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Inversed solid-phase grain boundary wetting in the Al–Zn system

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Abstract The microstructure of binary Al–10 at% Zn and Al–15 at% Zn alloys after long anneals (800–4000 h) was studied between 190 and 258 °C. The contact angles between (Zn) particles and (Al)/(Al) grain boundaries (GBs) were measured. They decrease with decreasing temperature. First (Al)/(Al) GBs completely wetted by the second solid phase (Zn) appear below $T_{wsAl0\%} = 205 \pm 5$ °C. Above $T_{wsAl0\%} = 205 \pm 5$ °C all (Al)/(Al) GBs are incompletely wetted by (Zn) solid phase. The extrapolation of the maximal contact angle θ to zero permits to obtain the $T_{wsAl100\%} = 125 \pm 10$ °C. Below this line all (Al)/(Al) GBs has to be completely wetted by (Zn) solid phase.

Introduction

Thin equilibrium GB or surface films in the one-phase area of a bulk phase diagram were first considered by Cahn [1] and Ebner and Saam [2]. They proposed the idea that the transition from incomplete to complete surface wetting is a phase transformation. Later this idea was successfully applied for GBs, and also old data on GB wetting were reconsidered from this point of view [3–6]. From the bulk Al–Zn phase diagram (Fig. 1a) it is obvious that the Al–Zn system belongs to the "classical" Cahn's systems with a critical point for a binary solution. GB wetting phase transformation proceeds at the temperature T_{wGB} where GB energy σ_{GB} becomes equal to the energy $2\sigma_{SL}$ of two solid/liquid interfaces (Fig. 2a). Above T_{wGB} GB is substituted by a layer of the melt. As a result, the new tie-line appeared in the two-phase area of a bulk phase diagram (Fig. 1a), namely that of the GB wetting phase transition. GBs can also be "wetted" by a second solid phase, the reversible transition from incomplete (Fig. 2c) to complete (Fig. 2d) solid phase wetting was observed for the first time in the Zn–Al system at a certain temperature T_{ws} [7].

The transition from incomplete to complete GB wetting by a liquid phase always proceeds with increasing temperature [3–6]. It is easy to understand because the entropy of a liquid phase is higher than that of a solid one. Therefore, $2\sigma_{SL}$ has a good reason to decrease with increasing temperature steeper than σ_{GB} (see scheme in Fig. 2a). In the first studies on the GB wetting by a second solid phase the same tendency was observed [7, 8]. Namely, the (Zn)/(Zn) GBs became completely wetted by the (Al) solid phase with increasing temperature [7]. The (Al)/(Al) GBs also became completely wetted by the Al_3Mg_2 phase with increasing temperature [8]. However, there is no unambiguous reason for the GB wetting by a second solid phase, why the transition from incomplete (Fig. 2c) to complete (Fig. 2d) GB wetting cannot proceed by decreasing temperature. Recently the authors observed the GB wetting followed by the dewetting in the Co–Cu system [9]. This phenomenon occurs close to the Co Curie point, and it is known that if a paramagnet matrix becomes ferromagnetic, the additional

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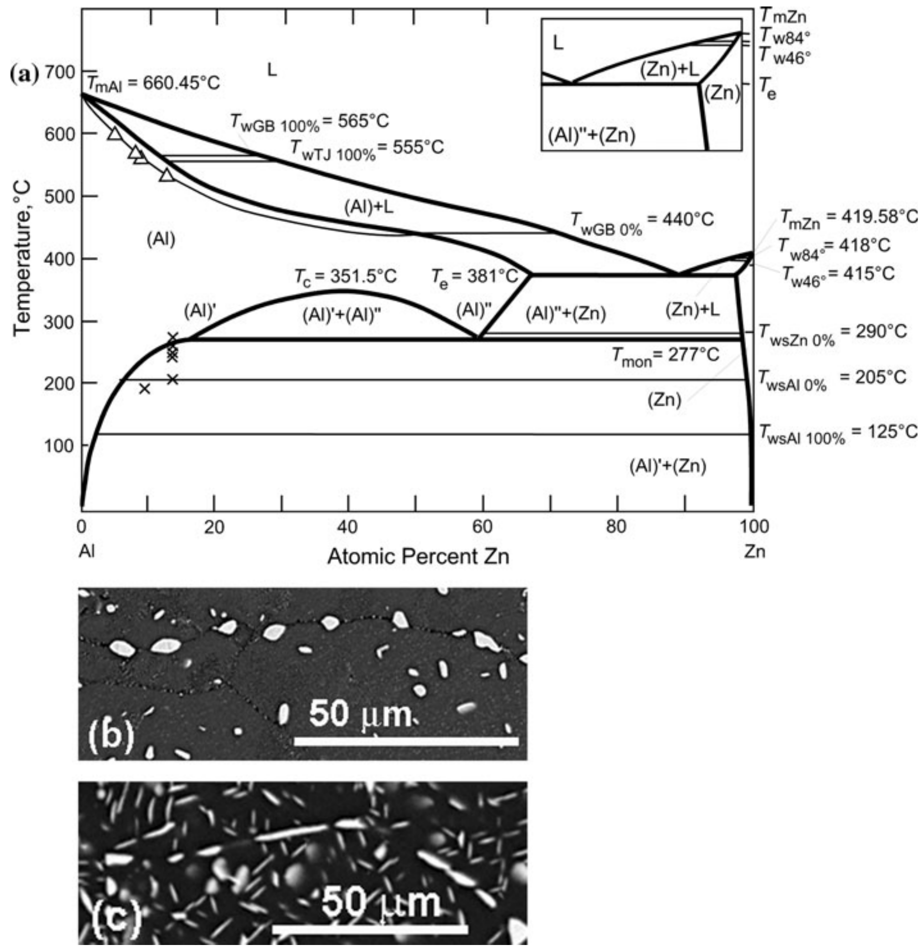

Fig. 1 **a** Al–Zn phase diagram constructed using the data [7, 14–17, 20]. *Thick lines* denote bulk phase transformations [19]. *Thin lines* denote GB phase transformations [7, 14–17, 20]. *Open triangles* denote TEM and DSC data for the GB prewetting line [15, 17]. *Crosses* mark the experimental points for the measurements of contact angle θ. The *inset* shows the Zn-rich corner of the diagram. **b** and **c** Micrographs illustrating the morphology of GB (Zn) precipitates at **b** 260 °C and **c** 190 °C. (Al) matrix appears **black**

attraction between grains may "squeeze" the diamagnetic wetting phase from a GB [10–13]. The goal of this study is to check, whether the transition from incomplete to complete GB wetting by a second solid phase can proceed by decreasing temperature in "pure" case, without any additional phase transformations in a matrix like in [9]. In this case the temperature dependences of the GB energy σ_{GB} and energy of two solid–solid interfaces $2\sigma_{SS}$ would also intersect at T_{ws} (Fig. 2b). However, in this case GB becomes completely wetted by a second solid phase below T_{ws} and not above T_{ws} like in refs. [7–9]. The authors started to search for this phenomenon in the Al–Zn alloys. First, it was obtained some preliminary results in the previous investigations of GB and triple junctions wetting phenomena in these alloys [7, 14–17]. Second, the nanograined Al–Zn alloys reveal the unusual ductility increase by the decreasing temperature [18].

Experimental

Al-based alloys with 10 and 15 at% Zn were investigated. They were prepared of high purity components (5N5 Al and 5 N Zn) by vacuum induction melting. The 2 mm thick slices were also cut from the ∅ 10 mm cylindrical Al–Zn ingots and sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Samples were annealed at temperatures 190 °C (4000 h), 205 °C (1200 h), 242 °C (1000 h), 253 °C (800 h), and 258 °C (800 h), and then quenched in water. The accuracy of the annealing temperature was ± 2 °C. After quenching, samples were embedded in resin and then mechanically ground and polished, using 1 μm diamond paste in the last polishing step, for the metallographic study. After etching, samples were investigated by means of the light microscopy, and scanning electron microscopy (SEM). SEM investigations have been carried out in a Philips XL30 scanning microscope equipped by the LINK ISIS energy-dispersive spectrometer produced by Oxford Instruments. Light microscopy has been performed using Neophot-32 light microscope equipped with 10 Mpix Canon Digital Rebel XT camera. A quantitative analysis of the wetting transition was performed adopting the following criterion: every (Al)/(Al) GB was considered to be completely wetted only when a layer of (Zn) solid solution had covered the whole GB (Figs. 1b, 2c); if such a layer

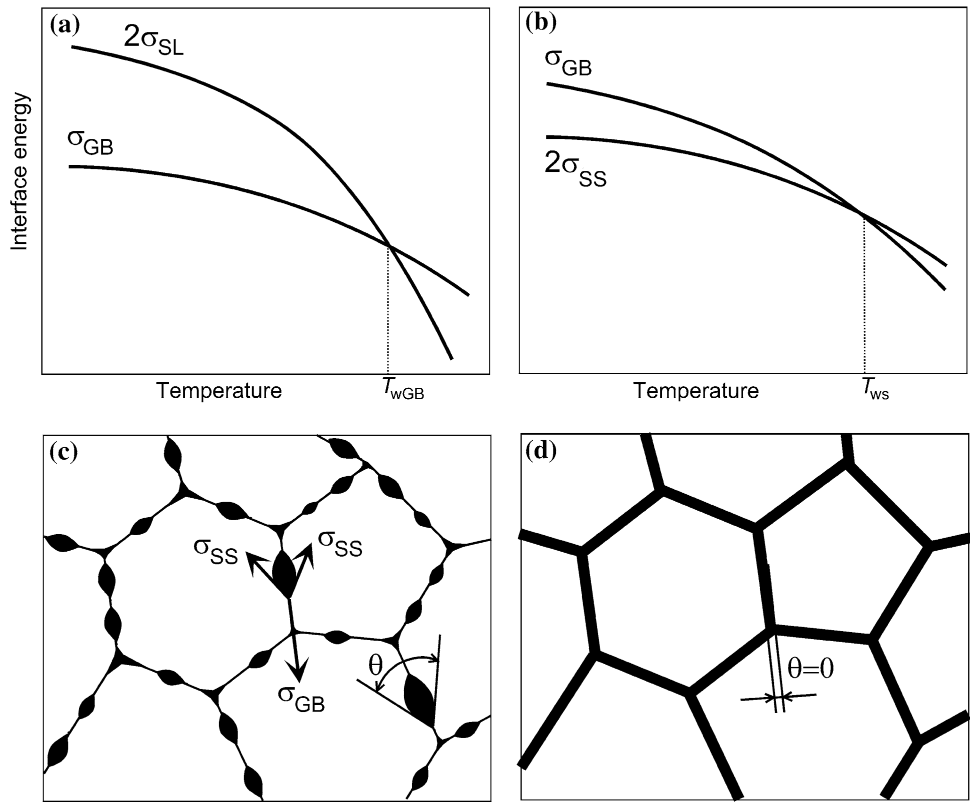

Fig. 2 **a**, **b** Scheme of the temperature dependence of GB energy σ_{GB} and energy of two wetting interfaces $2\sigma_{SL}$ and/or $2\sigma_{SS}$. **a** Transition from incomplete to complete wetting by a liquid phase at T_{wGB} with increasing temperature. **b** Transition from incomplete to complete wetting by a second solid phase at T_{ws} with decreasing temperature. **c** Scheme of the polycrystal with GBs incompletely wetted by a second solid phase (*black*). $\sigma_{GB} < 2\sigma_{SS}$, second solid phase forms individual particles along GBs and in the triple junctions of the matrix solid phase, the contact angle $\theta > 0$. **d** Scheme of the polycrystal with GBs completely wetted by a second solid phase. $\sigma_{GB} > 2\sigma_{SS}$, second solid phase forms continuous layers along GBs, the contact angle $\theta = 0$

appeared to be interrupted, the GB was regarded as incompletely (Figs. 1c, 2d) wetted. In case of incompletely wetted (Al)/(Al) GBs the contact angle θ between (Al)/(Al) GB and (Zn) solid solution was measured (Figs. 1b, 2c). At least 100 GBs were analysed at each temperature. Typical micrographs obtained by SEM are shown in Figs. 1b, c.

Results and discussion

In this study the authors measured the mean contact angle between (Al)/(Al) GBs and GB particles of (Zn) phase in the Al–10 at% Zn and Al–15 at% Zn polycrystals after long anneals below the monotectoid temperature $T_{mon} = 277$ °C (crosses in Fig. 1a). In Fig. 3 the temperature dependences of the maximal θ_{max} (circles), mean θ_{mean} (diamonds), and minimal θ_{min} (hexagons) values of the contact angle θ are shown. θ decreases with decreasing temperature. The value θ_{min} reaches zero at $T_{wsAl\ 0\%} = 205 \pm 5$ °C. The extrapolation of θ_{mean} to zero gives $T_{wsAl\ 50\%} = 167 \pm 10$ °C. Figure 1b, c shows the shape of GB Zn particles at 260 and 190 °C. The extrapolation of the θ_{max} to the low temperatures permits to estimate the temperature of the GB wetting transition as $T_{wsAl100\%} = 125 \pm 10$ °C. It means that at the room temperature the condition of complete wetting is fulfilled for all (Al)/(Al) GBs. In other words, all (Al)/(Al) GBs should be completely substituted by the Zn layer. As a result, two new lines of GB phase transformations appear in the Al–Zn phase diagram (Fig. 1a). The first tie-line is the $T_{wsAl0\%} = 205 \pm 5$ °C. Above this line all (Al)/(Al) GBs are incompletely wetted by (Zn) solid phase. Below this line the first (Al)/(Al) GBs completely wetted by (Zn) solid phase appear (Fig. 1c). The second tie-line is the $T_{wsAl100\%} = 125 \pm 10$ °C. This is the result of extrapolation of the upper plot $\theta_{max}(T)$ in Fig. 3. Below this tie-line $T_{wsAl100\%} = 125 \pm 10$ °C all (Al)/(Al) GBs has to be completely wetted by (Zn) solid phase. Above this tie-line first (Al)/(Al) GBs appear which are incompletely wetted by (Zn) solid phase.

Other lines of GB phase transformations obtained recently are also shown in the Al–Zn phase diagram (Fig. 1a) For example, in the (Al) + L two-phase region of the Al–Zn system the GB transformation for the (Al) GBs wetting by Zn-containing melt occurs [20]. The completely wetted GBs in the Al–Zn polycrystals do not exist below $T_{wGB0\%} = 440$ °C. $T_{wGB0\%}$ is the wetting temperature for a GB with maximal energy σ_{GBmax}. Above $T_{wGB100\%} = 565$ °C all high-angle GBs in (Al) are completely wetted by the melt (Fig. 2a) [16, 20]. $T_{wGB100\%}$ is the wetting temperature for a GB with minimal energy σ_{GBmin}. Between $T_{wGB0\%}$ and $T_{wGB100\%}$ the wetting tie-lines for GBs with intermediate $\sigma_{GBmax} > \sigma_{GB} > \sigma_{GBmin}$ are positioned in the (Al) + L area (Fig. 1a). GB triple junctions (TJs) become completely wetted at the temperature $T_{wTJ100\%} = 555$ °C below $T_{wGB100\%}$ [16]. The GB wetting phase transition in the

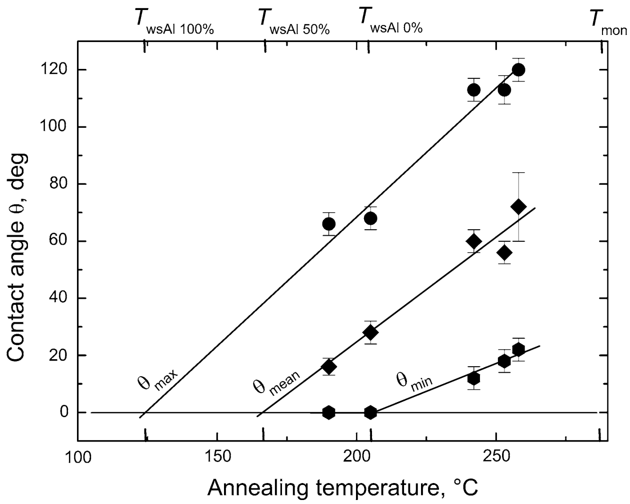

Fig. 3 Temperature dependences of maximal θ_{max} (*circles*), mean θ_{mean} (*diamonds*), and minimal θ_{min} (*hexagons*) values of the GB contact angle θ between (Al)/(Al) GBs and (Zn) particles (see scheme in Figs. 2c, d). The value θ_{min} reaches zero at $T_{wsAl\ 0\%} = 205$ °C. The extrapolation of θ_{mean} to $\theta = 0$ gives $T_{wsAl\ 50\%} = 167$ °C. At this temperature 50% of (Al)/(Al) GBs are completely wetted by (Zn) and another 50% of (Al)/(Al) GBs are incompletely wetted by (Zn). The extrapolation of the θ_{max} to the low temperatures until $\theta = 0$ permits to estimate the temperature of the GB wetting transition as $T_{wsAl100\%} = 125$ °C. Below $T_{wsAl100\%}$ all (Al)/(Al) GBs should be completely wetted by (Zn)

(Al) + L two-phase region of the Al–Zn system is of first order (discontinuous). The GB wetting phase transition in the (Zn) + L two-phase region is of second order (continuous) [14]. The tie-lines for the tilt $[11\bar{2}0]$ GBs with misorientation angles $\phi = 46°$ and $\phi = 84°$ are shown in the (Zn) + L two-phase region at $T_{w84°} = 418$ °C and $T_{w46°} = 415$ °C (Fig. 1a, see also insert in the upper right corner).

Following the Cahn's generic phase diagram, the more sophisticated theories of GB phases, segregation and wetting layers were developed [21–23]. Thin films of interfacial phases were observed in GBs in metals (studies of J. Luo and co-workers [24–26]), in oxides ([27], see also concept of complexions by Harmer and co-workers [28–32]), in interphase boundaries (Kaplan and co-workers [33–35]). According to those developments the GB wetting tie-lines continue as prewetting (or GB solidus or solvus) lines in the one-phase (Al) area. Just one prewetting line for $T_{wGB0\%}$ is shown for simplicity in Fig. 1a. The experimental evidence for the existence of a GB liquid-like phase between GB prewetting line and bulk solidus line was obtained by transmission electron microcopy [13] and differential scanning calorimetry (DSC) [36] (open triangles in Fig. 1a). In the area between GB solidus and bulk solidus, GB contains the thin layer of a GB phase. The energy gain (σ_{GB}–$2\sigma_{SL}$) above T_{wGB} permits to stabilize such thin layer of a GB phase between the abutting crystals, which is metastable in the bulk and become stable in the GB. The formation of metastable phase layer of thickness l leads to the energy loss $l\Delta g$ (Δg is the additional free enthalpy needed to create the layer of a metastable liquid phase). Finite thickness l of the GB phase is defined be the equality of the energy gain (σ_{GB}–$2\sigma_{SL}$) and energy loss $l\Delta g$. In this simplest model, the prewetting GB layer of finite thickness l suddenly appears by crossing the prewetting (GB soludus) line $c_{bt}(T)$. Thickness l logarithmically diverges close to the bulk solidus. It is due to the fact that the thickness of a wetting phase is thermodynamically infinite in the two-phase area. Physically, in the two-phase area, its thickness is defined only by the amount of the wetting phase. Several monolayer (ML) thick liquid-like GB layers possessing high diffusivity were observed in the Cu–Bi [37–41], Al–Zn [13, 36], Fe–Si–Zn [11–13] and W–Ni alloys [25, 26]. GB liquid-like phase drastically influences also the GB segregation [38], GB mobility [42], GB energy and electrical resistivity [43, 44]. The direct HREM evidence for thin GB films and triple junction "pockets" of the liquid-like phase has been recently obtained in metallic W–Ni [25, 26] and Al–Zn [13] alloys. The authors can imagine that additional lines, similar to the GB solidus, can also continue the tie-lines $T_{wsAl0\%} = 205 \pm 5$ °C and $T_{wsAl00\%} = 125$ °C into the one-phase (Al) area. Such continuations would form a kind of GB solvus lines for GBs with various energies. The search of such GB solvus lines will be the subject of the future study.

In summary, the authors observed the GB "wetting" by a second solid phase. The reversible GB transition from incomplete to complete wetting by a liquid phase always proceeds with increasing temperature since the temperature dependence $2\sigma_{SL}(T)$ is always more steep than the dependence $\sigma_{GB}(T)$, due to the fact that a liquid phase possesses higher entropy in comparison with a solid one. In case of solid state wetting, there are no obvious thermodynamic reasons for the drastic difference between temperature derivatives for GB energy σ_{GB} and for the energy of two solid/solid interphase boundaries $2\sigma_{SS}$. As a result, σ_{GB} may decrease with increasing temperature quicker than the energy of two solid/solid interphase boundaries $2\sigma_{SS}$. In this case, the transition from incomplete GB wetting to the complete one would proceed with decreasing temperature, like in the case in the Al–Zn system. The new GB tie-lines at $T_{wsAl0\%} = 205 \pm 5$ °C and $T_{wsAl100\%} = 125 \pm 10$ °C appeared in the Al–Zn phase diagram (Fig. 1a). Between $T_{wsAl0\%}$ and $T_{wsAl100\%}$ some (Al)/Al) GBs are completely wetted by the layers of solid (Al) phase. Below $T_{wsAl100\%}$ all (Al)/(Al) GBs has to be completely wetted by (Zn) solid phase.

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