

Influence of the Grain Boundary Phase Transitions on the Diffusion-Related Properties

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Abstract. Grain boundary (GB) phase transitions can change drastically the properties of polycrystals. The GB wetting phase transition can occur in the two-phase area of the bulk phase diagram where the liquid (L) and solid (S) phases are in equilibrium. The GB wetting tie-line appears in the L+S area. Above the temperature of the GB wetting phase transition a GB cannot exist in equilibrium contact with the liquid phase. The liquid phase has to substitute the GB and to separate both grains. The experimental data on GB wetting phase transitions in the systems Al–Sn, Al–Ga, Al–Sn–Ga, Cu–In, Cu–Bi, Fe–Si–Zn, Mo–Ni, W–Ni, Zn–Sn and Zn–In are analysed. The GB wetting tie-line can continue in the one-phase area of the bulk phase diagram as a GB solidus line. This line represents the GB premelting or prewetting phase transitions. The GB properties change drastically when GB solidus line is crossed by a change in the temperature or concentration. The experimental data on GB segregation, energy, mobility and diffusivity in the systems Cu–Bi, Al–Ga, Al–Pb and Fe–Si–Zn obtained both in polycrystals and bicrystals are analysed. In case if two solid phase are in equilibrium, the GB “solid state wetting” (or covering) can occur. In this case the layer of the solid phase 2 has to substitute GBs in the solid phase 1. Such covering GB phase transition occurs if the energy of two interphase boundaries between phase 1 and 2 is lower than the GB energy in the phase 1. The data on the “solid state wetting” GB phase transitions in systems Al–Zn, Zr–Nb, Fe–C, W–Ni, Mo–Ni and W–Cu are analysed. The tie-lines of the covering phase transitions can also have the continuation in the one-phase areas of the bulk phase diagrams. In that case one can speak about GB solvus lines and formation of equilibrium GB layers of the phases unstable in the bulk. The GB phase transitions lead to the drastic change of the GB properties, particularly their diffusion permeability. As a result, the GB phase transition influence such diffusion-controlled properties as liquid-phase and activated sintering, superplasticity, soldering, processing of semi-solid materials etc.

Introduction

The properties of modern materials, especially those of superplastic, nanocrystalline or composite materials, depend critically on the properties of internal interfaces such as grain boundaries (GBs) and interphase boundaries (IBs). All processes which can change the properties of GBs and IBs affect drastically the behaviour of polycrystalline metals and ceramics [1]. GB phase transitions are one of the important examples of such processes [2]. Recently, the lines of GB phase transitions began to appear in the traditional bulk phase diagrams [2–7]. The addition of these equilibrium lines to the bulk phase diagrams ensures an adequate description of polycrystalline materials.

Grain Boundary Wetting Phase Transitions

In this work GB wetting, prewetting and premelting phase transitions are considered. The GB melting, GB faceting transition and the “special GB – random GB phase transitions” are analyzed elsewhere [8–10]. One of the most important GB phase transitions is the *GB wetting transition*.

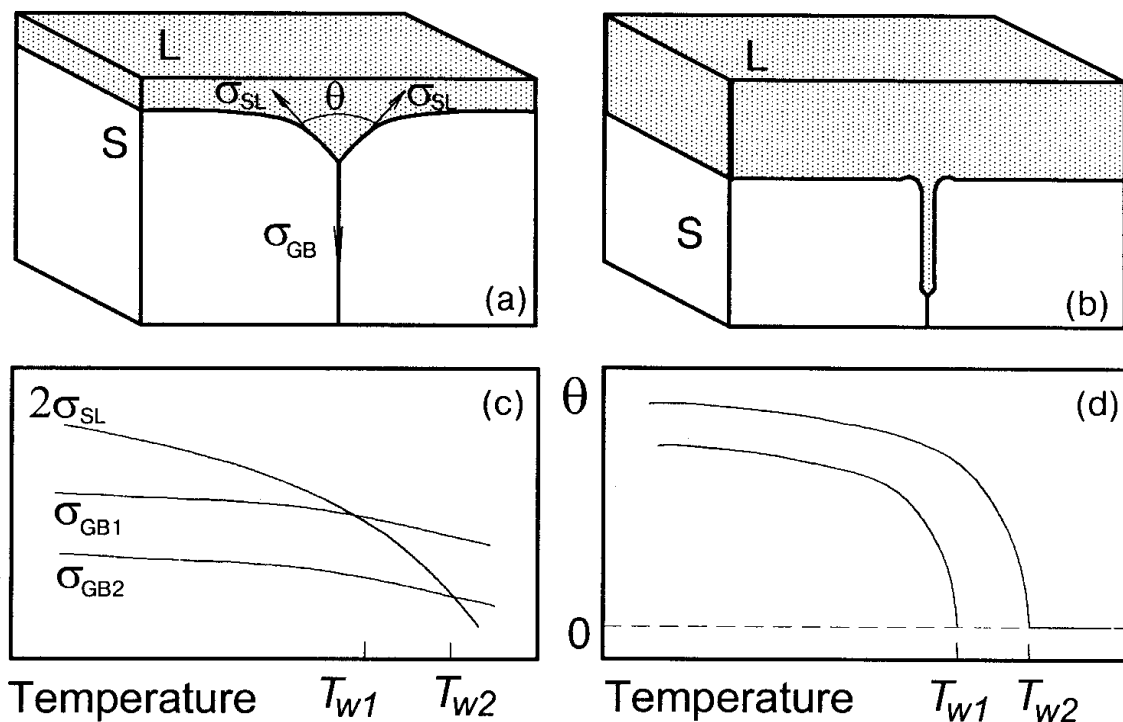


Fig. 1 (a) Scheme of the equilibrium contact between the grain boundary in the solid phase S and the liquid phase L (incomplete wetting). (b) Complete GB wetting. (c) Scheme of the temperature dependence for the GB energy σ_{GB} (for two different GBs) and the energy of two solid-liquid interface boundaries σ_{SL} . (d) Scheme of the temperature dependence of the contact angle θ for two grain boundaries with energies σ_{GB1} and σ_{GB2} . T_{w1} and T_{w2} are the temperatures of the GB wetting phase transition

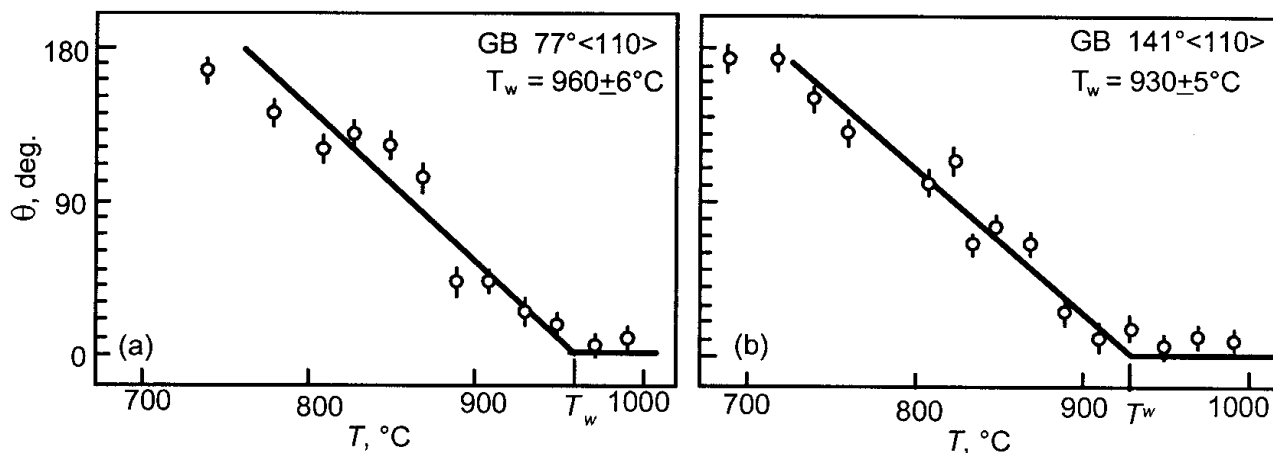


Fig. 2 Temperature dependences of the contact angle θ at the Cu GB tip in contact with (In) melt for the tilt GB $77^\circ \langle 011 \rangle$ ($T_w = 960 \pm 6^\circ\text{C}$) and for the tilt GB $141^\circ \langle 011 \rangle$ ($T_w = 930 \pm 5^\circ\text{C}$) [4]

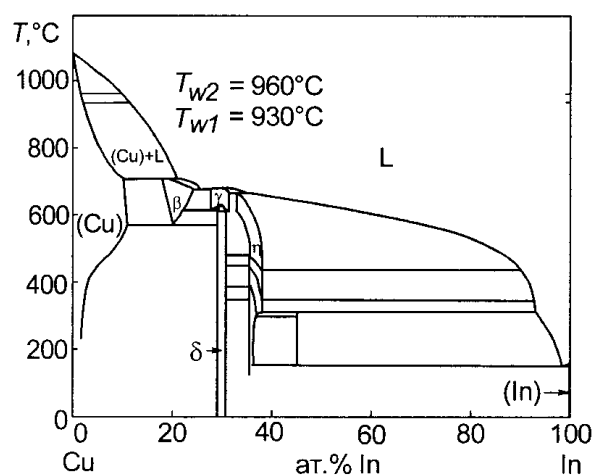


Fig. 3 The Cu-In phase diagram. Thick lines represent the bulk phase transitions. Thin lines at $T_{w2} = 960^{\circ}\text{C}$ and $T_{w1} = 930^{\circ}\text{C}$ are the tie-lines of the GB wetting phase transitions in the (Cu)+L two phase area [4]

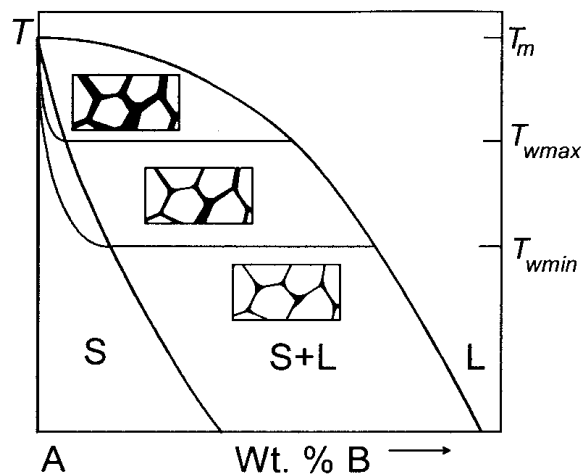


Fig. 4. Scheme of the phase diagram with lines of bulk and GB phase transitions. Thick lines represent the bulk phase transitions. Thin lines represent the tie-lines of the GB wetting phase transition in the $S + L$ area for the high angle GBs having maximal and minimal possible energy and the GB premelting phase transition in the solid solution area S

Since their prediction by Cahn [11] the study of wetting phase transitions has been of great experimental and theoretical interest, primarily for planar solid substrates and fluid mixtures [12–14]. 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 [15,16]. 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. 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: $\sigma_{GB} = 2 \sigma_{SL} \cos(\theta/2)$. If $\sigma_{GB} < 2\sigma_{SL}$, the GB is incompletely wetted and the contact angle $\theta > 0$ (Fig. 1a). At the temperature T_w of the GB wetting phase transition $\sigma_{GB} = 2\sigma_{SL}$, and at $T \geq T_w$ the GB is completely wetted by the liquid phase and $\theta = 0$ (Fig. 1b). If two GBs have different energies the temperatures of their GB wetting transitions will also differ: the lower σ_{GB} , the higher T_w (Figs. 1c and 1d). 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 $[\partial\sigma_{GB}/\partial T - \partial(2\sigma_{SL})/\partial T]$ [11,16]. If the GB wetting phase transition is of second order, $\partial\sigma_{GB}/\partial T = \partial(2\sigma_{SL})/\partial T$ at T_w . The theory predicts also the shape 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 $\tau = (T_w - T)/T_w$] and concave for a second order wetting transition: $\theta \sim \tau^{3/2}$ [12]. Nowadays, the GB phase transitions of the second order were not observed experimentally.

Consider the contact between a bicrystal and a liquid phase L . If the GB energy σ_{GB} is lower than the energy of two solid/liquid interfaces $2\sigma_{SL}$, the GB is not completely wetted and the contact angle $\theta > 0$ (Fig. 1a). If $\sigma_{GB} > 2\sigma_{SL}$ the GB is wetted completely by the liquid phase and $\theta = 0$

(Fig. 1b). If the temperature dependences $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ intersect, then the GB wetting phase transition proceeds at the temperature T_w of their intersection (Fig. 1c). The contact angle θ decreases gradually with increasing temperature down to zero at T_w . (see also the Fig. 2 for the system Cu–In) At $T > T_w$ the contact angle $\theta = 0$ (Figs. 1d and 2). The *tie-line of the GB wetting phase transition* appears at T_w in the two-phase region ($S+L$) of the bulk phase diagram (Fig. 3). Above this tie line GBs with an energy σ_{GB} cannot exist in equilibrium with the liquid phase. The liquid phase forms a layer separating the crystals.

In Fig. 3 two GB wetting tie lines are shown for two GBs with different energies obtained by measurements of $\theta(T)$ dependences (Fig. 2). In polycrystals the whole spectrum of GBs exist with various energies. Therefore, in polycrystals the maximal T_{wmax} and minimal T_{wmin} can be found for high-angle GBs with minimal and maximal energy σ_{GBmin} and σ_{GBmax} , respectively. The tie-lines at T_{wmax} and T_{wmin} are shown in the schematic phase diagram (Fig. 4). At the temperature between T_{wmax} and T_{wmin} some GBs are wetted by the liquid phase and other GBs are not wetted. In this case the non-diffusional penetration of the liquid phase into the polycrystal would proceed inhomogeneously. The example of inhomogeneous penetration of liquid phase (Ni) into W polycrystal is shown in Fig. 5. With increasing temperature between and the fraction of the wetted GBs increase from 0 at T_{wmin} to 100% at T_{wmax} (see the example for Cu–Bi polycrystals in Fig. 6)

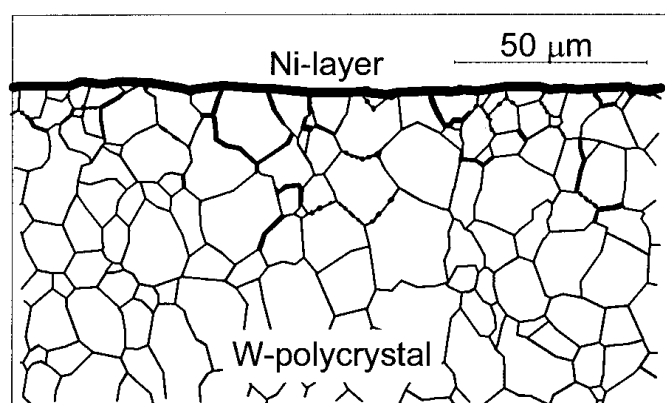


Fig. 5 Microstructure of W polycrystal with the liquid Ni-layer deposited on its surface after annealing at 1600°C [29]

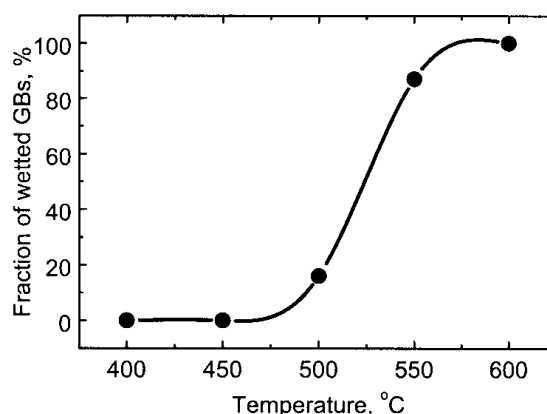


Fig. 6 Temperature dependence of the fraction of wetted GBs in Cu–Bi polycrystals [30]

First indications of the GB wetting phase transitions were found by measuring of the contact angles in polycrystals [17]. Correct measurements were later performed using metallic bicrystals with individual tilt GBs in the Al–Sn, Cu–In (Figs. 2 and 3) [4], Al–Pb–Sn [3,18,19], Al–Ga, Al–Sn–Ga [20,21], Cu–Bi (Fig. 6) [5,22,23,30], Fe–Si–Zn [24–27], Mo–Ni [28], W–Ni (Fig. 5) [29] and Zn–Sn [7] systems. The tie-lines of the GB wetting phase transition were constructed basing on the experimental data [3,4,7,18–29]. The difference in the GB wetting phase transition temperature was experimentally revealed for GBs with different energies [4,18]. The precise measurements of the temperature dependence of the contact angle revealed also that the GB wetting phase transition is of the first order [18]. The indications of presence of the liquid-like phase along the dislocation lines were also found [23].

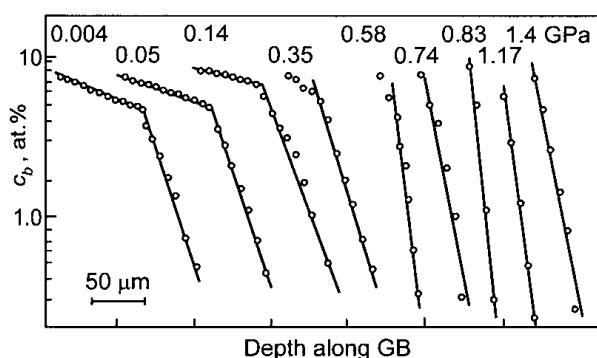


Fig. 7 Depth dependences of the GB Zn concentration c_b at 905°C and various pressures for the GB diffusion in Fe-5 at. % Zn alloy [27]

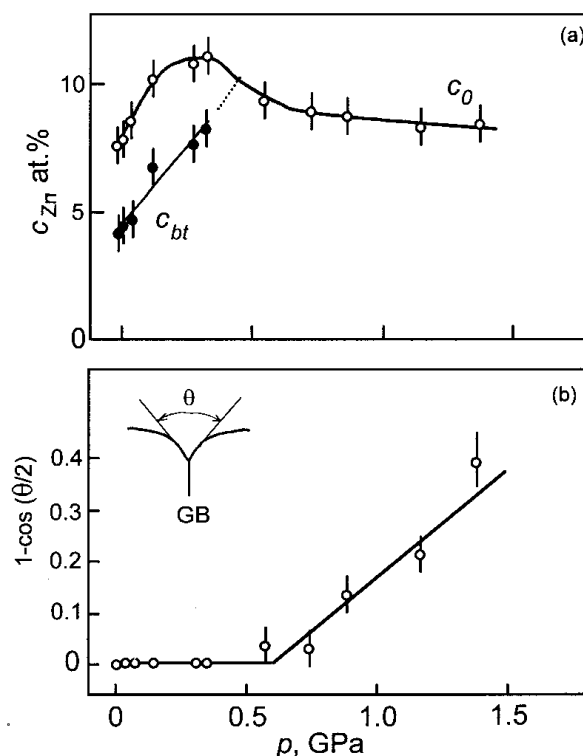


Fig. 8 Pressure dependences for (a) Zn solubility c_0 and GB concentration of the sudden change of the GB diffusivity c_{bt} and (b) $1-\cos(\theta/2)$ value in the Fe-5 at. % Zn alloy. θ is the contact angle at the GB contact with the melt [27]

Grain Boundary Prewetting (Premelting) Phase Transitions

It was pointed out by Cahn [31] that, when the critical consolution point of two phases is approached, GBs of one critical phase should be wetted by a layer of another critical phase, and in the one-phase region of a phase diagram there should be a singularity connected with an abrupt transition to a microscopic wetting layer. We distinguish two possible situations: the first one, when a layer of the new phase is formed on the GB (*prewetting transition*), and the second one, when the GB is replaced by a layer of the new phase (*premelting phase transition*). At the prewetting transition the difference between two phases must be small, while at the premelting transition the wetting phase may differ from that of the bulk dramatically. The lines of the GB prewetting or premelting phase transitions appear in the one-phase areas of the bulk phase diagrams where only one bulk phase can exist in the thermodynamic equilibrium (e.g. solid solution S , see Fig. 4). These lines continue the tie-lines of the GB wetting phase transitions and represent the GB solidus (Fig. 4). The thin liquid-like layer of the GB phase exists on the GBs between the bulk solidus and GB solidus in the phase diagram. During the GB premelting phase transition this layer appears abruptly on the GB by the intersection of GB solidus. As a result, the GB properties (diffusivity, mobility, segregation) change dramatically.

In other words, above the GB wetting tie-line T_w in the $S+L$ area of the bulk phase diagram $\sigma_{GB} > 2\sigma_{SL}$. This is true also if we intersect the bulk solidus at $T = \text{const}$ and move into the one-phase area S of the bulk phase diagram. The GB energy σ_{GB} in this part of the one-phase region is still higher than the energy $2\sigma_{SL}$ of two solid-liquid interphase boundaries. Therefore, the GB still can be substituted by two solid-liquid interfaces, and the energy gain $G = \sigma_{GB} - 2\sigma_{SL}$ appears by this substitution. G permits to stabilize the GB layer of the liquid-like phase. The appearance of the

liquid-like phase (otherwise unstable in the bulk) between two S/L interfaces instead of GB leads to the energy loss Δg per unit thickness and unit square. Therefore, the GB layer of the liquid-like phase has the thickness l defined by the equation $\sigma_{GB} - 2\sigma_{SL} = \Delta g l$. Thickness l depends on the concentration and temperature and becomes $l = 0$ at the line of GB premelting (or prewetting) phase transition.

The premelting transition has been revealed in the ternary Fe–Si–Zn system by measurements of Zn GB diffusivity along tilt GBs in the Fe–Si alloys [24–27]. It was found that the penetration profiles of Zn along GBs consist of two sections (Fig. 7), one with a small slope (high GB diffusivity) at high Zn concentrations and one with a large slope (low GB diffusivity) at low Zn concentrations. The transition from one type of behavior to the other was found to occur at a definite Zn concentration c_{bt} at the GB, which is an equilibrium characteristic of a GB and depends on the temperature and pressure (Fig. 7). The GB diffusivity increases about two orders of magnitude which is an indication of a quasi-liquid layer present in the GBs at high Zn concentration. The line of GB premelting phase transition in the one-phase area of the bulk phase diagram continues the line of the GB wetting phase transition in the two-phase $L+S$ area: by pressure increase both the GB wetting and the GB enhanced diffusivity disappear together at the same pressure value (Fig. 8) [27].

The GB mobility was studied for two tilt GBs in bicrystals grown of high purity 99.999 wt.% Al and of the same material doped with 50 wt. ppm Ga [21]. The GB mobility increased about 10 times by addition of the Ga content for the both GBs studied. Normally, the addition of a second component can only decrease the GB mobility due to the solution drag [32]. The increase of the GB mobility can only be explained by the formation of the liquid-like Ga-rich layer on the GBs as a result of a premelting phase transition

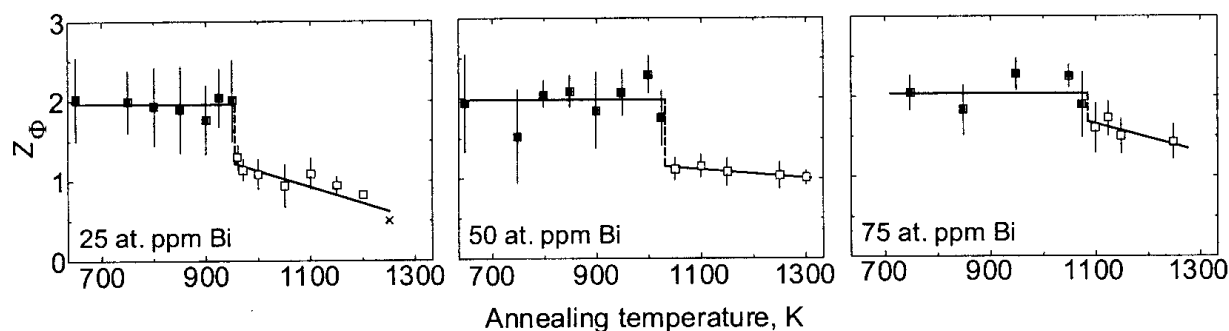


Fig. 9 Temperature dependence of the GB Gibbsian excess Z_{Φ} of Bi in Cu(Bi) polycrystals of various compositions, measured by AES [5,23,33,34]

The GB segregation of Bi in Cu was studied in the broad temperature and concentration interval [5,22,23,33,34]. It was shown that at a fixed Bi concentration the GB segregation Z_{Φ} changes abruptly at a certain temperature (Fig. 9). Below this temperature the GB Bi concentration is constant and corresponds to a thin layer of pure Bi (GB phase). Above this temperature the GB segregation is lower than one monolayer of Bi and decreases gradually with increasing temperature according to the usual laws. These features indicate also the formation of a thin layer of a GB phase in the one-phase area of the bulk Cu–Bi phase diagram (Fig. 10). The points of the abrupt change of the GB segregation form the GB solidus line in the bulk Cu–Bi phase diagram [22,23,33,34]. GB segregation was measured with the aid of Auger electron spectroscopy (AES) on the GB fracture surfaces in samples broken *in situ* in the AES instrument. In other words, the multilayer GB segregation in Cu–Bi alloys leads to the increased GB brittleness. In Fig. 10 the (retrograde) bulk

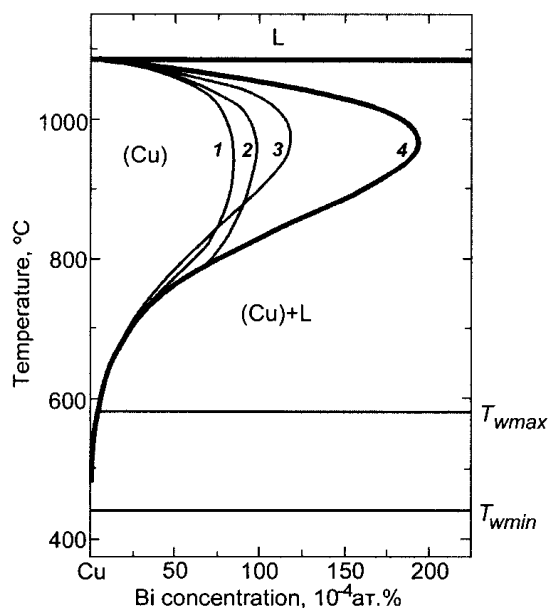


Fig. 10 Cu-Bi phase diagram. Curves 1 and 2 are the GB solidus lines obtained on two different individual tilt GBs [35]. Curve 3 is the GB solidus line obtained on the Cu-Bi polycrystals [5,23,33]. Curve 4 is the (retrograde) bulk solidus line [22]. The GB wetting phase transition tie-lines at T_{wmax} and T_{wmin} are also shown in the two-phase $S+L$ area (see Fig. 6)

solidus line (curve 4 [22]) is shown together with the GB solidus line obtained on the Cu-Bi polycrystals (curve 3 [5,23,33]) and on two different individual tilt GBs (curves 1 and 2 [35]). The GB wetting phase transition tie-lines at T_{wmax} and T_{wmin} are also shown in the two-phase $S+L$ area. Both latter lines were constructed using the data on fraction of wetted GBs (Fig. 6 [30]). The GB solidus lines (curves 1, 2 and 3) lie completely in the one-phase S area of the Cu-Bi bulk phase diagram. The lines of individual GBs (curves 1 and 2) intersect the GB solidus for the polycrystals. This is due to the fact that the GB fracture in the polycrystals “chooses” the most brittle GBs, which are different at different temperatures. It is also clearly seen that the GB solidus lines are positioned completely above the GB wetting tie-lines. Therefore, the GB solidus lines in the one phase S area of Cu-Bi phase diagram can be considered as continuation of the GB wetting tie-lines in $S+L$ two-phase area. In [36] the GB energy was measured in Cu-Bi alloys using individual $\Sigma 19$ GB in bicrystals with the aid of the GB thermal grooves. The thermal groove profile was obtained with the aid of atomic force microscopy. The GB Bi segregation was measured simultaneously in the same conditions. The abrupt change of the segregation coincides with the *discontinuity of GB energy*. This fact demonstrates that the GB premelting (or prewetting) phase transition is of first order. The low-temperature measurements of resistivity temperature coefficient dp/dT and residual resistivity ρ_0 at 4 K were performed in [34] using the Cu-Bi polycrystals annealed at high temperature and subsequently quenched. Both dp/dT and ρ_0 demonstrate well pronounced break exactly at the same position where the sudden change of GB segregation was observed. In other words, the formation of GB layers of liquid-like phase leads to the measurable changes of the resistivity.

Grain Boundary Wetting (Covering) by Solid Phase

The situation illustrated in Fig. 1 can repeat in case if second phase (β) is not liquid but also solid. In other words, if in the phase α the GB energy $\sigma_{\alpha\alpha}$ is lower than the energy of two α/β solid/solid interfaces, the GB $\alpha\alpha$ has to be substituted by the layer of the second solid phase β . Such process can be called the GB wetting (or covering) by solid phase. It is clear, that the kinetics of the equilibration processes in case GB wetting (or covering) by solid phase is much slower than in case of wetting by liquid phase. Our preliminary experiments with Al-95 wt.% Zn alloy demonstrate,

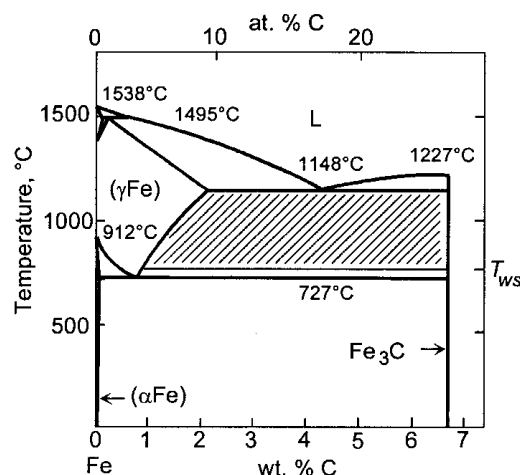


Fig. 11 Phase diagram Fe–C with lines of the bulk phase transitions (thick solid lines [37]) and the tie-line of the GB covering phase transition slightly above the eutectoid temperature of 727°C (thin solid line). In the dashed area the austenite GBs are not stable against the formation of Fe_3C GB layers (so-called cementite network [38]).

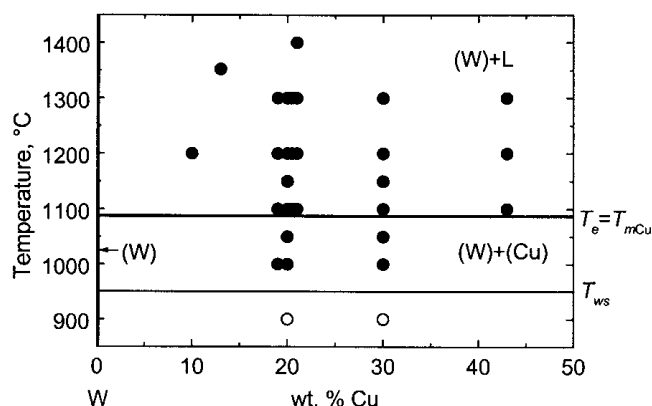


Fig. 12 Phase diagram W–Cu with lines of the bulk phase transitions (thick solid lines [37]) and the tie-line of the GB covering phase transition at 950°C (thin solid line). The experimental points correspond to the two different GB morphologies in the W–Cu polycrystals [39–44]. Solid circles: GBs in W are wetted by the layers of liquid (Cu) phase or covered by the solid (Cu) phase. Open circles: GBs in W are not covered by the solid (Cu) phase

that after about 1 month of annealing the difference in the morphology of Al-rich phase precipitates (Al) at the (Zn)/(Zn) GBs in Zn-rich phase can be observed. Namely, at high temperatures just below the eutectic temperature in the Al–Zn system, more than 50% of (Zn)/(Zn) GBs are covered by continuous layer of the Al-rich phase. With decreasing temperature the portion of the (Zn)/(Zn) GBs covered by the (Al) layer decreased, and at the temperatures just below the eutectoid point all (Al) precipitates at the (Zn)/(Zn) GBs have the shape of isolated particles. Another examples of the GB covering phase transitions can be found by the analysis of the data published in the literature. In Fig. 11 the phase diagram iron-cementite is shown. Thick solid lines represent the bulk phase transitions [37] and the tie-line of the GB covering phase transition is slightly slightly above the eutectoid temperature of 727°C (thin solid line). In the dashed area the austenite GBs are not stable against the formation of Fe_3C GB layers (so-called GB cementite network [38]). In Fig. 12 the W–Cu phase diagram is shown with lines of the bulk phase transitions (thick lines [37]) and the tie-line of the GB covering phase transition at 950°C (thin line). The experimental points correspond to the two different GB morphologies in the W–Cu polycrystals obtained by liquid phase sintering or activated sintering [39–44]. Solid circles correspond to the GBs in W are wetted by the layers of liquid (Cu) phase or covered by the solid (Cu) phase. Open circles denote the GBs in W which are not covered by the solid (Cu) phase

Conclusions

The GB phase transitions can be observed both in two-phase and one-phase areas of bulk phase diagrams. In the two-phase $S+L$ area where solid and liquid phases are in equilibrium the GB

wetting phase transition can take place at T_w . Above T_w the GB disappears being substituted by two solid/liquid interfaces and the (macroscopically thick) layer of the liquid phase. The tie-lines of the GB wetting phase transition must have a continuation (GB solidus) in the one-phase S area of the bulk phase diagram. By intersection of GB solidus line the GB prewetting or premelting phase transition proceeds. Between the lines of GB and bulk solidus the grain boundary is substituted by two solid/liquid interfaces and the thin layer of the liquid-like phase. This liquid-like phase is stable in the GB and unstable in the bulk. The liquid-like phase is stabilized in GB due to the energy gain which appears as a result of substitution of GB by two solid/liquid interfaces. The GB wetting and prewetting (premelting) phase transitions observed up-to-date are of first order. If the GB energy is higher than the energy of two solid/solid interfaces, the GB solid state wetting (covering) phase transition can occur in a two-phase S_1+S_2 area of the phase diagram.

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Discussion

- H. Mehrer:** You discussed the microstructure of two-phase Al–Zn alloys in the terms of solid-state grain boundary wetting. Could you please comment on the possible influence of Ostwald ripening?
- B. Straumal:** If grain boundaries are not “wetted” (covered) by the second solid phase, the GB particles will grow as usual according the Ostwald ripening laws. The large particles will grow, and the small ones will disappear. This process will be controlled most possible by GB diffusion. If the GB energy is lower than the energy of two interphase boundaries between two solid phases, the GB particles of the second solid phase have to grow and to merge together forming finally the continuous layer covering GB

Yu. Nechaev: Could you comment about

- (1) mechanism of premelting phase transition,
- (2) activation volume of GB diffusion in case of premelting and
- (3) non-equilibrium boundaries under superplastic deformation?

B. Straumal: (1) The equilibrium premelted layer on the GBs can form, for example, as a result of GB diffusion;

(2) In principle, the activation volume of GB diffusion in case of premelting would be possible to measure, for example, for Zn diffusion along the GBs in Fe–Si alloys. Unfortunately, in our experiments the GB wetting disappears (together with premelting layers) at rather low pressure of about 0.4 GPa. In this narrow pressure interval there was no measurable difference in GB diffusivity.

(3) Our data on GB phase transitions demonstrate that the GB layers of second phase can be the elements of equilibrium structure. It means that at least in certain cases the intensive superplastic deformation permits to obtain the *equilibrium* GB structure which is otherwise not obtainable at low temperatures due to the “frozen” kinetics.

F. Rustichelli: One could use the small-angle neutron scattering in order to investigate *in situ* the phase transitions at grain boundaries in the definitive way, especially in nanocrystalline materials.

B. Straumal: Sure. The first examples you can find in the works of E. Pereiro-López et al. and O. Lame et al. presented at this conference. And these are just first steps in this direction by using very powerful methods of *in situ* investigations of GB phase transitions!

L. Klinger: What is the physical meaning of this line in one-phase region?

B. Straumal: To the left side of the GB premelting (or prewetting) phase transition line, e.g. at smaller concentration of the second component, the GB is “clean” and contains only the ordinary GB segregation layer. To the right side of the GB premelting (or prewetting) phase transition line, e.g. between this GB line and bulk solidus, the GB contains the thin layer of the liquid-like phase, which is unstable in the bulk. In other words, the GB energy σ_{GB} in this part of the one-phase region is still higher than the energy $2\sigma_{SL}$ of two solid-liquid interphase boundaries. Therefore, the GB is substituted by two solid-liquid interfaces, and the energy gain $G = \sigma_{GB} - 2\sigma_{SL}$ permits to stabilize the GB layer of the liquid-like phase. The appearing of the liquid-like phase (otherwise unstable in the bulk) leads to the energy loss Δg per unit thickness and unit square. Therefore, the GB layer of the liquid-like phase has the thickness l defined by the equation $\sigma_{GB} - 2\sigma_{SL} = \Delta g l$. Thickness l depends on the concentration and temperature and becomes $l = 0$ at the line of GB premelting (or prewetting) phase transition.

J. Philibert: Looking at your last micrographs (Al–Zn system), this looks like continuous precipitates of a second phase along GB. What is the difference?

B. Straumal: The GB “plates” in the Al–Zn system are really continuous precipitates of a second phase along GB. We just stress out that there can be the transition from the individual precipitates to the continuous precipitate of the second phase at GB. And this transition (for example, with increase of the temperature) has the same simple

thermodynamic reason as the GB wetting phase transition in case when second phase is liquid.



D. sc. B. Straumal