2989 (1991).
8. B.B. Straumal and L.S. Shvindlerman, *Acta Metall.* **33**, 1735 (1985).
9. B. Straumal, T. Muschik, W. Gust, and B. Predel, *Acta Metall. Mater.* **40**, 939 (1992).
10. J.H. Rogerson and J.C. Borland, *Trans. Am. Inst. Met. Engrs.* **227**, 2 (1963).
11. T.B. Massalski et al. (editors), *Binary Alloy Phase Diagrams* (ASM International, Materials Park, Ohio), 1990, p. 216.
12. E.L. Maksimova, L.S. Shvindlerman, and B.B. Straumal, *Acta Metall.* **36**, 1573 (1988).
13. E.L. Maksimova, L.S. Shvindlerman, and B.B. Straumal, *Acta Metall.* **37**, 2855 (1989).
14. G. Hasson and C. Goux, *Scripta Metall.* **5**, 889 (1971).