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GRAIN BOUNDARY PHASE TRANSITIONS

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Phase transitions and wetting phenomena belong to the most important topics in the field of thermodynamics of condensed matter. Only in the last few decades it was 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**). Recently the lines of the grain boundary (**GB**) phase transitions begin to appear in the bulk phase diagrams [1,2]. The addition of these equilibrium lines to the bulk phase diagrams ensures the adequate description of polycrystalline materials. In some cases the complete phase diagrams showing also GB lines should help to understand the processes of microstructure formation in various important technologies like liquid phase sintering [3] or isothermal solidification [4].

One of the most important GB phase transitions is the *GB wetting transition*. Consider the contact between a bicrystal and a liquid phase L (Fig.1). If the GB energy σ_{GB} is lower than $2\sigma_{SL}$ (σ_{SL} being the energy of solid-liquid interface), the GB is not wetted and the contact angle $\theta > 0$ (Fig.1a). If $\sigma_{GB} > 2\sigma_{SL}$ the GB is wetted by the liquid phase and $\theta = 0$ (Fig.1b). If the temperature dependencies $\sigma_{GB}(T)$ 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 (Fig.1d). 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 conode 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 polycrystalline samples: Zn–Sn [5], Al–Sn [6,7], Al-Cd [7], Al–In [7], Al–Pb [6] and Ag–Pb [8]. In later measurements bicrystals with individual GBs are also used: (Fe–Si)–Sn [9], (Fe–Si)–Zn [9,10], and Cu–In [1].

If two GBs have different energies σ_{GB1} and σ_{GB2} the temperatures of GB wetting transitions T_{w1} and T_{w2} will also differ: the lower σ_{GB}, the higher T_w (Fig.1d). Therefore, 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. The experiments show that this difference is not negligible. For example, the difference between T_w for GBs in Cu bicrystals in contact with an In-rich melt is about 30°C [1]. Therefore, it is not correct to measure T_w in polycrystals. For the construction of GB wetting transition conodes in the bulk phase diagram bicrystals with GBs having different σ_{GB} values must be used.

Figure 2 shows the Al–Sn bulk phase diagram along with the conodes 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 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 [5] or Al–Cd [7] the GB wetting temperatures coincide also with temperatures where the liquidus line has a low concentration slope. This is not surprising

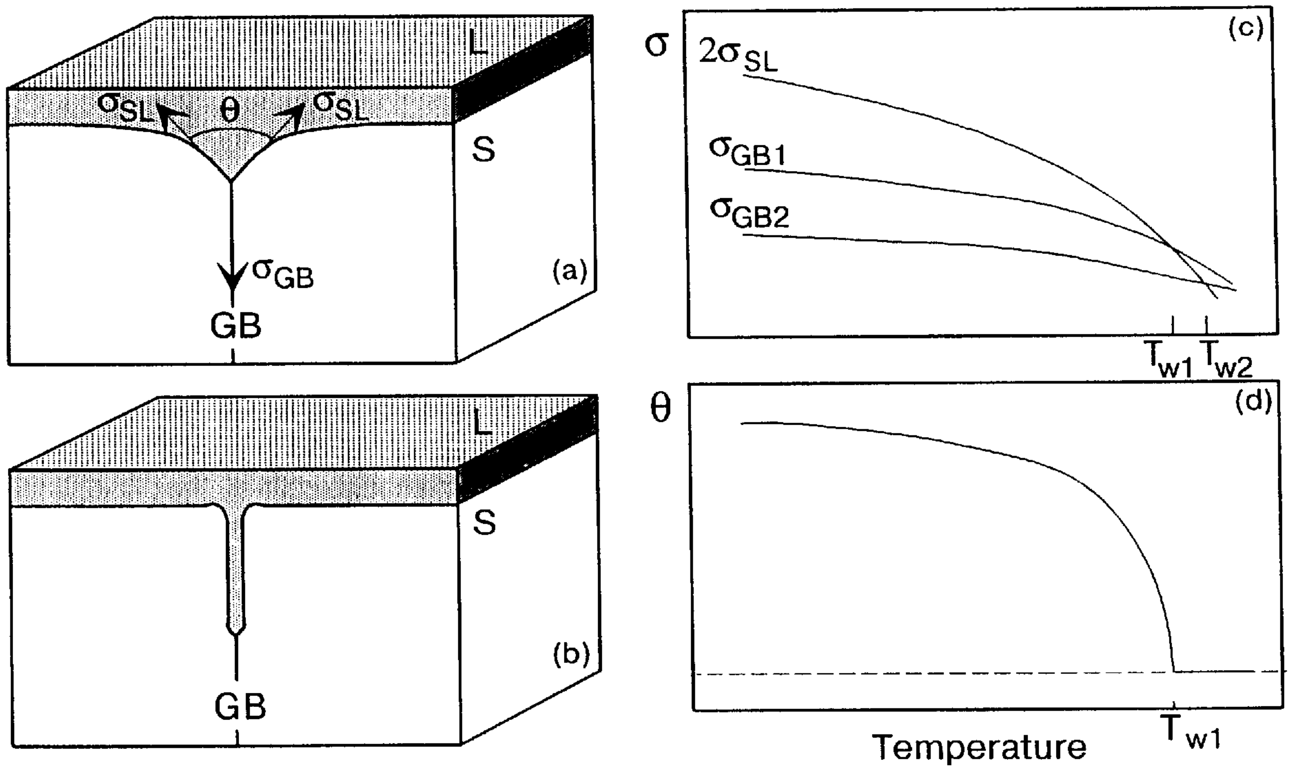

Fig.1. (**a**) Bicrystal in contact with a liquid phase. GB is not wetted: θ>0. (**b**) GB is wetted: θ=0. (**c**) Schematic temperature dependencies of GB energy $\sigma_{GB}(T)$ and energy of two solid-liquid interphase boundaries $2\sigma_{SL}(T)$. They intersect at temperatures T_{w1} and T_{w2} of GB wetting phase transition. (**d**) Schematic temperature dependency of contact angle θ corresponding to the scheme in Fig.1c.

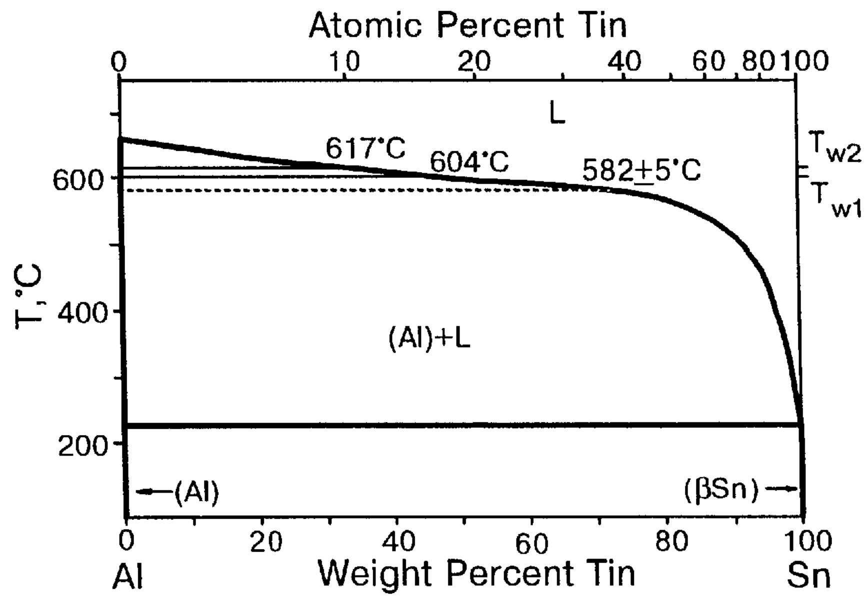

Fig. 2. Al–Sn bulk phase diagram (thick solid lines) [14] along with the tie lines of GB wetting transition (thin solid lines) at T_{w1} = 604±1°C for the tilt 32°<011>{001} GB and at T_{w2} = 617±1°C for the tilt 38.5°<011>{001} GB. The extrapolated *minimal possible temperature* of GB wetting phase transition T_{wmin} = 582±5°C for the GBs with *maximal energy* is also shown (dotted line).

because in this case the difference between 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.

Figure 3 shows a schematic bulk phase diagram with lines of GB wetting phase transition. The most important feature of the GB phase transition is that below T_w the GBs can exist in equlibrium 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. Of course, this penetration process has its own kinetics and needs a distinct time. In Fig.3 three lines of GB wetting phase transitions are schematically shown analogously to Fig.2. The microstructures of two-phase polycrystals are also schematically shown for four different temperature intervals. Below T_{wmin} all contact angles $\theta>0$ and the liquid phase has the form of isolated droplets. Above T_{wmin} and between lines of wetting phase transition for other GBs 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 the limit of zero misorientation angle ($\phi\to0$) also the GB energy $\sigma_{GB}\to0$ and $T_w \to T_m$, where T_m is the melting temperature.

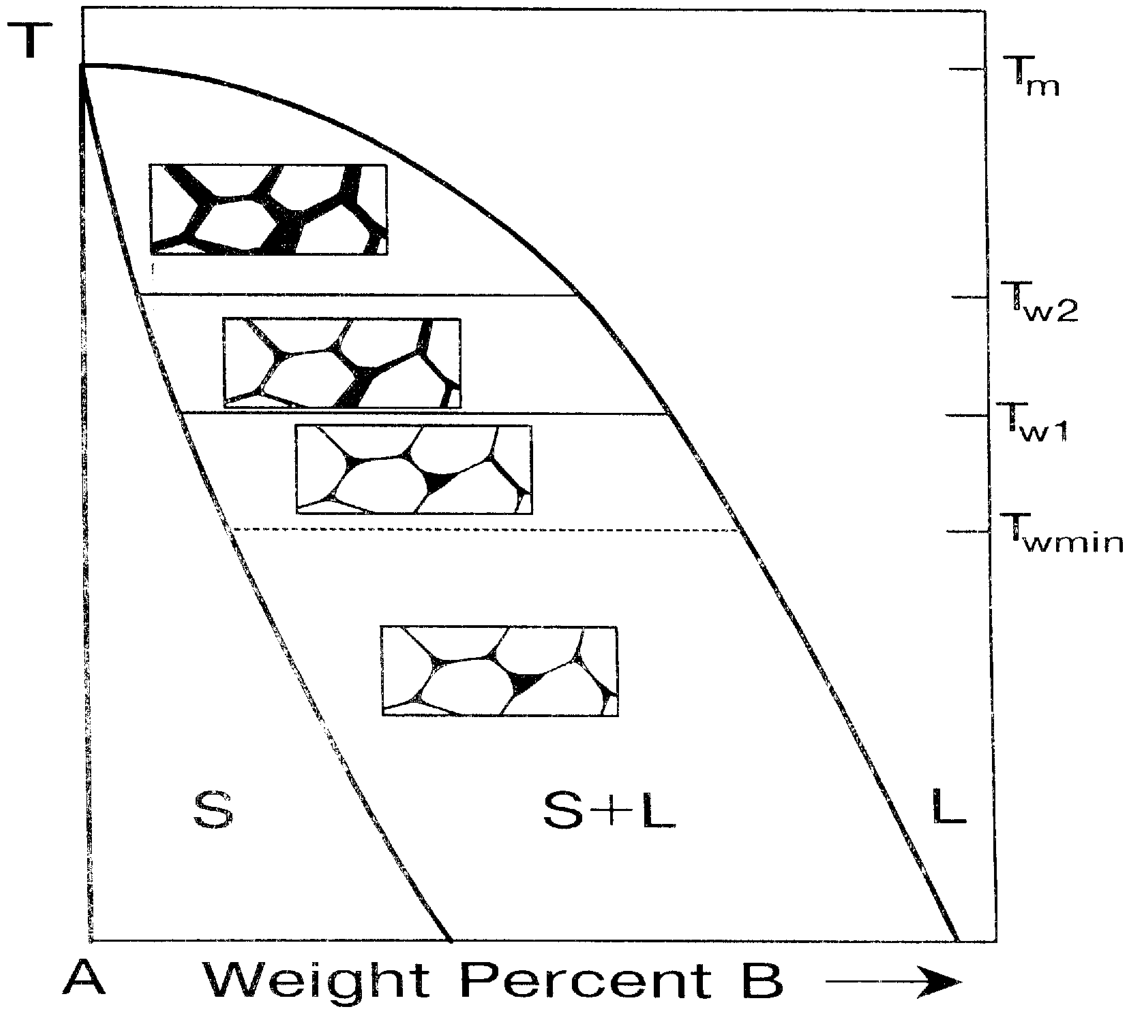

Fig.3. A schematic phase diagram showing the lines of GB wetting phase transitions and the corresponding microstructures of two-phase polycrystals.

The information about GB wetting phase transitions is important not only for the two-phase alloys. In homogeneous solid solutions other GB phase transitions can take place [2,11] which can essentially alter the GB properties [9,10,12,13] and therefore those of polycrystals. The lines of GB phase transitions like **prewetting or premelting** must begin at the end of the conode of GB wetting transition on the solidus line [10,11]. In case of prewetting phase transition a microscopic quasi-liquid layer appears on the GB in the conditions when the liquid is not thermodynamically stable.

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