

Wetting and premelting of triple junctions and grain boundaries in the Al–Zn alloys

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Received 22 March 2007; received in revised form 31 August 2007; accepted 14 September 2007

Abstract

Phase transitions in grain boundaries (GBs) and GB triple junctions (TJs) can change drastically the properties of polycrystals. The GB and TJ wetting phase transition can occur in the two-phase area of the bulk phase diagram where the liquid and solid phases are in equilibrium. The GB and TJ wetting tie-lines can continue in one-phase area of the bulk phase diagram as a GB or TJ solidus line. This line represents the GB or TJ premelting phase transition. The structure and composition of grain boundaries and GB triple junctions were studied by high-resolution electron microscopy and analytical transmission electron microscopy in the Al–5 at.% Zn polycrystals and by differential scanning calorimetry (DSC) in the Al–7.5 at.% Zn polycrystals. Between bulk solidus and GB or TJ solidus the metastable Zn-rich β_m -phase was observed in the GB triple junctions of quenched samples. This phase appears neither in the samples annealed above the bulk solidus nor in those annealed below the GB solidus. Zn-content in this β_m -phase corresponds to that of bulk liquidus. This is a structural indication that if the melt wets the GBs or TJs, the GB (or TJ) solidus line appears in the bulk phase diagram, and the liquid-like phase exists in GBs and TJs between bulk solidus and GB (or TJ) solidus lines. The structural observation of this phase is also supported by our data obtained by means of DSC.

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Keywords: Grain boundaries; Triple junctions; Phase transitions; Al–Zn alloy

1. Introduction

Wetting of grain boundaries (GBs) and GB triple junctions (TJs) in metallic alloys can either improve or deteriorate the properties of polycrystalline materials. The melt completely wets a GB (Fig. 1a and b) if the energy of two solid–liquid interfaces $2\sigma_{SL}$ is lower than the GB energy σ_{GB} . The GB wetting transition proceeds if the temperature dependences $2\sigma_{SL}(T)$ and $\sigma_{GB}(T)$ intersect at T_{wGB} (Fig. 1e). If a melt wets GBs in an alloy, it may wet also GB triple junctions. In this case a trigonal prism filled by a liquid phase (Fig. 1d) substitutes a GB triple junction (Fig. 1c). A star of three GBs (Fig. 1c) is substituted by a triangle of solid–liquid interphase boundaries (Fig. 1d). In the simplest case of an ideal symmetrical triple junction with equal σ_{GB} val-

ues 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 (Fig. 1e). 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_{wGB} . 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_{wGB} . Therefore, in the temperature interval between T_{wTJ} and T_{wGB} the completely wetted GBs are absent in a polycrystal, but completely wetted triple junctions may be present.

If the alloys are in the (Al) + L area of the bulk phase diagram, i.e. above the solidus line (marked in Fig. 2 by points 1, 2 and 2'), the melt wets grain boundaries. A melt wets a GB only if the GB energy, σ_{GB} , is higher than the energy of two solid–liquid interfaces, $2\sigma_{SL}$. In this case a GB is substituted by the layer of the liquid phase (melt) and two solid–liquid interfaces. GB wetting has been observed recently

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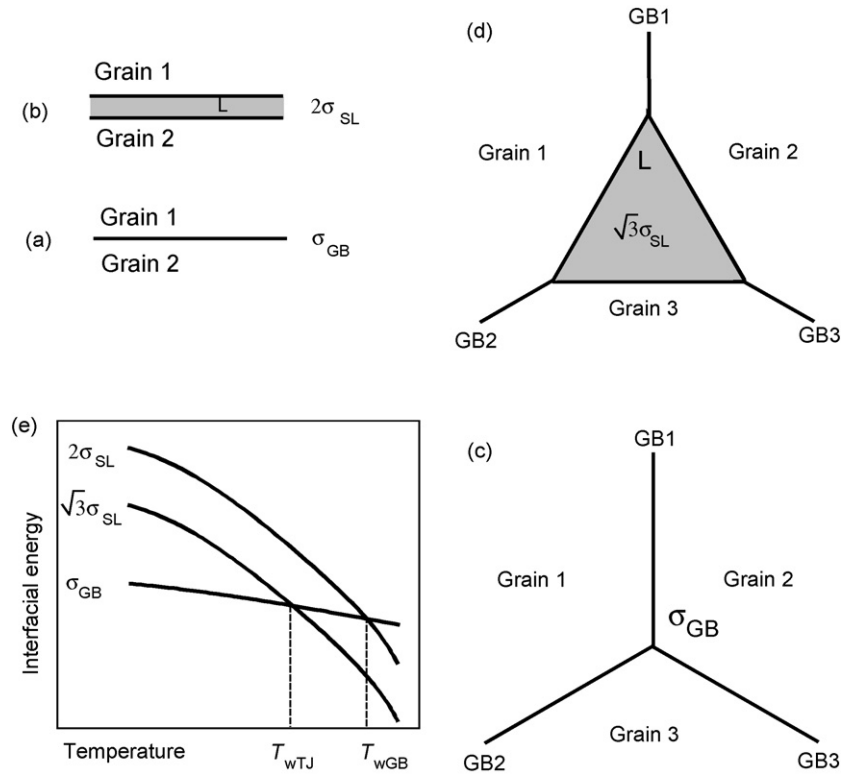


Fig. 1. (a) Pure GB with energy σ_{GB} (below T_{wGB}). (b) Completely wetted GB substituted by the melt L and two solid–liquid interfaces with energy $2\sigma_{SL}$ (above T_{wGB}). (c) Pure GB triple junction with energies σ_{GB} (below T_{wTJ}). (d) Completely wetted GB triple junction. The GB “star” is substituted by the melt L and triangle of solid–liquid interfaces with energy $\sqrt{3}\sigma_{SL}$. (e) Scheme of the temperature dependences $2\sigma_{SL}(T)$, $\sqrt{3}\sigma_{SL}(T)$ and $\sigma_{GB}(T)$ showing the appearance of wetting phase transition temperatures T_{wGB} for GB and T_{wTJ} for TJs.

in Al–Zn system [1]. The condition of full wetting, $\sigma_{GB} > 2\sigma_{SL}$, is fulfilled above T_{wGB} . At this temperature, T_{wGB} the GB wetting tie-line exists in the two-phase area (Al)+L area of the bulk phase diagram. The wetting transition temperature,

T_{wGB} , depends on GB energy, σ_{GB} . If σ_{GB} is high, T_{wGB} is low and visa versa. The minimal temperature $T_{w0\%}$ corresponds to the maximal GB energy σ_{GBmax} . Below $T_{w0\%}$ no wetted GBs (0%) are present in the polycrystal (area 1 in Fig. 2). The maximal temperature $T_{w100\%}$ corresponds to the minimal GB energy σ_{GBmin} . Above $T_{w100\%}$ all high-angle GBs in the polycrystal are wetted (area 2' in Fig. 1). Temperatures $T_{w0\%} = 440^\circ\text{C}$ and $T_{w100\%} = 620^\circ\text{C}$ were determined experimentally [1]. Between $T_{w0\%}$ and $T_{w100\%}$ (area 2 in Fig. 1) the portion of wetted GBs in the polycrystal increases with increasing temperature. In the area 2' above $T_{w100\%}$ the viscous flow of a polycrystal becomes possible even if the amount of melt is low [2,3]. Therefore, at low Zn concentrations melt lubricates the grains and they easily slide one over the other. Below $T_{w0\%}$ (the area 1) melt is enclosed in the surrounding solid phase. Therefore, at high Zn concentrations the strength of a polycrystal decreases only slightly if the solidus line is crossed from below.

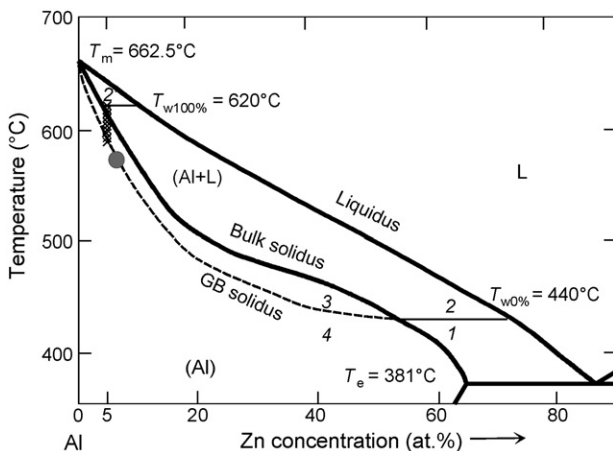


Fig. 2. A part of the Al–Zn phase diagram. Thick solid lines denote bulk phase equilibria [4]. (Al) is the single-phase region where only the Al-based solid solution is in equilibrium in the bulk. L is the single-phase region of liquid phase (melt). In the (Al) + L two-phase region Al-based solid solution and melt coexist. Thin solid lines in the (Al) + L region are the tie-lines of the GB wetting phase transformation experimentally obtained in Ref. [1]. The thin dashed line denotes the hypothetical GB solidus line. Between bulk solidus and GB solidus GBs contain a thin equilibrium layer of a liquid like-GB phase. Crosses and full circle denote the experimental points in this work.

If the alloys are slightly below the solidus line, i.e. in the (Al) area of the bulk phase diagram (marked as 3 in Fig. 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]. This is because the system needs the additional energy ΔG for the formation of a metastable liquid phase. This energy can be compensated if the condition of full wetting, $\sigma_{GB} > 2\sigma_{SL}$, is fulfilled and the energy gain $\sigma_{GB} - 2\sigma_{SL}$ 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 Fig. 2), ΔG further increases and $\sigma_{GB} - 2\sigma_{SL}$ cannot compensate ΔG any more. The liquid-like GB layer disappears below GB solidus line (dashed line in Fig. 2). GB solidus begins at the melting point T_m of the pure component (in case of Al $T_m = 662.5^\circ\text{C}$). 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 (hypothetic) GB solidus line corresponding to maximal GB energy σ_{GBmax} and minimal $T_{w0\%}$ is drawn in Fig. 2.

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 based on the Al–Zn system. Being nanograined, the 7xxx alloys possess very high elongation-to-failure ratios (up to 1250%) [2,3]. This phenomenon exists only in a narrow temperature interval, i.e. slightly below the solidus line. High superplasticity is also observable only below about 12 wt.% Zn and 5 wt.% Mg. This phenomenon remained unexplained for more than 10 years. However, 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 [1]. The necessary condition for the existence of GB solidus is fulfilled. The goal of this work is to clarify, whether liquid-like layers really exist in GBs and TJs in the Al–Zn system.

2. Experimental

The Al–5 at.% Zn and Al–7.5 at.% Zn alloys were prepared of high purity components (5N5 Al and 5N Zn) by vacuum induction melting. Slices (2 mm thick) were cut from a 10 mm diameter cylindrical Al–5 at.% Zn 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 K (crosses in Fig. 1), and then quenched in water. The accuracy of the annealing temperature was ± 1 K. After quenching, samples for transmission electron microscopy (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. As-cast disks of the Al–7.5 at.% Zn alloy obtained after grinding, sawing and chemical etching were subjected to high-pressure torsion (HPT) at room temperature under the pressure of 5 GPa in a Bridgman anvil type unit (5 torsions, duration of process about 300 s) [6]. All samples for the investigations were cut from the deformed disks at a distance of 5 mm from the sample centre. For this distance the shear strain is ~ 6 . These fine-grained samples [7] were studied with the aid of differential scanning calorimetry (DSC) using the TA Instruments calorimeters (models 910 and 1600) in the dry nitrogen atmosphere at the cooling and heating rates of 10 and 20 K/min.

3. Results and discussion

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

(a) Samples annealed above bulk solidus (620 °C) and quenched to room temperature: The metallographic study with SEM and LM reveals that all GBs were wetted by the melt. During quenching the liquid phase solidifies according to the phase diagram (Fig. 1). The last portions of a liquid phase decompose eutectically at $T_e = 381^\circ\text{C}$. After cooling, these areas consist of a very fine mixture of almost pure Zn and (Al–63 at.% Zn) phases (see eutectic line in Fig. 1). Such eutectic mixture is also visible in TEM samples (Fig. 3). The GBs and GB triple junctions were wetted by a layer of liquid phase during annealing. After quenching they split into a periodic sequence of elongated Zn-rich particles and (Al) regions. The Zn particles (Fig. 3) appear dark in the bright-field TEM image 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). Selected area electron diffraction pattern is shown in the insert. The most intense spots in the selected area electron diffraction pattern belong to the two crystallographic zones of (Al) lattice (1 1 0) and (1 1 4). 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 [7]. The concentration was determined to be about 2 at.% Al. This shows that the bulk melt phase wetted the GBs during annealing which gives the agreement with data [1]. Zn particles were observed only in samples annealed above bulk solidus.

(b) The HREM image (Fig. 4) and selected area electron diffraction 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 (1 1 0) projection plane. The smaller spots belong to the GB phase, some of them are marked by arrows and indexed. The c/a ratio for this phase is 1.62 which is quite close to that for ideal hexagonal close-packed structure

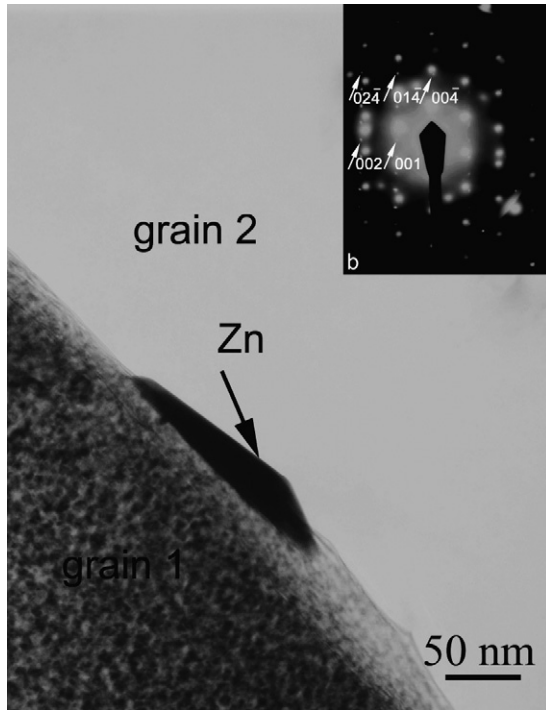


Fig. 3. Bright-field TEM image of a (Al)/(Al) GB in an Al-5 at.% Zn polycrystal annealed at 620 °C. Dark particles of almost pure Zn are observed in the GBs and in the TJs of (Al) grains. Selected area electron diffraction pattern is shown in the insert. The spots of the dark particle (shown by the arrow) are visible together with spots of the (Al) matrix. The analysis reveals that the structure of dark particle corresponds to that of Zn with hexagonal close-packed structure with lattice parameters $a = 0.266$ nm and $c = 0.497$ nm and with ratio $c/a = 1.87$.

($c/a = 1.633$). 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 [8]. 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 bulk solidus line and above 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. Therefore, our data does not exclude the presence of thin GB layers of a β_m -phase as well. An increased Zn content measured by EELS in GBs (~10 at.%) can serve as an indirect confirmation of this statement.

(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.

For 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 bulk solidus and GB solidus is broad enough (about 10–15 K) for the measurements. High plasticity has been observed in the Al-Zn-Mg alloys in a similar temperature interval of 10–15 K 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.

In the *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) →

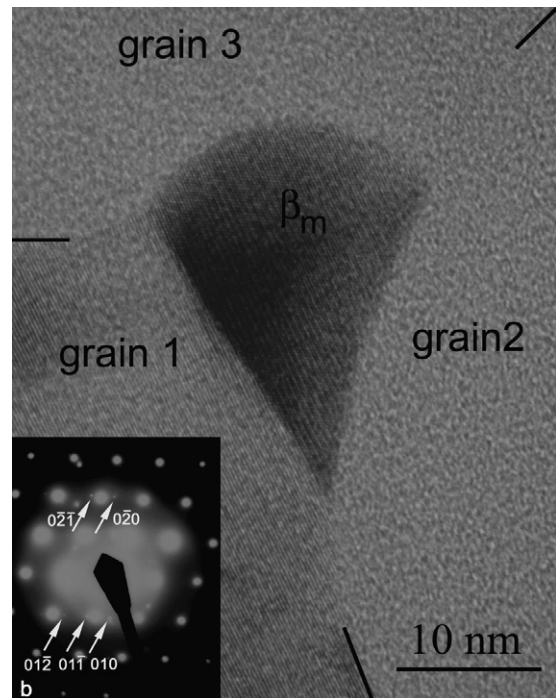


Fig. 4. HREM image of the (Al) GB triple junction in an Al-5 at.% Zn polycrystal after annealing at 605 °C. Al GBs are marked by short black lines. The GB triple junction contains the particle of a phase with 24 at.% Zn according to the EELS spectra. Electron diffraction pattern has spots of (Al) phase and metastable β_m -phase. Reflections corresponding to a metastable hexagonal close-packed β_m -phase with $a = 0.274$ nm, $c = 0.443$ nm and $c/a = 1.62$ are shown by arrows and indexed.

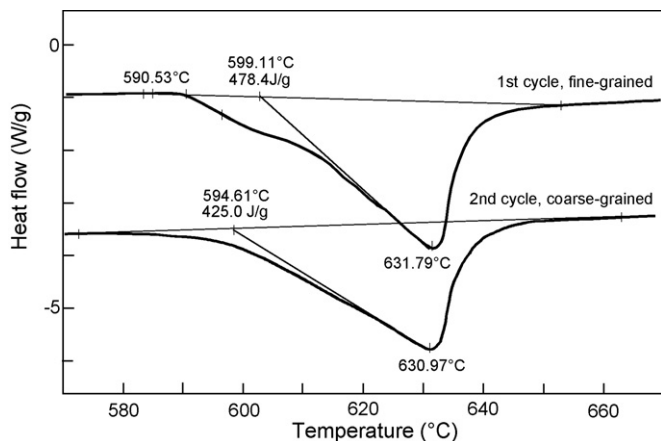


Fig. 5. Temperature dependence of heat flow (DSC curve) for the Al–20 wt.% Zn samples. Upper curve corresponds to the first heating of samples with grain size about 10–20 μm with heating rate 20 K/min. Lower curve was measured in a second circle, i.e. the melted sample was solidified, cooled down to about 500 $^{\circ}\text{C}$ and heated again to 670 $^{\circ}\text{C}$.

rhombohedral distorted f.c.c. α'_R -phase \rightarrow distorted f.c.c. α'_m -phase \rightarrow $\beta(\text{Zn})$ equilibrium phase. The metastable β_m -phase does not belong to this usual sequence. It was observed only once in rather unusual conditions [8]. 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 [9,10], high diffusivity [11–14] and high migration ability [15].

DSC measurements were made to confirm the structural observation of GB phase in Al–Zn alloys. The initial grain size of Al–7.5% Zn polycrystals after HPT was about 500 nm. TEM measurements of samples after heating in the DSC apparatus up to 400 $^{\circ}\text{C}$ revealed a grain size of about 20–30 μm . The experiments were carried out on the fine-grained material while it contains increasing amount of GBs and triple junctions and we could expect that the effect is high enough to be detected. In Fig. 5, DSC curves are shown for the Al–7.5% Zn samples for the heating from 20 to 670 $^{\circ}\text{C}$. The high-temperature part between 570 and 670 $^{\circ}\text{C}$ is shown. Temperature 570 $^{\circ}\text{C}$ is in the one-phase (Al) solid solution area of the Al–Zn phase diagram, i.e. below solidus point [4]. Temperature 670 $^{\circ}\text{C}$ is above liquidus point, i.e. in the one-phase liquid area of the Al–Zn phase diagram. Upper curve corresponds to the first heating of a HPT deformed sample with heating rate 20 K/min. At the end of heating curve the sample was completely liquid. The upper curve possess a broad minimum which corresponds to the melting of alloy between solidus and liquidus temperatures. Lower curve was measured in a second circle, i.e. the melted sample was solidified, cooled down to about 500 $^{\circ}\text{C}$ and heated again to 670 $^{\circ}\text{C}$. In this case the DSC curve also has a minimum, but it is narrower. The melting finishes at the same liquidus temperature of about 631 $^{\circ}\text{C}$, but starts about 5 K higher than melting the of deformed samples. According to these data, a point showing the region of existence for GB phase in Al–7.5% Zn, was drawn on the binary phase diagram (Fig. 2). During the repeated heating of the same samples no effect was observed on

the DSC traces. It is obviously connected to the recrystallization occurred in the sample during the first heating. Increasing grain size and decreasing GB numbers makes the expected effect non-observable.

4. Conclusions

- (i) Obtained data unambiguously shows that a GB phase really exists in the Al–Zn system.
- (ii) 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 (Fig. 2).
- (iii) Between 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.
- (iv) 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 bulk solidus or below GB solidus. This is an unambiguous proof that the liquid-like GB phase really exists in the Al-based alloys below the bulk solidus line.

Acknowledgements

The authors thank the Russian Foundation for Basic Research (contracts 06-03-32875 and 05-02-16528), German Federal Ministry for Education and Research (contract RUS 04/014), INTAS (contract 05-109-4951) and collaboration program between Polish and Russian Academies of Sciences. They also greatly appreciate Dr. W. Sigle (Max-Planck-Institut für Metallforschung, Stuttgart, Germany) for his help in the analytical microscopy investigations and Prof. R. Valiev (Ufa State Aviation Technical University, Ufa, Russia) for the HPT-treatment of the samples.

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