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Wetting of grain boundaries in Al by the solid Al$_3$Mg$_2$ phase

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Abstract The microstructure of binary Al$_{100-x}$–Mg$_x$ ($x = 10$, 15, 18 and 25 wt%) alloys after long anneals (600–4000 h) was studied between 210 and 440 °C. The transition from incomplete to complete wetting of Al/Al grain boundaries (GBs) by the second solid phase Al$_3$Mg$_2$ has been observed. The portion of completely wetted GBs increases with increasing temperature beginning from $T_{\mathrm{wsmin}} = 220$ °C. Above $T_{\mathrm{wsmax}} = 410$ °C all Al/Al GBs are completely wetted by the Al$_3$Mg$_2$ phase.

Introduction

The equilibrium and reversible transition from incomplete to complete wetting of grain boundaries (GBs) by the liquid phase (melt) has been experimentally observed in a number of systems like Zn–Sn, Ag–Pb, Al–Cd, Al–In, Al–Pb, W–Ni, W–Cu, W–Fe, Mo–Ni, Mo–Cu, Mo–Fe, Cu–In, Al–Sn [1–6]. The formation of continuous layers of a liquid phase between solid grains is broadly used, particularly in welding, soldering and liquid-phase sintering. Recently, this has been observed in the Zn–Al alloys that similar GB wetting transition can proceed even in case when a second phase wetting GBs is solid [7]. There are good reasons to expect that the complete wetting of GBs by a second solid phase can be observed in many technologically important systems. Especially "suspicious" are the alloys where the complete GB wetting by a melt was already observed, like for example the Al–Mg alloys [8]. The Al–Mg system forms a base of the important class of Al alloys. The eventual formation of equilibrium GB layers of a rather brittle Al$_3$Mg$_2$ phase can drastically influence the mechanical properties of the Al–Mg alloys. Therefore, the search for the conditions where the Al/Al GBs could be completely wetted by the second solid phase Al$_3$Mg$_2$ is very important.

Experimental

The Al–Mg alloys with 10, 15, 18 and 25 wt% Mg (Fig. 1) were prepared from the high-purity 5N Al and 4N5 Mg by a vacuum induction melting in a form of cylindrical ingots. The 2 mm thick slices were cut from the ⌀ 20 mm cylindrical Al–Mg ingots, each slice was cut into four segments, and each sample was sealed into evacuated silica ampoule with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Samples were annealed at temperatures between 210 and 440 °C (see experimental points in the Al–Mg phase diagram, Fig. 1) during long time (between 4000 h at 210 °C and 600 h at 440 °C), 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

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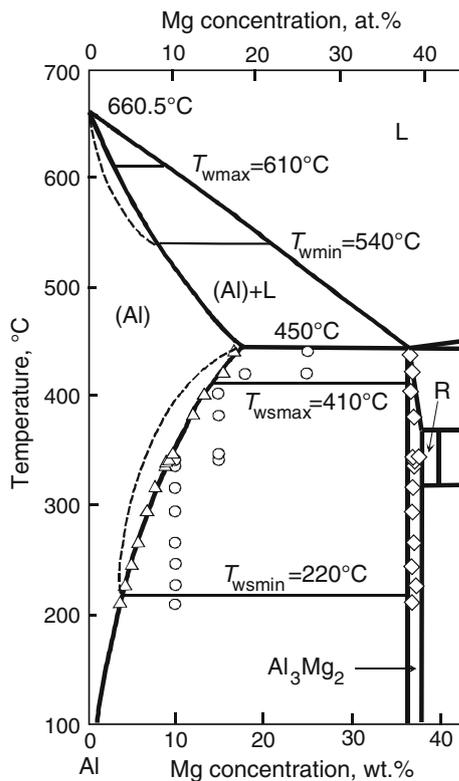
Fig. 1 Part of the Al–Mg phase diagram. *Thick lines* denote the bulk phase transitions and are taken from Ref. [9]. *Thin horizontal lines* are the tie-lines of GB wetting phase transitions. T_{wmax} and T_{wmin} for the GB wetting by a liquid phase are taken from Ref. [8]. T_{wsmax} and T_{wsmin} for the GB wetting by a second solid phase Al_3Mg_2 were determined in the present work. *Circles* denote the points where the wetting annealings were performed. *Triangles* denote the measured concentration in the (Al) solid solution. *Diamonds* denote the measured concentration in the Al_3Mg_2 solid phase. *Dotted lines* denote the hypothetical GB solidus and solvus

step, for the metallographic study. After etching, samples were investigated by means of the light microscopy and scanning electron microscopy (SEM). SEM investigations were carried out in a Tescan Vega TS5130 MM microscope equipped by the LINK energy-dispersive spectrometer produced by Oxford Instruments. Using the same equipment, the composition of various structural elements in the annealed and quenched samples was controlled with the aid of electron probe microanalysis. 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 Al_3Mg_2 had covered the whole GB; if such a layer appeared to be interrupted, the GB was regarded as a partially wetted. At least 100 GBs were analysed at each temperature. Typical micrographs obtained by SEM are shown in Fig. 2.
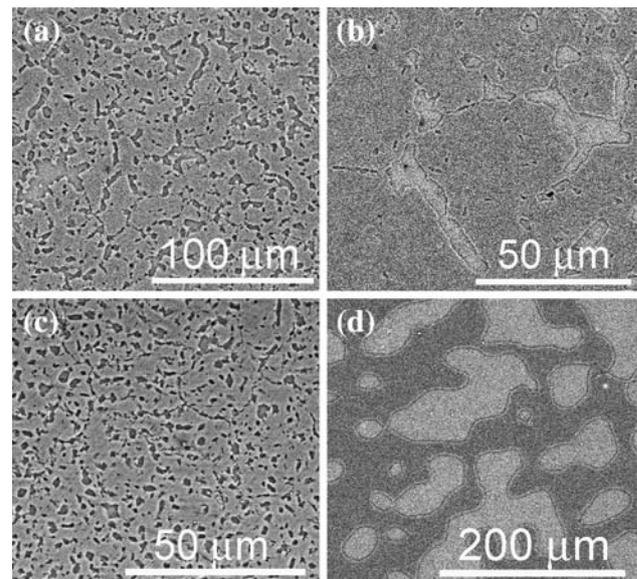

Fig. 2 SEM micrographs of Al–Mg alloys: **a** Al–10 wt% Mg alloy annealed at 210 °C, 4000 h; **b** Al–10 wt% Mg alloy annealed at 225 °C, 3600 h; **c** Al–10 wt% Mg alloy annealed at 335 °C, 2180 h; **d** Al–18 wt% Mg alloy annealed at 420 °C, 600 h. The Al-based solid solution grains appear *light grey*, the Al_3Mg_2 phase appears *dark grey* in all micrographs

Results and discussion

SEM micrograph of the Al–10 wt% Mg alloy annealed at 210 °C, 4000 h is shown in Fig. 2a. The particles of the Al_3Mg_2 phase (appears dark grey) form chains along Al/Al GBs. The grains of the Al-based solid solution appear light grey. It has to be underlined that the Al/Al_3Mg_2 interphase boundaries (IBs) are not smooth (like for example the Al/Zn interphase boundaries in the Al–Zn alloys are [7, 26, 27]). Most probably it is due to the strong anisotropy of the interfacial energy of Al/Al_3Mg_2 IBs. No Al/Al GBs completely wetted by the layers of the Al_3Mg_2 phase are visible. The contact angles between Al_3Mg_2 particles and Al/Al GBs are small, but not zero. The microstructure of the Al–10 wt% Mg alloy annealed at 225 °C, 3600 h is shown in Fig. 2b. First Al/Al GBs completely wetted by the continuous layers of the Al_3Mg_2 phase appear. Therefore, the temperature of the beginning of GB wetting transition is T_{wsmin} = 220 °C. With increasing temperature the portion of the Al/Al GBs completely wetted by the Al_3Mg_2 phase increases (see for example the micrograph of the Al–10 wt% Mg alloy annealed at 335 °C, 2180 h, Fig. 2c). Unfortunately, the Al/Al_3Mg_2 IBs are not smooth. It makes complicated the calculation of the portion of completely wetted GBs. Therefore, in order to distinguish between completely and incompletely wetted GBs we used the criterion from the Cahn's work [12]: "If the minor phase wets GBs, the major phase is distributed as droplets in the

minor phase". Above the maximal temperature of the GB wetting transition $T_{wsmax} = 410\,°C$ all Al/Al GBs are completely wetted by the Al_3Mg_2 phase and separated from each other by the continuous Al_3Mg_2 layers (see as example the micrograph of the Al–18 wt% Mg alloy annealed at 420 °C, 600 h, Fig. 2d). It is visible in Fig. 2d that the Al/Al_3Mg_2 IBs remain faceted at 420 °C, though they are slightly smoother than at lower temperatures. The thickness of the Al_3Mg_2 wetting layers depends on the amount of phase. Generally, it increases with increasing Mg content in the alloys. Therefore, we used the Al–Mg alloys with various Mg content in order to keep minimal the amount of Al_3Mg_2 phase at each annealing temperature (see Fig. 1) in order to distinguish the complete and incomplete GB wetting. Our goal was to prevent as long as possible the merging of Al_3Mg_2 particles into a continuous layer. The fraction of wetted GBs in the Al–Mg poly-crystals is shown as a function of the temperature in Fig. 3. Different symbols correspond to the different compositions of studied Al–Mg alloys. Between $T_{wsmin} = 220\,°C$ and $T_{wsmax} = 410\,°C$ the fraction of the wetted GBs gradually increases with increasing temperature from 0 to 100%.

Thin equilibrium GB or surface films were first considered by Cahn [10] and Ebner and Saam [11]. They proposed the idea that the transition from incomplete to complete surface wetting is a phase transformation. Cahn also analysed the case when wetting phase is solid [12]. Later the idea of wetting transformations was successfully applied for GBs, also old data on GB wetting were reconsidered from this point of view [3–6]. The phenomenon of the transition from incomplete to complete wetting is more general than the wetting under the consolute point
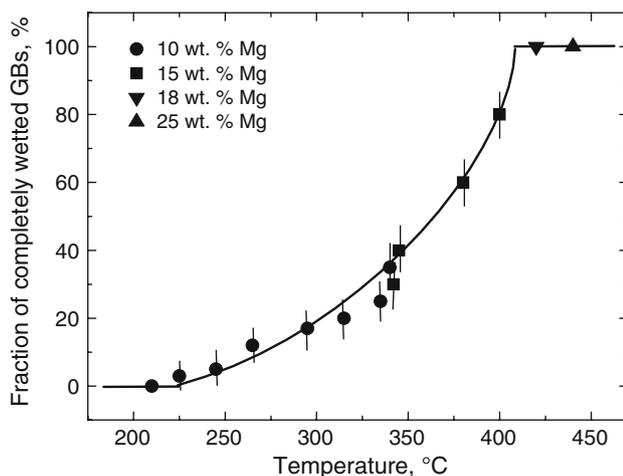
Fig. 3 Temperature dependence for the fraction of Al/Al GBs completely wetted by the Al_3Mg_2 phase. Different symbols correspond to the different compositions of studied Al–Mg alloys: *circles* 10 wt% Mg, *squares* 15 wt% Mg, *inverted triangle* 18 wt% Mg, *upright triangle* 25 wt% Mg

originally proposed by Cahn [10, 12] and analysed further in numerous works [13, 14]. The modified Cahn's model was developed based on the numerous experimental results [15]. The transition from incomplete to complete wetting occurs in all systems where the temperature dependences of interface energies intersect [15]. In particular GB wetting phase transformation proceeds at the temperature T_w where GB energy σ_{GB} becomes equal to the energy $2\sigma_{SL}$ of two solid/liquid interfaces. Above T_w GB is substituted by a layer of the melt. The tie-line of the GB wetting phase transition appears in the two-phase area of a bulk phase diagram. For example, in the (Al) + L two-phase region of the Al–Mg system the GB transformation for the Al/Al GBs wetting by Mg-containing melt occurs [8]. The completely wetted GBs in the Al–Mg polycrystals do not exist below $T_{wmin} = 540\,°C$. T_{wmin} is the wetting temperature for a GB with maximal energy σ_{GBmax}. Above $T_{wmax} = 610\,°C$ all high-angle GBs in (Al) are completely wetted by the melt [8]. T_{wmax} is the wetting temperature for a GB with minimal energy σ_{GBmin}. Between T_{wmin} and T_{wmax} the wetting tie-lines for GBs with intermediate $\sigma_{GBmax} > \sigma_{GB} > \sigma_{GBmin}$ are positioned in the (Al) + L area (Fig. 1). GBs can also be "wetted" by a second solid phase, as we can see in the present work, too [12, 14]. The reversible transition from incomplete to complete solid phase wetting was observed for the first time in the Zn–Al system [7].

Following the Cahn's generic phase diagram, the more sophisticated theories of GB phases, segregation and wetting layers were developed [13–15]. Thin films of interfacial phases were observed in GBs in metals (works of Luo and coworkers [16, 36, 37]), in oxides ([17], see also concept of complexions by Harmer et al. [18–22]), in interphase boundaries (Kaplan and coworkers [23–25]). According to those developments the GB wetting tie-lines continue as prewetting (or GB solidus or solvus) lines in the one-phase (Al) area. Such GB solidus and/or solvus lines should exist also in the Al–Mg system. Just one GB solidus line for T_{wmin} and one GB solvus line for T_{wsmin} is shown for simplicity in Fig. 1. The experimental evidence for the existence of a GB liquid-like phase between GB solidus line and bulk solidus line was obtained by transmission electron microcopy (TEM) [26] and differential scanning calorimetry (DSC) for the Al–Zn alloys [27]. 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 stabilise 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 being the additional energy needed to produce the thermodynamically 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 comes about from an assumption that the size of the system is infinite. Moreover, 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 [28–31], Al–Zn [26, 27], Fe–Si–Zn [32–35] and W–Ni alloys [36, 37]. GB liquid-like phase drastically influences also the GB segregation [29], GB mobility [38], GB energy and electrical resistivity [39, 40]. The direct HREM evidence for thin GB films and triple junction "pockets" has been recently obtained in metallic W–Ni [36, 37] and Al–Zn [26] alloys.

The observed splitting of the solidus line into conventional bulk solidus and novel GB solidus permitted explaining the mysterious phenomenon of the high strain-rate superplasticity (HSRS) observed in several nano-structured Al ternary alloys and nanostructured Al metal-matrix composites, containing Mg and Zn [41–47]. The maximal elongation-to-failure increased drastically from 200–300% upto 2000–2500% in a very narrow temperature interval of about 10 °C just below the respective solidus temperature. Very long time no satisfactory explanation was offered for this phenomenon. In Refs. [26, 27], we explained the extremely high plasticity in the Al-based alloys by the presence of thin liquid-like layers of the thermodynamically stable GB phase close to the bulk solidus line. Is it possible to explain the high plasticity in the Al-based alloys at room temperature using similar wetting phenomena?

In summary, the GB wetting phase transition proceeds in the Al-rich alloys in the Al–Mg system. The new GB tie-lines appear in the Al–Mg phase diagram (Fig. 1). Below the tie-line at $T_{wsmin} = 220$ °C no Al/Al GBs wetted by the second solid phase Al_3Mg_2 are present in the polycrystals. Above the tie-line at $T_{wsmax} = 410$ °C all Al/Al GBs are wetted by the second solid phase and separated from each other by the continuous Al_3Mg_2 layers. This phenomenon can be used for the tailoring of mechanical properties of the Mg-doped Al alloys. The novel information on GB wetting tie-lines will be used for the search of thin GB phases above T_{wsmin} close to the bulk solvus line in the Al–Mg system.

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