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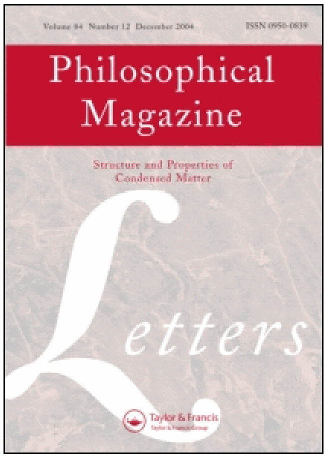

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Grain boundary phase observed in Al–5 at.% Zn alloy by using HREM

B. B. STRAUMAL†‡, A. A. MAZILKIN*†‡, O. A. KOGTENKOVA†,
S. G. PROTASOVA†‡ and B. BARETZKY‡

†Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka,
Moscow district, Russia
‡Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3,
70569 Stuttgart, Germany

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The nature and behaviour of grain boundary (GB) phases is very important since they can control strength, plasticity, resistivity, grain growth, corrosion resistance, etc, especially in nanocrystalline materials. For nanocrystalline Al-based light alloys, extremely high plasticity has been observed in restricted temperature and concentration intervals close to the solidus line. This phenomenon is not fully understood. It can be explained by formation of GB phases not included in the bulk phase diagram. Therefore, the structure of GB phases, as well as thermodynamic conditions for their existence, has to be carefully studied. In this work the structure and composition of GBs and GB triple junctions in Al–5 at.% Zn polycrystals annealed in the temperature region above and below the bulk solidus line were studied by high-resolution electron microscopy and analytical transmission electron microscopy. Evidence has been obtained that a thin layer of a liquid-like phase exists in GBs and GB triple junctions slightly below the bulk solidus line.

1. Introduction

The Al–Zn system is the basis of high-strength Al alloys of the 7xxx series [1]. As nanograined materials, several 7xxx alloys possess extremely high elongation-to-failure ratios (up to 1250%) [2, 3]. This phenomenon was observed only in a very restricted temperature and concentration interval, i.e. slightly below the solidus line and below about 12 wt% Zn and 5 wt% Mg. The physical reasons why the superplasticity disappears with slight changes of temperature and concentration have remained unexplained for more than ten years. The high plasticity (as well as many other phenomena) may be explained by the appearance of equilibrium liquid and/or liquid-like grain boundary (GB) phases [4].

If the alloys are *above the solidus line*, in the (Al) + L area of the bulk phase diagram (marked also as 1, 2 and 2′ in figure 1), the melt can wet grain boundaries.

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*Corresponding author. Email: mazilkin@issp.ac.ru

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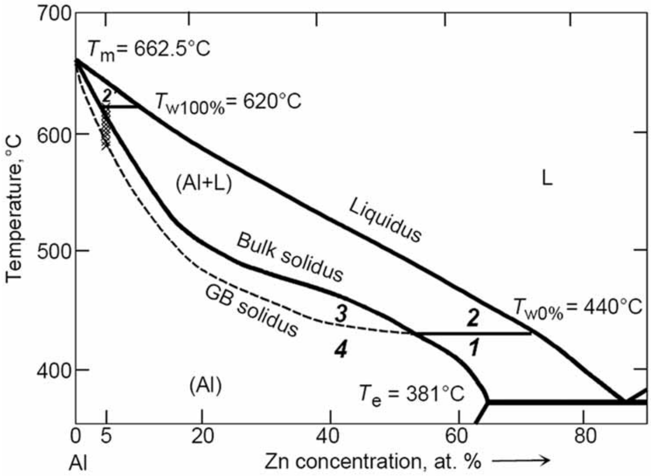

Figure 1. A part of the Al–Zn phase diagram. Thick solid lines denote bulk phase equilibria [10]. (Al) is the single-phase region where only the Al-based solid solution is in equilibrium in the bulk. L is the single-phase region of liquid phase (melt). In the (Al) + L two-phase region, Al-based solid solution and melt coexist. Thin solid lines in the (Al) + L region are the tie-lines of the GB wetting phase transformation obtained experimentally by Straumal *et al.* [4]. The thin dashed line denotes the hypothetic GB solidus line. Between bulk solidus and GB solidus, GBs contain a thin equilibrium layer of a liquid-like GB phase. Crosses denote the experimental points in this work.

Zn concentration in the melt is governed by the liquidus line. Melt wets a GB if the GB energy, σ_{GB}, is higher than the energy of two solid–liquid interfaces, $2\sigma_{\mathrm{SL}}$. In order to minimize the total energy of the system, a GB has to be substituted by the layer of the liquid phase (melt) and two solid–liquid interfaces. GB wetting has been observed in the Al–Zn system [4]. The condition of full wetting, $\sigma_{\mathrm{GB}} > 2\sigma_{\mathrm{SL}}$, is fulfilled above certain temperature, T_{w}, called GB wetting transition temperature. At this temperature T_{w} the GB wetting tie-line exists in the two-phase area (Al) + L of the bulk phase diagram. The wetting transition temperature, T_{w}, depends on GB energy, σ_{GB}. High-angle GBs in a polycrystal have different energies in an interval between σ_{GBmin} and σ_{GBmax}, depending on their misorientation and inclination angles. If σ_{GB} is high, T_{w} is low and visa versa. The minimal temperature $T_{\mathrm{w0\%}}$ corresponds to the maximal GB energy σ_{GBmax}. Below $T_{\mathrm{w0\%}}$ no wetted GBs (0%) are present in the polycrystal (area 1 in figure 1). The maximal temperature $T_{\mathrm{w100\%}}$ corresponds to the minimal GB energy σ_{GBmin}. Above $T_{\mathrm{w100\%}}$ all high-angle GBs in the polycrystal are wetted (area 2′ in figure 1). Temperatures $T_{\mathrm{w0\%}} = 440°\mathrm{C}$ and $T_{\mathrm{w100\%}} = 620°\mathrm{C}$ were determined experimentally [4]. Between $T_{\mathrm{w0\%}}$ and $T_{\mathrm{w100\%}}$ (area 2 in figure 1) the portion of wetted GBs continuously increases in the polycrystal with increasing temperature. In the area 2′ above $T_{\mathrm{w100\%}}$ the viscous flow of a polycrystal becomes possible even if the amount of melt is low [2, 3]. Melt lubricates the grains and they easily slide one over the other. Below $T_{\mathrm{w0\%}}$ (the area 1) melt is enclosed by the surrounding solid phase, and strength of a polycrystal does not substantially decrease if the solidus line is crossed.

If the alloys are *slightly below the solidus line*, i.e. in the (Al) area of the bulk phase diagram (marked as 3 in figure 1), a thin layer of the liquid-like phase can be formed in GBs. In this area the liquid phase can be formed in the GBs even though it is metastable in the bulk [5]. The additional energy ΔG needed for the formation of this phase can be compensated if the condition of full wetting, $\sigma_{\mathrm{GB}} > 2\sigma_{\mathrm{SL}}$, is fulfilled and the energy gain $\sigma_{\mathrm{GB}} - 2\sigma_{\mathrm{SL}}$ is higher than the energy loss ΔG. In this case a thin layer of a liquid-like phase may appear in the GB. Zn concentration in the liquid-like phase is also given by the liquidus line at the respective annealing temperature.

If the alloys are *deeply below the solidus line* in the (Al) area of the bulk phase diagram (area 4 in figure 1), ΔG further increases and $\sigma_{\mathrm{GB}} - 2\sigma_{\mathrm{SL}}$ cannot compensate ΔG any more. The liquid-like GB layer disappears below GB solidus line (dashed line in figure 1). GB solidus begins at the melting point T_{m} of the pure component (in case of Al $T_{\mathrm{m}} = 662.5°\mathrm{C}$). GB solidus finishes at the intersection between GB wetting tie-line and bulk solidus. Each GB with its σ_{GB} has its own wetting tie-line and respective GB solidus. Only one (hypothetical) GB solidus line corresponding to maximal GB energy σ_{GBmax} and minimal $T_{\mathrm{w0\%}}$ is drawn in figure 1.

The thin layer of an equilibrium liquid-like GB phase between bulk and GB solidus line can explain the phenomenon of unusually high plasticity of 7xxx alloys. High plasticity exists only in a narrow temperature interval (about 10°C) below bulk solidus and at low contents of alloying elements. It can be easily explained by GB solidus line based on our model of GB phases [5]. It follows from previous investigations that the GB wetting transitions occur in the (Al) + L area of the Al–Zn bulk phase diagram [4]. The necessary condition for the existence of GB solidus is fulfilled.

Do the liquid-like layers exist in GBs in the Al–Zn system in a measurable temperature interval? Is it possible to observe liquid-like GB layers directly *in situ* or modified after quenching? The goal of this work is to answer these questions.

2. Experimental procedure

An Al–5 at.% Zn alloy was prepared of high purity components (5N5 Al and 5N Zn) by vacuum induction melting. This concentration was selected because in this alloy almost all GBs are wetted above the bulk solidus line. This facilitates the observation of the GB phases by transmission electron microscopy (TEM). Slices (2 mm thick) were cut from the 10 mm diameter cylindrical ingot and sealed into evacuated silica ampoules with a residual pressure of approximately 4×10^{-4} Pa at room temperature. Samples were annealed for 0.5 h at temperatures between 585 and 630°C, in steps of 5°C (crosses in figure 1), and then quenched in water. The accuracy of the annealing temperature was ±1°C. After quenching, samples for TEM investigations were cut from the specimens. The residual material was 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 (LM) and scanning electron microscopy (SEM). High-resolution transmission electron microscopy (HREM) investigations were carried out in a JEM-4000FX microscope at an accelerating voltage of 400 kV. The concentration of Zn in TEM samples was measured by means of electron energy loss spectroscopy (EELS). The spatial resolution of the EELS analysis was about 5 nm. For EELS experiments, a dedicated scanning transmission electron microscope VG HB 501 was used. The microscope was operated at 200 keV. It is equipped with a cold field-emission gun and an electron energy-loss spectrometer (Gatan UHV Enfina 766). A power law function was used to remove the background and to quantify the composition.

3. Experimental results and discussion

The observed phenomena are split into three groups according to the annealing temperature.

(a) For samples annealed *above the bulk solidus* (620°C) and quenched to room temperature, the metallographic study with SEM and LM reveals that all GBs are wetted by the melt. Previous investigations of GB wetting in Al-based alloys like Al–Zn [4], Al–Mg [6] and Al–Sn [7] demonstrate that the melt layer wetting the GBs at the annealing temperature easily undercools following water quenching. As a result, a primary (Al) solid solution does not crystallize from the melt by rapid cooling, and the previously liquid GB layer solidifies as a fine eutectic mixture of the (Al) grains and the grains of respective second phase (Zn, Al_3Mg_2 or Sn). This (originally melted) GB layer appears grey in LM micrographs. Its morphology represents the distribution of the melt between solid grains during the annealing. The mean composition of this GB layer is equal to the liquidus concentration at the annealing temperature (about 11 at.% Zn in this work). TEM reveals the fine structure of the GBs and GB triple junctions, which were liquid during the annealing above bulk solidus (figure 2a). After quenching they split into a periodic sequence of elongated Zn-rich particles and (Al) regions along the GB between grains 1 and 2 (figure 2a). The Zn particles appear dark in the bright field TEM micrograph in contrast to Al-rich regions, which appear bright. Such contrast is due to the atomic mass difference and indicates that the atoms in the (Zn) regions are heavier than in surrounding (Al). The selected area electron diffraction pattern and corresponding scheme are shown in figures 2b and c. The most intense spots belong to the two crystallographic zones of (Al) lattice (110) and (114). The third set of reflections (small spots) belongs to a single Zn-rich particle. Some of these reflections are marked by arrows and indexed. The dark regions have a hexagonal close-packed (hcp) structure with lattice parameters $a = 0.266$ nm and $c = 0.497$ nm and with ratio $c/a = 1.87$ slightly different from that of pure Zn. The concentration of Al in the particle was estimated using the lattice parameter concentration dependence in (Zn) solid solution [8]. The concentration was determined to be about 2 at.% Al. Thus, the undercooled liquid phase wetted the GBs during annealing and decomposed eutectically

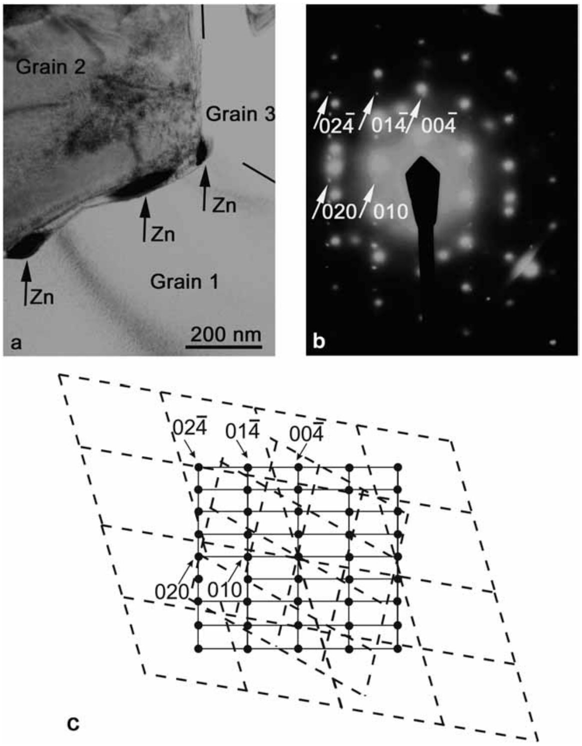

Figure 2. (a) Bright field TEM micrograph of a (Al)/(Al) GBs in an Al–5 at.% Zn polycrystal annealed at 620°C. Dark particles of almost pure Zn are observed in the GB and in the junction of three adjacent (Al) grains. (Al)/(Al) GBs are marked by short black lines. (b) Selected area electron diffraction pattern. The spots of the dark particle (shown by arrows) are visible together with spots of the (Al) matrix. The analysis reveals that the structure of dark particles corresponds to that of Zn with hcp structure with lattice parameters $a = 0.266$ nm and $c = 0.497$ nm and with ratio $c/a = 1.87$. (c) Scheme of the electron diffraction pattern for Zn particles (rectangular net with filled circles) and (Al) grains (nets of dashed lines).

at the water quenching as observed by Straumal *et al.* [4]. Zn particles were observed only in samples annealed above bulk solidus.

(b) Samples annealed *slightly below the bulk solidus* (between 600 and 615°C) do not contain a Zn phase. This is because no bulk melt (able to solidify as almost pure Zn) was present in the samples during annealing. However, in several GB triple junctions the "pockets" of another Zn-enriched phase were observed between 600 and 615°C (figure 3). The HREM micrograph (figure 3a) and selected area electron diffraction with corresponding scheme (figures 3b and c) of the samples annealed at 605°C show "pockets" that contain hcp phase β_m with the lattice parameters $a = 0.274$ nm and $c = 0.443$ nm. The spots with high intensity belong to the (Al) matrix with (110) projection plane. The smaller spots belong to the GB phase, some of which are marked by arrows and indexed. The c/a ratio for this phase is 1.62 which is quite close to that for an ideal hcp structure ($c/a = 1.633$).

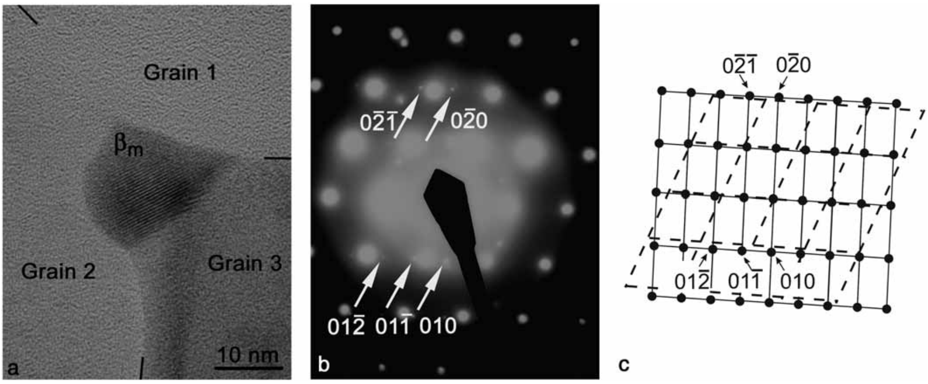

Figure 3. (a) HREM micrograph of the (Al) GB triple junction in an Al–5 at.% Zn polycrystal after annealing at 605°C. Al GBs are marked by short black lines. The GB triple junction contains the particle of a phase with 24 at.% Zn, according to the EELS spectra. (b) Electron diffraction pattern with spots of (Al) phase and metastable β_m-phase. Reflections corresponding to the metastable hcp β_m-phase with $a = 0.274$ nm, $c = 0.443$ nm and $c/a = 1.62$ are shown by arrows and indexed. (c) Scheme of the electron diffraction pattern for β_m-phase (rectangular net with filled circles) and (Al) grain (net of dashed lines).

According to the EELS data Zn content in the "pockets" is about 24 at.%, i.e. rather close to the liquidus concentration at 605°C. This Zn concentration indicates that the observed phase was formed during cooling from a liquid-like GB phase. It does not belong to the metastable phases that usually appear in Al-based alloys by cooling. Previously, a phase with similar parameters has only been observed in thin Al–5 at.% Zn samples annealed at 120°C for 4 days [9]. It was called β_m-phase and found to be metastable. The β_m-phase in GB triple junctions was found only in those samples annealed between 600 and 615°C, i.e. below the bulk solidus line and above the GB solidus line. The intensity of β_m spots in the electron diffraction patterns, measured for samples annealed between 600 and 615°C, is much higher than would be expected for polycrystals, where the β_m-phase exists only in triple junctions. An increased Zn content in GBs (~10 at.%) and depleted (Al) solid solution in the neighbouring grains (~4 at%) measured by EELS can serve as an indirect confirmation of this statement. An estimation of a possible thickness of the β_m-phase along the GB gives a value of about two monolayers. That is more than an ordinary segregation. Therefore, our data does not exclude the presence of thin GB layers of a β_m-phase as well.

(c) Below 600°C (i.e. *deeply below the bulk solidus*) all observed GBs and GB triple junctions were "clean". They contained neither almost pure Zn [as in case (a)] nor Zn-rich β_m-phase [as in case (b)]. Consequently, the GBs contained neither bulk liquid phase nor thin GB liquid-like phase during annealing.

From these results we can determine the GB solidus temperature for the Al–5 at.% Zn alloys; it is between 600 and 605°C. This means that the temperature interval for the existence of GB liquid-like phase between the bulk solidus and GB solidus is broad enough (about 10–15°C) for the measurements. High plasticity has been observed in the Al–Zn–Mg alloys in a similar temperature interval of 10–15°C below bulk solidus [2, 3]. This is one more indication that the high plasticity in the nanograined 7xxx alloys is caused by the formation of a liquid-like GB phase.

We were only able to detect the β_m-phase in triple junctions because thin layers of the GB phases can only be observed in HREM if the grains on both sides of a GB are in a transmitting position. Unfortunately, we did not find such grain couples in our (rather coarse-grained) samples. It is possible that the GB liquid-like phase remained in the triple junctions and disappeared in GBs by cooling: This may be because the liquid-like "pockets" in triple junctions are thicker than GB layers. However, there is a much more complex explanation as well. Since a melt wets GBs in an alloy, it may wet also a triple junction. In this case a triangular prism filled by a liquid phase substitutes a triple junction. A star of three GBs is substituted by a triangle of solid/liquid interphase boundaries. In the simplest case of an ideal symmetrical triple junction with equal σ_{GB} values for all three GBs the wetting condition is $\sigma_{GB} \geq \sqrt{3}\sigma_{SL}$. This criterion is weaker than similar one for GB wetting $\sigma_{GB} \geq 2\sigma_{SL}$. Both σ_{GB} and σ_{SL} decrease with increasing temperature because of entropy. If the temperature dependences of $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ intersect below a melting (liquidus) temperature T_m, a GB wetting phase transformation takes place at T_w. However, the temperature dependence $\sqrt{3}\sigma_{SL}(T)$ lies below the dependence $2\sigma_{SL}(T)$ and intersects with $\sigma_{GB}(T)$ at a temperature T_{wTJ} which is below T_w. Therefore, in the temperature interval between T_{wTJ} and T_w the completely wetted GBs are absent in a polycrystal, but completely wetted triple junctions may be present.

In *ex situ* experiments one must deal with a state obtained after quenching of a sample. Thin GB layers can easily disappear during the cooling due to the diffusion processes. The Zn diffusivity in Al is rather high even at room temperature. This is shown by the Guinier–Preston II zones observed in the bulk of all studied samples. When the supersaturated Zn-rich Al-based solid solution dissolves, the particles of an equilibrium β(Zn)-phase do not appear immediately in the bulk: the pre-precipitates and metastable phases with increasing Zn content appear one after another. The usual sequence is: Guinier–Preston (GP) I zones (spherical pre-precipitates coherent with Al-matrix) → GP II zones (semi-coherent ellipsoidal pre-precipitates) → rhombohedral distorted fcc α'_R-phase → distorted fcc α'_m-phase → β(Zn) equilibrium phase. The metastable β_m-phase does not belong to this usual sequence. It was observed only once in rather unusual conditions [9]. There is indirect evidence that in our case the β_m-phase formed from the unusual starting state, i.e. liquid-like GB layers. In other metallic alloys the liquid-like GB layers reflect themselves in the multilayer GB segregation [11, 12], high diffusivity [13–16] and high migration ability [17].

4. Summary

In conclusion, the data obtained unambiguously show that a GB phase really exists in the Al–Zn system. It has been expressed by adding a GB solidus line into the Al–Zn phase diagram. This line appears in the single-phase (Al) region due to the GB wetting transformation in the two-phase (Al) + L region (figure 1). Between the bulk solidus and GB solidus lines a liquid-like layer exists in GBs and GB triple junctions with a Zn content equal to the liquidus concentration. The liquid-like GB phase transforms during quenching into the metastable Zn-rich β_m-phase with almost ideal hcp lattice and 24 at.% Zn. The β_m-phase does not appear in samples annealed above the bulk solidus or below the GB solidus. This is first unambiguous proof that the liquid-like GB phase really exists in the Al-based alloys below the bulk solidus line.

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