

Lines of Grain Boundary Phase Transitions in Bulk Phase Diagrams

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Abstract. Different grain boundary (**GB**) phase transitions are classified and the GB wetting phase transition is defined. Methods of investigation of GB wetting phase transitions with aid of individual GBs in bicrystals are explained. The order of a GB wetting phase transition is discussed. The experimental data on the GB tie lines in bulk phase diagrams, the influence of the GB wetting phase transition on the microstructure of polycrystals, the penetration of a liquid phase along GBs and the influence of pressure on the GB wetting phase transition are presented. The possible formation of stable thin GB layers of a phase, which is unstable in the bulk (GB premelting or GB prewetting transition), is described.

1. Introduction

Phase transitions are among the most important topics in the field of thermodynamics of condensed matter. It has been shown that in grain boundaries (**GBs**) specific GB phase transitions can occur which do not proceed in the bulk [1]. Certain GB phase transformations are closely related with the GB geometry and can proceed only in GBs having particular crystallographic parameters. These are the „special GB – general GB“ phase transition [2–5] and the *GB faceting* phase transition [6–8]. It is well known that GBs with a misorientation angle which is close to a coincidence misorientation („special GBs“) possess properties different from the properties of the so-called general GBs. It has experimentally been shown that this difference in the properties between special and general GBs can suddenly disappear at certain misorientation angles and temperatures. The temperature and misorientation intervals for the existence of special GBs depend on the reciprocal density of coincidence sites Σ for a coincidence misorientation ϕ_{Σ} , on temperature T , impurity concentration etc. [2–5]. For a special GB with a misorientation close to ϕ_{Σ} a limited number of inclinations exist which are thermodynamically stable. If the flat special GB possesses an inclination slightly different from any stable one, it decomposes into facets having the stable inclinations. In other words, the GB faceting transformation occurs [6–8]. Other GB phase transitions have a more „chemical“ nature and do not depend so critically on the crystallographic GB parameters. The lines of these GB phase transitions can be plotted in the traditional bulk phase diagrams together with the usual lines of bulk phase transitions. Such GB phase transitions can strongly influence the properties of polycrystals. Because real materials are in general polycrystalline, it is important to add the GB lines into the bulk phase diagrams. The most important GB phase transitions of this kind are the *wetting* and *prewetting* (or *premelting*) transitions.

2. GB wetting phase transition

Only in the last few decades was it understood that the transition from incomplete (contact angle $\theta > 0$) to complete ($\theta = 0$) wetting of a solid substrate by a liquid phase proceeds like a normal phase transition (wetting phase transition). Since prediction of these transitions by Cahn [9] the study of wetting phase transitions has been of great experimental and theoretical interest, primarily for planar solid substrates and fluid mixtures [10–12]. It has experimentally been shown that the wetting transition is of the first order. The discontinuity in the surface energy has been measured, and the hysteresis of the wetting behaviour has been observed [13,14]. The experimental data on wetting phenomena at solid/solid interfaces, for example on grain boundaries (**GBs**), are much poorer [15]. The important difference is that in the case of GB wetting only two phases coexist, namely a liquid phase and a solid one containing the boundary between the misoriented grains (Fig.1). Therefore, the contact angle θ also depends only

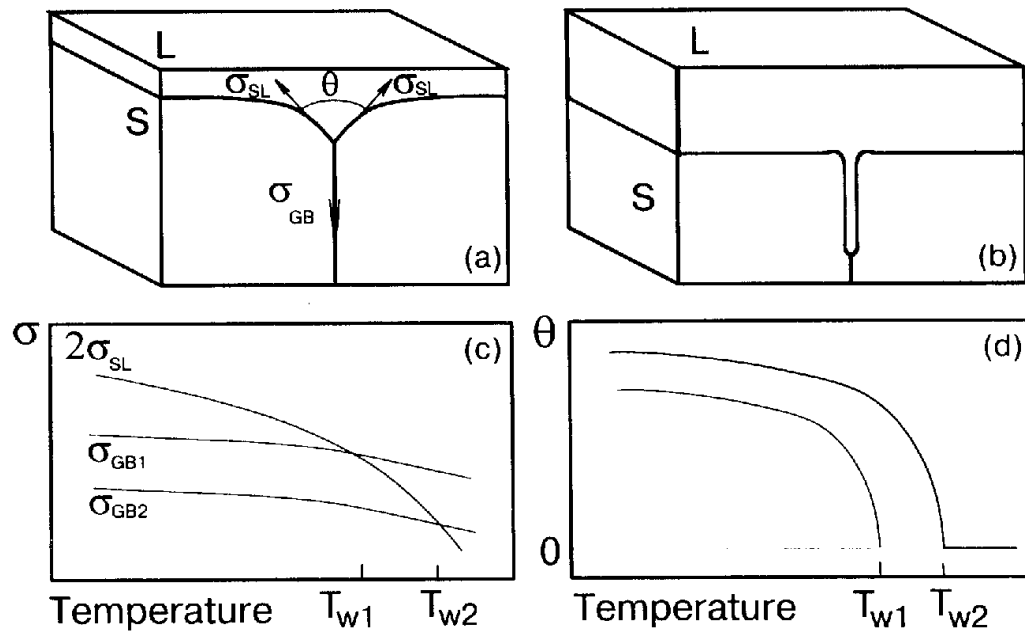


Fig. 1. (a) A bicrystal in contact with a liquid phase at $T < T_w$. The GB is incompletely wetted. The contact angle $\theta > 0$. (b) The GB is completely wetted, $T > T_w$, $\theta = 0$. (c) Schematic dependencies of $2\sigma_{SL}(T)$ together with $\sigma_{GB1}(T)$ and $\sigma_{GB2}(T)$ for two different GBs. They intersect at the temperatures T_{w1} and T_{w2} of the GB wetting phase transition. (d) Schematic temperature dependencies of the contact angle θ corresponding to the curves drawn in Fig. 1(c).

on two different surface energies (the GB energy σ_{GB} and the energy of the solid/liquid interphase boundary σ_{SL}) instead of three in the usual experiments (Fig. 1(a)):

$$\sigma_{GB} = 2\sigma_{SL} \cos(\theta/2). \quad (1)$$

We consider the contact between a bicrystal and a liquid phase L (Fig. 1). If the GB energy σ_{GB} is lower than $2\sigma_{SL}$, the GB is incompletely wetted and the contact angle $\theta > 0$ (Fig. 1(a)). If $\sigma_{GB} > 2\sigma_{SL}$, the GB is completely wetted by the liquid phase and $\theta = 0$ (Fig. 1(b)). If the temperature dependencies $\sigma_{GB}(T)$ and $2\sigma_{SL}(T)$ intersect, the GB wetting phase transition proceeds at the temperature T_w of their intersection (Fig. 1(c)). The contact angle θ decreases gradually with increasing temperature down to zero at T_w (Fig. 1(d)). At $T > T_w$ the contact angle $\theta = 0$. 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. 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. The decreasing of the contact angle θ down to 0 at T_w was firstly observed in the following systems: Zn-Sn [16], Al-Sn [17, 18], Al-Cd [18], Al-In [18], Al-Pb [17] and Ag-Pb [19].

The data obtained on polycrystals cannot be used for a correct description of the GB wetting transition because the GBs are randomly inclined towards the section plane preventing precise measurements of θ , and only the θ values averaged over many GBs can be obtained. By the averaging of θ important features of the GB wetting transitions are smeared out because the properties of GBs depend strongly on their crystallographic parameters. Therefore, θ should be measured on *individual GBs in oriented bicrystals*. In this case the GB lies perpendicular to the section plane, and the crystallographic parameters of the GB can be predetermined by the bicrystal production.

If two GBs have different energies the temperatures of their GB wetting transitions will also differ: the lower σ_{GB} , the higher T_w (Fig. 1(c, d)). There is a family of GB wetting transition tie lines in the two-phase region ($S+L$) of the bulk phase diagram which correspond to GBs with different energies. Therefore, it is not correct to measure T_w in polycrystals. For the construction of GB wetting transition tie lines in the bulk phase diagram bicrystals with GBs having different σ_{GB} values must be used.

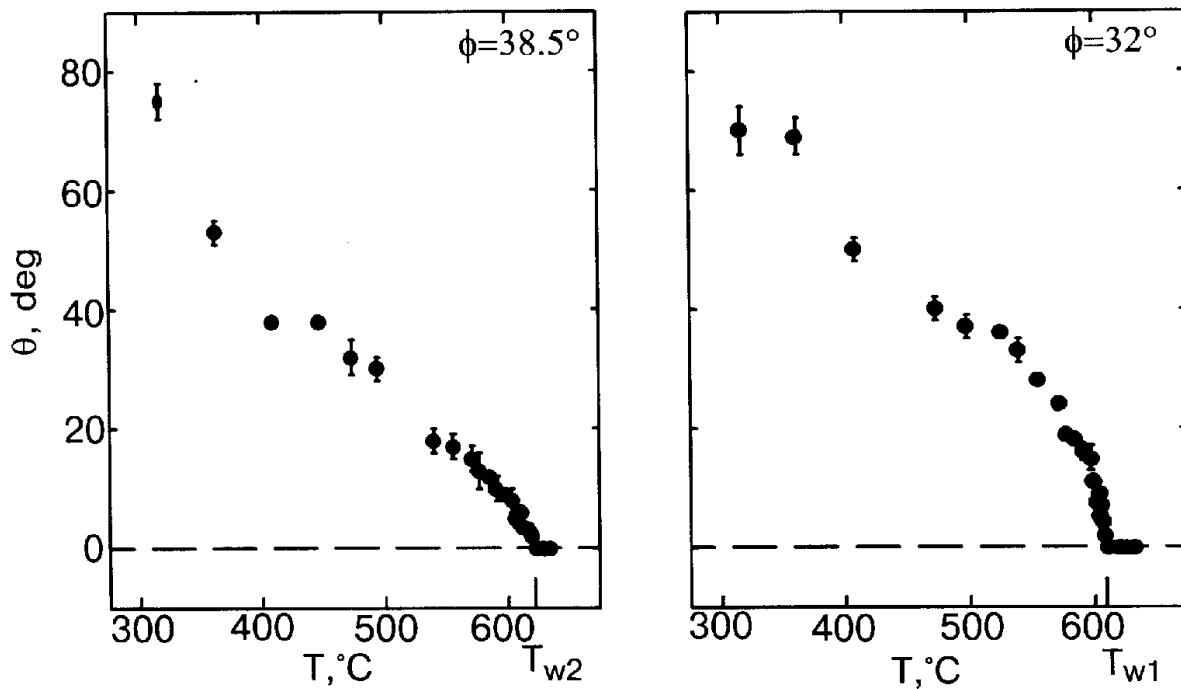


Fig. 2. The temperature dependencies of the contact angle θ for $32^\circ\langle 011\rangle\{001\}$ and $38.5^\circ\langle 011\rangle\{001\}$ symmetrical tilt GBs in Al.

If the GB wetting phase transition is of first order, there is a discontinuity Δ in the temperature derivative of the GB energy at T_w which is equal to $[\partial\sigma_{GB}/\partial T - \partial(2\sigma_{SL})/\partial T]$ [9,11]. If the GB wetting phase transition is of second order then $\partial\sigma_{GB}/\partial T = \partial(2\sigma_{SL})/\partial T$ at T_w . In order to be able to determine the order of a GB phase transition, the $\theta(T)$ dependencies must be measured with a high accuracy. Unfortunately, in the works made on polycrystals the temperature intervals between the experimental points are too large for allowing a decision about the actual form of the $\theta(T)$ dependency close to T_w .

3. Investigations of GB wetting phase transitions with individual GBs

The most accurate measurements of the contact angle at temperatures near a GB wetting phase transition were made in the Al-Sn system [20]. This system was chosen for the measurements because the data for polycrystals show that there is a GB wetting phase transition somewhere between 580 and 620°C [18]. Besides, the solubility of Sn in solid Al is very low (max. 0.25 wt.%) [21]. Therefore, the contact between the Al bicrystal and the Sn-rich melt is very close to the equilibrium at all temperatures studied. If the solubility of the second component in a material of the bicrystal is high and temperature dependent, uncontrollable equilibration processes in the solid phase during the annealing influences the value of θ , making precision measurements difficult. A special (tilt angle $\phi=38.5\pm 1^\circ$; near the $\Sigma 9$ coincidence misorientation) and a general ($\phi=32\pm 0.5^\circ$) symmetrical tilt $\langle 011\rangle\{001\}$ GB were chosen for the measurements. Experimental data and computer modelling of such GBs in Al indicate that the GB with a tilt angle of 38.5° has a low energy and the other GB has a high energy [22].

The bicrystals were produced from Al of 99.999 wt.% purity using a modified Bridgman technique. At intermediate stages of the bicrystal production specially etched single crystalline seeds were oriented by laser optics directly on the spark erosion machine used for cutting. Finally, the orientation parameters of the bicrystals were controlled using Laue back reflection. The flat bicrystals were grown in high-purity graphite crucibles in an atmosphere of high-purity argon (with an oxygen content equivalent to the vacuum of 10^{-5} Pa). For the wetting experiments the samples were covered with Sn. For this purpose the Al bicrystals were etched and brought in contact with liquid Sn of 99.9999 wt.% purity at about 240°C. The surface layer at the end of the bicrystal dissolves in the liquid Sn and saturates the melt up to the liquidus concentration. The contact between the molten Sn(Al) and the Al bicrystal forms within a few seconds. All individual samples were cut from the same bicrystal. The bicrystalline samples coated with a Sn-rich layer were placed together with an oxygen getter (a piece of a Ta foil) in evacuated silica capsules. Each sample was annealed at a prescribed temperature and subsequently quenched in water

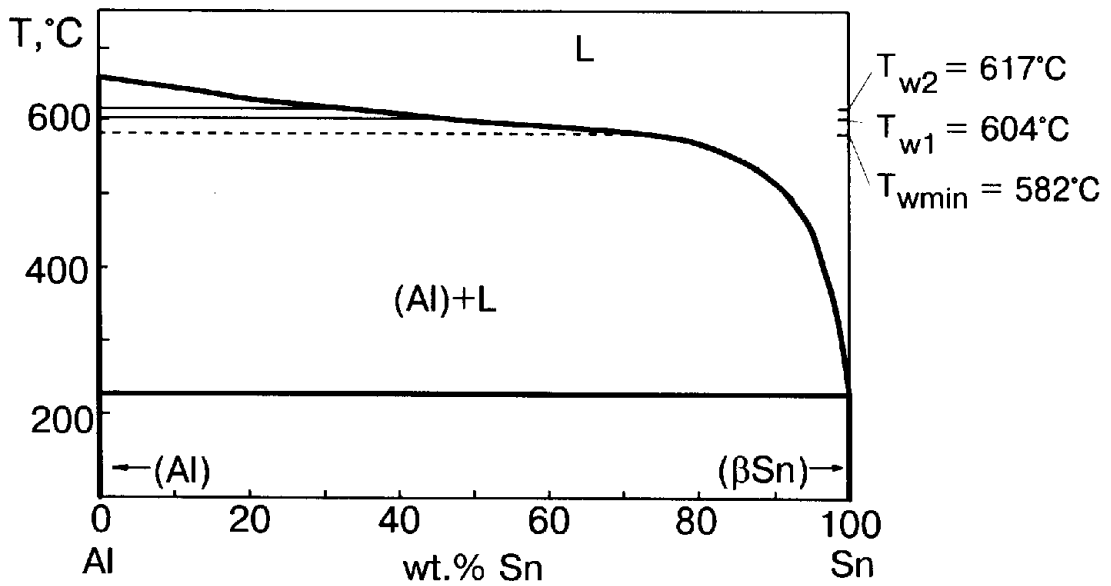


Fig. 3. The Al-Sn bulk phase diagram (thick solid lines) [21] along with the tie lines of the GB wetting transition (thin solid lines) at T_{w1} for the $32^\circ\langle 011\rangle\{001\}$ tilt GB and at T_{w2} for the $38.5^\circ\langle 011\rangle\{001\}$ GB. The extrapolated *minimal possible temperature* of the GB wetting phase transition, T_{wmin} , for GBs with *maximal energy* is also shown (dotted line).

with a cooling rate of 10^2 K/s. The measured θ values begin to differ from the equilibrium value only at cooling rates of about 10^{-2} K/s.

After quenching, the samples were embedded in a holder and mechanically ground and polished to make a polished surface parallel to the $\{011\}$ surface of the Al bicrystal and perpendicular to the GB and solid/liquid interface. The polished surface was etched, the contact area between the GB and the interphase boundary was photographed in an optical microscope, and the contact angle θ was measured. The errors associated with the θ measurements were defined by subsequent measurements of θ at different distances from the former surface after removing 100–200 μm thick layers. It is very important that all annealing temperatures are higher than the coating temperature and some Al dissolves in the Sn-rich melt according to the liquidus line. During this dissolution process the interphase boundary moves a distance of about 100–1000 μm from the former position and the contamination initially present on the interphase boundary due to the coating process dissolves in the melt. It is also important that a 200–300 μm thick layer is mechanically removed before the measurements. Therefore, the contact angle is measured deep in the sample where θ is determined only by σ_{GB} and σ_{SL} in equilibrium with the (very clean) bulk Al and Sn-Al melt without any influence of the (eventually contaminated) surface. The temperature dependencies of the contact angles of both GBs studied are shown in Fig. 2. Both $\theta(T)$ dependencies are convex in the broad temperature interval below T_w . At all temperatures below T_{w2} the contact angles for the GB with $\phi=38.5^\circ$ are smaller than those for the GB with $\phi=32^\circ$. This means the energy σ_{GB2} is really lower than σ_{GB1} as expected from the selection of the GB misorientation parameters. At the temperature T_w the GB wetting phase transition occurs and for $T > T_w$ the contact angle $\theta=0^\circ$. The GBs studied have different temperatures for the wetting phase transition: $T_{w1} = 617 \pm 1^\circ\text{C}$ for $\phi=38.5^\circ$ and $T_{w2} = 604 \pm 1^\circ\text{C}$ for $\phi=32^\circ$.

4. The order of GB wetting phase transition

If the energies σ_{GB} and σ_{SL} depend linearly on the temperature, the phenomenological theory [9] predicts for a wetting phase transition of first order—analogously to fluids on a solid substrate—that the temperature derivative of the macroscopic GB energy has a discontinuity Δ at T_w given by

$$\partial(2\sigma_{SL})/\partial T - \partial\sigma_{GB}/\partial T = -2\sigma_{SL} \partial(\cos \theta)/\partial T. \quad (2)$$

This equation is obtained by differentiating the law of cosines for the triangle built by σ_{SL} , σ_{GB} and σ_{SL} (Fig. 1(a)) at T_w where $\cos \theta = 1$. The $\theta(T)$ dependencies measured close to T_w permit us to estimate

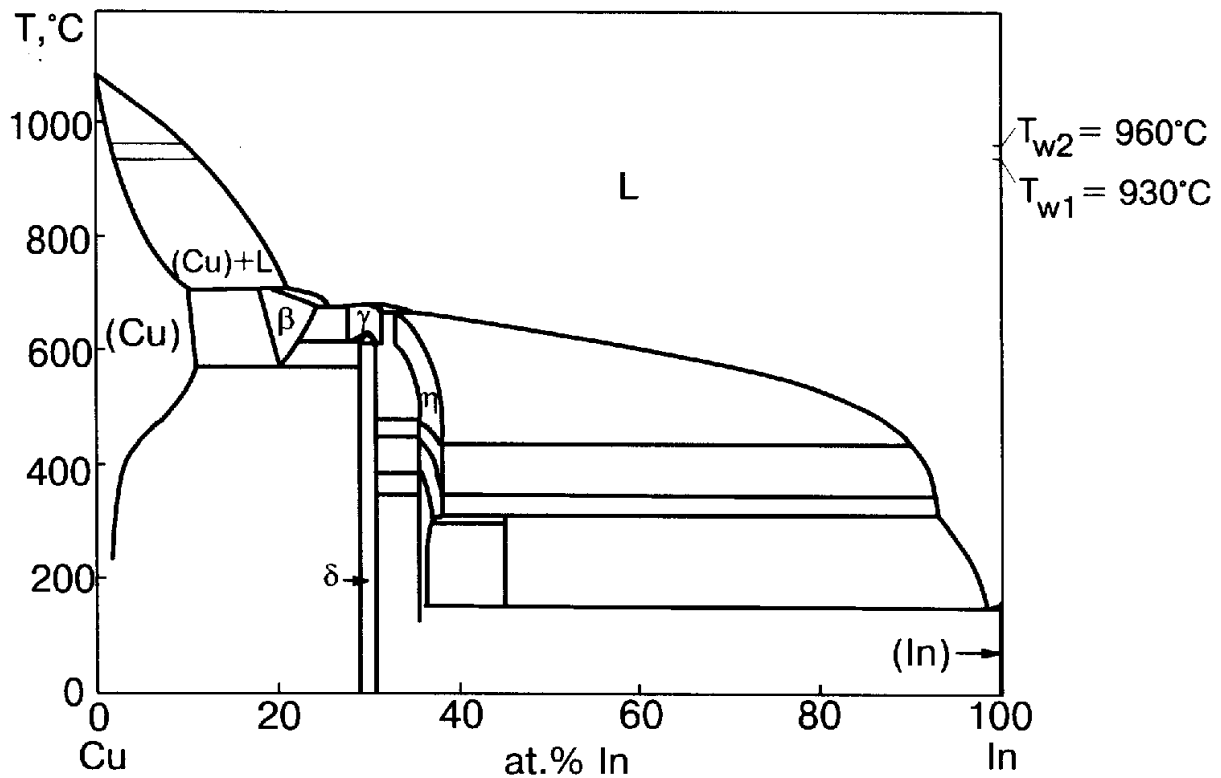


Fig. 4. The Cu–In bulk phase diagram (thick lines) [21] along with the conodes of the GB wetting transition (thin lines) at T_{w1} for the $141^\circ\langle 011\rangle\{001\}$ tilt GB and at T_{w2} for the $77^\circ\langle 011\rangle\{001\}$ tilt GB.

the values of $\partial(\cos \theta)/\partial T$ in the temperature interval where the $\theta(T)$ dependencies can be treated as linear (from T_w to about $T_w - 70$ K). We can estimate the right-hand part of Eq.(2) knowing that $2\sigma_{SL} = \sigma_{GB}$ at T_w and using the value $\sigma_{GB} = 350$ mJ/m² for Al near the melting temperature T_m [22] because in our case T_w is close to T_m (660°C). For the $32^\circ\langle 011\rangle\{001\}$ GB $\Delta = -17$ mJ/m²K and for the $38.5^\circ\langle 011\rangle\{001\}$ GB $\Delta = -5.6$ mJ/m²K. Therefore, the discontinuity of σ_{GB} is much lower for the special (near $\Sigma 9$) GB than for the general one. Both Δ values are higher than for fluorocarbon-alcohol fluid ($\Delta = -0.9$ mJ/m²K [14]) due to the high surface energies of metals.

5. Bulk phase diagrams with tie lines of GB wetting phase transition

Figure 3 shows the Al–Sn bulk phase diagram along with the tie lines T_{w1} and T_{w2} of the GB wetting transition for the GBs studied. The borders of bulk phase fields are represented by thick lines and the GB wetting tie lines by thin lines. The tie lines of the GB wetting transition lie in the temperature interval where the solubility of Sn in the liquid phase decreases very fast. In systems like Zn–Sn [16] or Al–Cd [18] the GB wetting temperatures coincide also with temperatures for which the liquidus line has a low concentration slope. This is not surprising because in this case the difference between the liquidus and solidus concentrations decreases very fast with increasing temperature. The same is true for the surface tension of the solid/liquid interface σ_{SL} . Therefore, it is possible that $2\sigma_{SL}$ will be lower than σ_{GB} above a certain temperature. The individual GBs were chosen so that the energy of most other GBs in Al lie between σ_{GB1} and σ_{GB2} [22]. Therefore, the values of T_w for most Al GBs wetted by a Sn(Al) melt lie also between $T_{w1} = 604^\circ\text{C}$ and $T_{w2} = 617^\circ\text{C}$. We see that T_{w2} (being the wetting transition temperature for the GB with the lower energy) really coincides with the temperature where most GBs in a polycrystal are wetted by a Sn-rich melt [18]. Using the data about GB energies, the minimal temperature $T_{wmin} = 582^\circ\text{C}$ was determined at which the GBs having highest energy first begin to be wetted. At a temperature of 580°C no wetted GBs exist in a polycrystal where the averaged contact angle is $\theta = 25^\circ$ [18]. Figure 4 shows the Cu–In bulk phase diagram along with the tie lines T_{w1} and T_{w2} of the GB wetting transition for two symmetrical tilt GBs [23]. The energy of the $77^\circ\langle 011\rangle\{011\}$ GB is about 40% lower than that of the $141^\circ\langle 011\rangle\{011\}$ GB. The difference between T_{w1} and T_{w2} is 30°C .

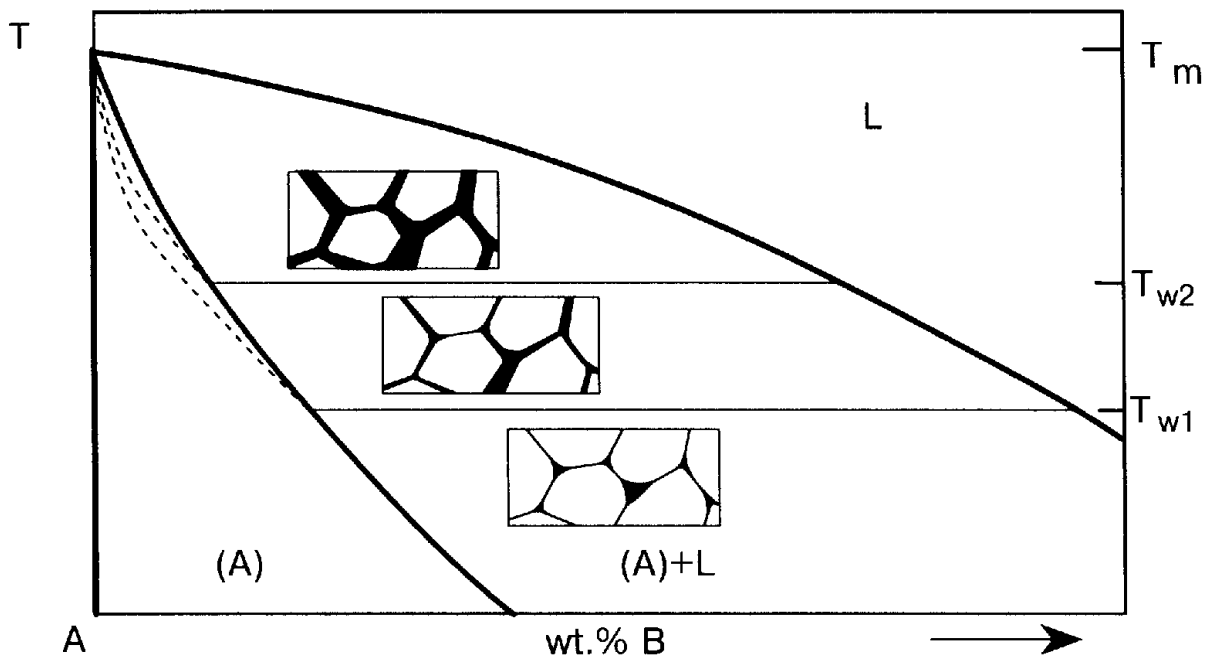


Fig. 5. A schematic phase diagram showing the lines of GB wetting phase transitions and the corresponding microstructures of two-phase polycrystals.

6. Influence of the GB wetting phase transition on the microstructure of polycrystals

Figure 5 shows a schematic bulk phase diagram with tie lines of the GB wetting phase transition. The most important feature of the GB phase transition is that below T_w the GBs can exist in equilibrium with a melt. Above T_w conversely the same GBs cannot exist in contact with a melt having the equilibrium liquidus concentration. The melt will penetrate along the GBs. In Fig. 5 the lines of GB wetting phase transitions are drawn. The microstructures of two-phase polycrystals are schematically shown for three different temperature intervals. Below T_{w1} all contact angles $\theta > 0$ and the liquid phase has the form of isolated droplets. Above T_{w1} some GBs are wetted and other are not wetted. Above T_{w2} most GBs are wetted and the solid phase may exist only as isolated single crystalline "islands" in the "sea" of melted phase. In principle the GBs with very low energy (twin GBs, low angle GBs) can have very high T_w . In a study of the melting of polycrystalline Cu-In solid solutions [24] it was shown that the wetting of GBs and the subsequent migration of liquid films at the GBs play an important role during the melting process. In particular, in alloys quenched from the temperatures a few degrees above the solidus small droplets of a liquid phase were observed at the ends of twin plates, while the coherent twin boundaries of the same twin plate were not wet [23]. This indicates that the annealing temperature (before quenching) was above T_w for incoherent GBs (at the ends of the twin plate) with high energy but below T_w for the coherent twin GB which has a very low energy.

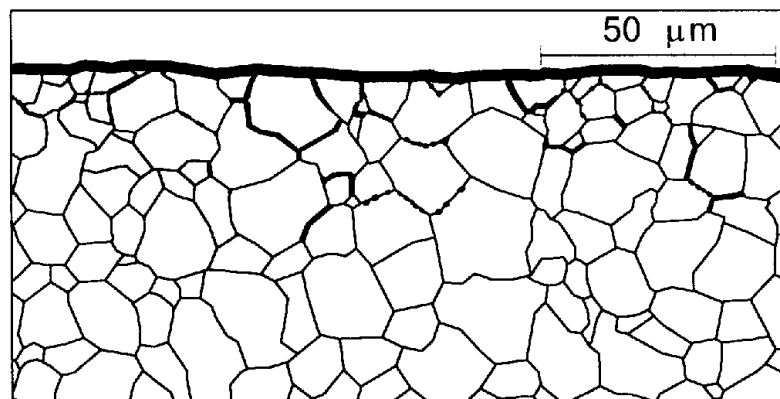


Fig. 6. The microstructure of a W polycrystal after penetration of a Ni-rich melt from the surface at 1600°C for 1h.

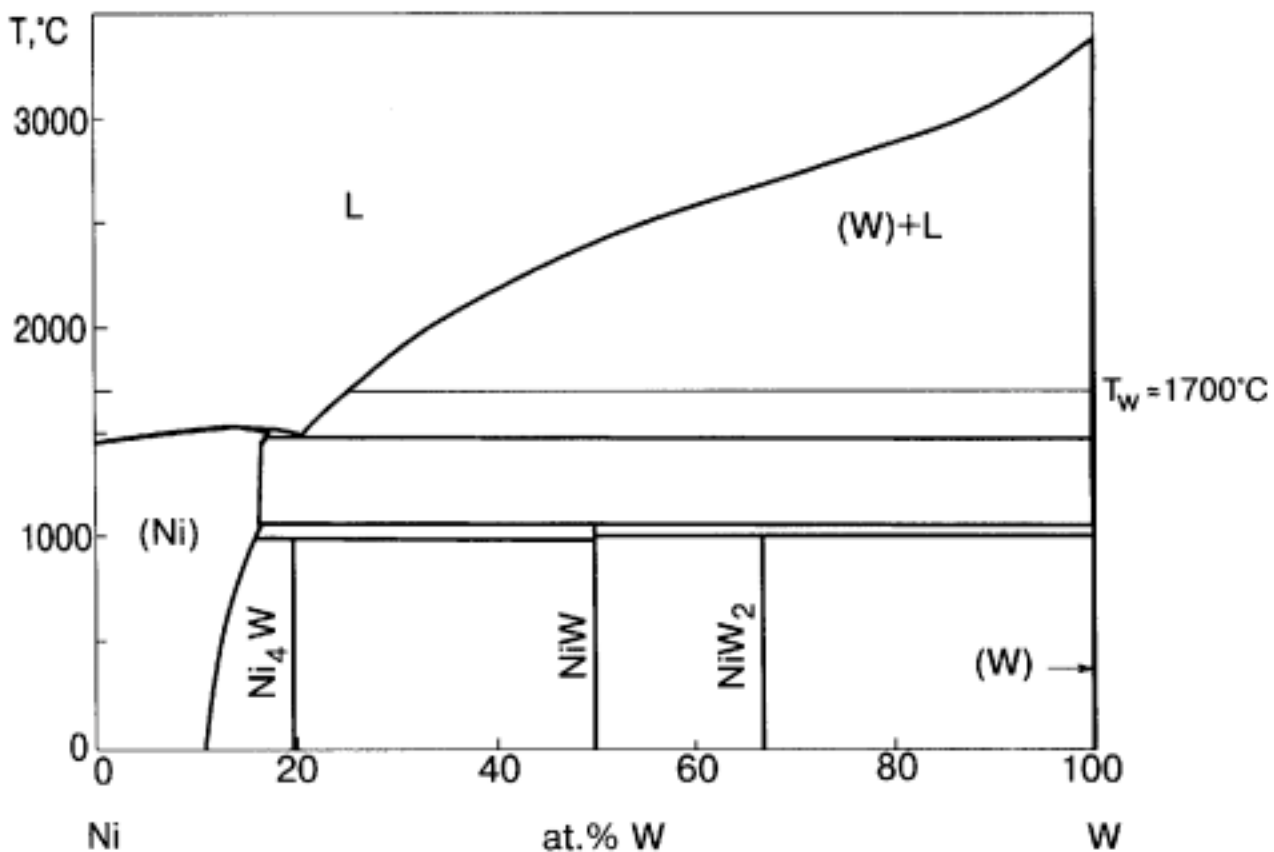


Fig. 7. The W-Ni phase diagram along with a tie line of the GB wetting phase transition.

7. Penetration of a liquid phase along GBs

The penetration and distribution of a liquid phase along GBs play a very important role in liquid phase sintering of refractory metals. Complete wetting of the solid by the liquid is believed necessary for a full densification during the liquid phase sintering of materials containing a high volume fraction of the solid phase. The parameters of liquid phase sintering (for example, the spacing between the solid particles) depend critically on the wetting angles θ in the contacts between the liquid phase and particles [25, 26]. Liquid bridges between particles with different θ may assume different forms [26], and the spacing dependencies of the force between such particles are also very different for different values of θ [27]. For low wetting angles the force F between the particles is attractive and during the sintering it presses the particles together [25]. For large θ the force F is repulsive at little spacings and is attractive only at large spacings [25]. In this case during the sintering an equilibrium spacing exists and at lower spacings the particles repel each other. This difference between the forces for high and low θ values controls the process of particle rearrangement. It was shown that in W-Ni alloys during the initial stages of sintering the original polycrystalline W powder dissolved into single crystals due to the penetration of liquid Ni along the GBs. However, after long sintering periods, microstructural studies clearly indicate that some of the W single crystals move about within the liquid and subsequently contact and coalesce into a single particle. This indicates that in some temperature interval above the eutectic temperature T_e in the W-Ni system the low energy GBs are not wet and the high energy GBs are wet by the liquid phase. The penetration of a Ni-rich melt into W polycrystals was investigated at 1600, 1800 and 2000°C [29]. After annealing at 1600°C the Ni-rich phase penetrated along the GBs to a depth of about 50 μm into the W polycrystal. This temperature lies about 100°C above the eutectic temperature of the W-Ni system. In the penetration layer there are three types of GBs (Fig. 6):

- GBs which were wet with a Ni-rich melt at the annealing temperature. The Ni-rich phase formed a uniform flat thick layer on these GBs;
- GBs which were partially wet with a Ni-rich melt at the annealing temperature. The Ni-rich phase formed droplets on these GBs;

GBs which were not wet with a Ni-rich melt at the annealing temperature. There are no visible macroscopic layers or particles of the Ni-rich phase on these GBs.

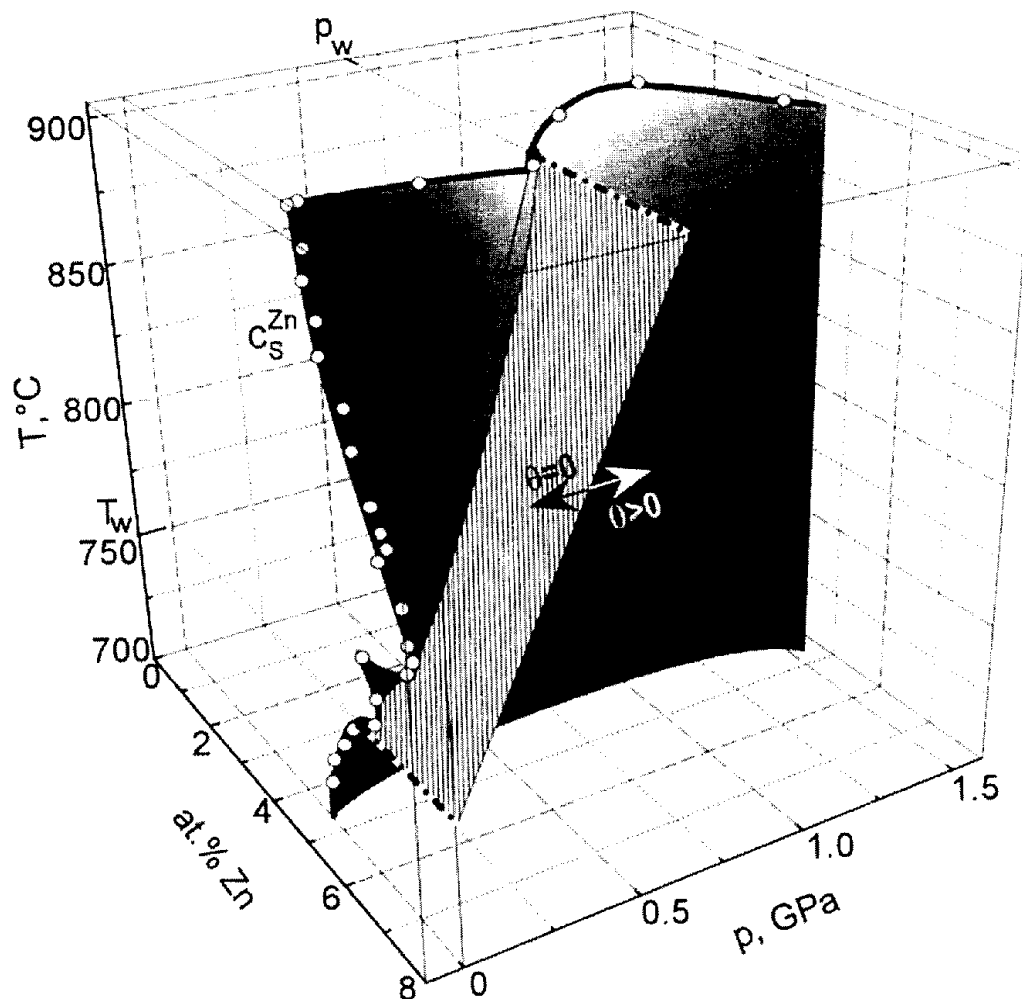


Fig. 8. The Fe-12 at.% Si-Zn three-dimensional bulk phase diagram in the coordinates "Zn concentration-temperature-pressure" along with the surface of wetting/dewetting phase transition (light) for a $38^\circ\langle 001 \rangle \{001\}$ tilt GB. This surface divides the two-phase area of the bulk phase diagram into two subspaces where the complete (low p , high T) and the partial (high p , low T) wetting of the GB by the Zn-rich melt occur.

At the higher temperatures investigated (1800 and 2000°C) Ni also penetrates along the GBs into the W polycrystal. But in these cases the penetration is more uniform: in the penetration layer there are no partially wet GBs with droplets of the Ni-rich phase. Therefore, the temperature above which practically all GBs are wetted in the W-Ni system lies at about 1700°C (see the phase diagram in Fig. 7).

8. Pressure influence on the GB wetting phase transition

The specific volume of the liquid phase is higher than that of the solid one. Therefore, if the GB is wetted by a liquid phase (above T_w), an increase of the pressure at constant temperature can lead to the dewetting of the GB. The studies of the wettability of GBs in Fe-Si alloys under high hydrostatic pressure show that the wetting of GBs by the Zn-rich melt disappears as the pressure increased. In Fig. 7 three-dimensional phase diagrams are shown in the coordinates "Zn concentration-temperature-pressure" and "Zn concentration-Si concentration-pressure". They show the surfaces of the Zn solubility limit (solidus and solvus) in Fe-Si solid solutions together with the surfaces of the GB wetting phase transition. The pressure of the GB dewetting transition decreases with increasing of the Si content in the alloy.

9. GB phase transitions in the bulk solid solution (prewetting or premelting)

The GB wetting phase transitions occur in a two-phase area of the bulk phase diagram where the solid and liquid phases are in equilibrium. Above the tie line of the GB wetting transition the GB cannot exist in equilibrium with the melt and is substituted for a layer of a liquid bulk phase. It is possible from the

