

Grain boundary wetting-related phase transformations in Al and Cu-based alloys. Review

B. B. Straumal^{1-4,†}, O. A. Kogtenkova¹, A. B. Straumal^{1,4}, B. Baretzky³

[†]straumal@issp.ac.ru

¹Institute of Solid State Physics of RAS, 2 Ac. Ossipyan str., Chernogolovka, 142432, Russia

²Chernogolovka Scientific Center of RAS, 9 Lesnaya str., Chernogolovka, 142432, Russia

³Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology,

Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

⁴National University of Science and Technology «MISIS», 4 Leninskii ave., Moscow, 119049, Russia

The phase transformations can proceed not only in the bulk phases but also on free surfaces and in grain- and interphase boundaries. In this review we consider the grain boundary phase transformations in Cu- and Al-based alloys. In particular, among those transformations are the transitions between complete and incomplete grain boundary wetting. The wetting phase can be either liquid or solid. If the wetting phase is solid, the fraction of wetted grain boundaries can increase also with decreasing temperature. The transition itself can be discontinuous (of the first order) or continuous (of the second order). The thin layers of grain boundary phases (called also the grain boundary complexions) can occur in the conditions (temperature, pressure and concentration) where only one volume phase is thermodynamically stable. The phenomenon of the pseudo-incomplete (or pseudo-partial) grain boundary wetting is also discussed. In this case the wetting phase characterized by non-zero grain boundary contact angle coexists with a thin continuous layer of grain boundary phase. The new lines of respective grain boundary phase transformations appear in the conventional phase diagrams for the bulk phases. The grain boundary phase transitions can strongly influence the properties of grain boundaries themselves and those of polycrystals as a whole. For example, the presence of grain boundary layers can increase the plasticity (if the phase is ductile) or decrease it (if the grain boundary phase is brittle). The effect of grain boundary phase transitions on properties of polycrystalline material increases with decreasing grain size and becomes critical in nanograined materials.

Keywords: grain boundaries, phase transformations, metastable phases, Al-Zn, Al-Mg, Cu-Ag, Cu-Co.

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Фазовые превращения в сплавах меди и алюминия, связанные со смачиванием границ зерен. Обзор

Страумал Б. Б.^{1-4,†}, Когтенкова О. А.¹, Страумал А. Б.^{1,4}, Баретцки Б.³

[†]straumal@issp.ac.ru

¹Институт физики твердого тела РАН, ул. Академика Осипьяна 2, Черноголовка, 142432, Россия

²Черноголовский научный центр РАН, ул. Лесная 9, Черноголовка, 142432, Россия

³Технологический Институт Карлсруэ, Институт нанотехнологий,
пл. Германа фон-Гельмгольца, 1, 76344 Эггенштайн-Леопольдсхафен, Германия

⁴НИТУ МИСиС, Ленинский пр-т 4, Москва, 119049, Россия

Фазовые превращения могут происходить не только в объеме, но и на внешних поверхностях, а также на границах зерен и межфазных границах. В этом обзоре рассмотрены фазовые превращения на границах зерен в сплавах на основе меди и алюминия. В частности, к таким превращениям относятся переходы между полным и неполным смачиванием границ зерен. Фаза, смачивающая границу зерен, может быть как жидкой так и твердой. Если смачивающая фаза является твердой, доля полностью смоченных границ может возрастать с понижением температуры. Переход между полным и неполным смачиванием границ зерен может быть как первого, так и второго рода (непрерывным).

Тонкие слои зернограничных фаз могут также возникать в условиях (температура, давление и концентрация), где термодинамически устойчива только одна объемная фаза. Также в обзоре обсуждается явление псевдо-неполного (или псевдо-частичного) смачивания границ зерен. В этом случае смачивающая фаза характеризуется ненулевым граничным краевым углом с границей зерен, сосуществующим с тонким сплошным слоем зернограничной фазы. Новые линии фазовых превращений на границах зерен появляются на обычных фазовых диаграммах для объемных фаз. Зернограничные фазовые переходы сильно влияют как на свойства границ зерен так и поликристаллов в целом. Например, наличие пограничных слоев зерен может увеличить пластичность (если зернограничная фаза является пластичной) или уменьшить ее (если зернограничная фаза хрупкая). Влияние фазовых переходов на границах зерен на свойства поликристаллического материала возрастает с уменьшением размера зерен и становится критическим в наноразмерных материалах.

Ключевые слова: границы зерен, фазовые превращения, метастабильные фазы, Al-Zn, Al-Mg, Cu-Ag, Cu-Co.

1. Introduction

The can phase transformations can proceed not only between bulk phases but also in free surfaces, grain boundaries (GBs) and interphase boundaries (IBs). It has been theoretically predicted for the first time in 1970ies by Cahn [1] and Ebner and Saam [2]. Experimental evidences of GB phase transformations obtained later were described in numerous review papers [3–13]. As a result, new lines of GB phase transformations were added to the conventional bulk phase diagrams [14–27]. In this review we will discuss the GB phase transformations in Cu- and Al-based alloys.

It is relatively easy to observe the GB phase transitions which take place in the two-phase (or multiphase) regions of the bulk phase diagrams, like for example the GB wetting-dewetting phase transformations [8, 28–32]. In this case the thickness of a GB layer of a second (wetting) phase is macroscopic, reaches several microns and it can be observed even in the light microscope [33–35]. However, the GB phase transformations can take place also in the one-phase (or solid solution) regions of the bulk phase diagrams (like GB premelting, prewetting etc.) [8, 18, 36–45]. In this case the few-nm-thin layers of a second phase are formed in the GBs, and such phase is stable in GB but not stable in the bulk [18, 46–48]. There are several experimental troubles in observing such intergranular films (IGFs), their formation and disappearance. First, such IGFs are quite thin, and only recently appeared the reliable methods of their investigation like high-resolution transmission electron microscopy (HRTEM) in the aberration-corrected microscopes [17, 47, 49–52] as well as three-dimensional atom probe tomography (APT) [10, 48, 53, 54].

2. Main features of wetting-related GB phase transformations

In many cases the GB phase transformations take place at high temperatures, and the samples have to be quenched down to room temperature (RT) in order to be studied by HRTEM or 3D-APT. After such quenching one is never sure that the GB structure remained the same as it was at high temperature. From this point of view, the nitrides and oxides permit to “freeze” the high temperature structure easier than metallic alloys [9, 23, 55–63]. Therefore, it is not surprising that the first thin IGFs were observed in silicon nitride [64]. In case of metals, the quenching only seldom permits to conserve the high-temperature IGFs or their unambiguous

tracks [10, 22, 24, 47, 48, 65–68]. There are a big variety of intergranular films or phases and respective transformations between them [18–20, 62, 66, 67, 69–72]. Since seminal work of S. J. Dillon et al. [73] they are called GB complexions [11, 17, 18, 21, 22, 44, 47, 62, 63, 67, 72, 73–79]. Fortunately, even in the case if GB phases cannot be quenched down to RT from the high temperature for *ex-situ* studies, the GB phase transformations manifest themselves in change of GB properties or the properties of polycrystal as a whole [54, 80, 81]. These changes can be used for *in-situ* studies, i.e. measurements at temperatures where such GB transitions take place indeed. One can measure the GB migration rate [23, 82–84], GB diffusivity [85–88], GB energy or faceting/roughening [60, 78, 89–94], GB sliding [95–99] (GBs can become very ductile [100–102] or — oppositely — very brittle [103–105]), GB segregation [49–51, 53, 66, 70, 74, 104, 105–108] etc. One can study the GB-controlled properties of polycrystals like creep [100], superductility [109–119], strength [76, 120–122], grain growth [54, 56–59, 63, 75, 76, 79, 80, 83, 106, 123–130], densification by sintering [26, 57, 81, 131–136], electric conductivity [9, 95, 137–141], magnetic properties [142, 143] or thermal conductivity [144, 145]. The bulk phase transformations can be either endo- or exothermal. Therefore, they can be studied, for example, by the differential scanning calorimetry (DSC) [146, 147]. Fortunately, if the specific area of GBs in a polycrystal is high enough (fine grains), the thermal effect of GB phase transition also become measurable with the aid of DSC [114, 148–150]. The GB phase transformations (with formation of IGFs) also manifest themselves in the abnormal grain growth [54, 56–59, 63, 75, 76, 79, 80, 83, 106, 123–130].

According to conventional concepts of the bulk phase diagrams of binary systems, no phase transitions can occur in the bulk in a single-phase region (like in a solid solution). Nevertheless, thin layers of the second phase can be observed in grain boundaries and in GB triple junctions in the conditions where only one phase is stable in the bulk (see for example [8, 45, 68, 114, 148–150] and references therein). Usually, such thin GB layers are observed in the immediate vicinity of the solidus (or solvus) line. However, in the literature appear more and more indications that something unusual can proceed also “deep” in the solid-solution area, namely at temperature and/or concentration far away from solidus or solvus lines. For example, (a) the Al-based alloy exhibits anomalous superplasticity around 400°C [155], (b) the additional peaks in the differential scanning

calorimetry (DSC) curves appear in a single-phase region after heating of the fine-grained alloys obtained by different methods (ball milling, solidification under high pressure, etc.) [156, 157]; (c) hardening and softening behavior changes during plastic deformation at room temperature of aluminum alloys of the Al–Zn system after preliminary heat treatment in a single-phase region [158]. These phenomena were observed in fine grained materials and can indicate that GB phase transformation could occur in solid solutions also far away from solidus or solvus lines.

3. Wetting-related GB phase transformations in Al–Zn and Al–Mg alloys

The Al–Zn binary system is very rich on various GB phase transition phenomena. First, the transition from partial to complete wetting of (Al)/(Al) GBs by the melt has been observed in the two-phase (Al) + L area of the Al–Zn phase diagram [28]. In the (Al) + L area the (Al) solid solution is in equilibrium with the melt. The first (Al)/(Al) GBs completely wetted by the Al + Zn liquid phase appear above temperature $T_{wmin} = 440^\circ\text{C}$. The respective tie-line at $T_{wmin} = 440^\circ\text{C}$ is shown in Fig. 1a by the thin solid line. With increasing temperature the portion of completely wetted (Al)/(Al) GBs increases and reaches 100% at $T_{wmax} = 565^\circ\text{C}$ [28]. Above $T_{wmax} = 565^\circ\text{C}$ all (Al)/(Al) GBs are completely wetted by the Al + Zn melt. This GB wetting phase transition is of the first order. Namely, the temperature dependence of the contact angle between GB and melt is convex, and its first derivative has a discontinuity (or break) at T_w . Thermal effect of GB wetting phase transition can be observed by DSC [148]. The GB wetting phase transition of the second order (or continuous transition) has been observed in the two-phase (Zn) + L area of the Al–Zn phase diagram (marked as T_{w1} and T_{w2} in Fig. 1a) [29]. In this case the temperature dependence of the contact angle between GB and melt is concave, and its first derivative has no discontinuity at T_{w1} or T_{w2} .

The tie-lines of the GB wetting phase transition have a continuation in the one-phase (Al) area of the Al–Zn phase diagram, namely the so-called GB solidus line. The GB solidus is shown in Fig. 1a by the dotted line starting at $T_{wmin} = 440^\circ\text{C}$. The GBs between bulk solidus and GB solidus contain the thin layer of a liquid-like phase [68, 88, 159–165]. The experimental indications of this GB solidus (or premelting transition) have been observed using TEM by comparison of the samples quenched from the temperatures above and below bulk solidus line [68]. The GB premelting transition manifests itself also in the DSC curves. It has been shown that in nanocrystalline or UFG samples, the melting of GBs begins earlier than the melting of the volume (see the line of GB solidus) [68, 114, 166, 167]. These data allowed us to determine the temperature of GB solidus in Al–Zn alloys.

The presence of a thin liquid-like layer in GBs between bulk solidus and GB solidus makes the polycrystals very ductile. Thus, two teams of experimentalists independently observed the unusual superplastic behavior with maximal elongation up to 2500% in the Al–Zn–Mg UFG polycrystals in the very narrow temperature interval below solidus line [115–119]. This high superplasticity disappears with increasing concentration of Mg and Zn in the alloys. These

effects remained unexplained until the observation of the GB wetting transition in Al–Zn and Al–Mg binary alloys as well as in the Al–Zn–Mg ternary system [109–119, 166, 167]. The respective tie-lines at $T_{min} = 540^\circ\text{C}$ and $T_{max} = 610^\circ\text{C}$ are shown in the Al–Mg phase diagram (Fig 1b). Due to the GB wetting transitions in the two-phase (Al,Mg,Zn) + L area the respective GB solidus lines continue the wetting tie-lines into (Al,Mg,Zn) solid solution area and, therefore, are the reason of liquid-like GB layers leading to the high ductility [109–114, 168].

In the Al–Zn also another class of GB phase transitions occurs, namely when a grain boundary is wetted not by a liquid, but by a second solid phase. The thermodynamic condition of such a wetting remains the same. It means that a GB becomes substituted by a continuous layer of a second phase (no matter, liquid or solid) in case if the GB energy σ_{GB} becomes higher than the energy of two interphase boundaries, solid/liquid $2\sigma_{SL}$ or solid α /solid β $2\sigma_{\alpha\beta}$. For the first time such a transition has been observed in the two-phase area of the Al–Zn binary phase diagram where the (Zn) solid solution is in the equilibrium with the Zn-rich (Al) solid solution, just below the eutectic point at $T_e = 381^\circ\text{C}$ (see Fig. 1a) [169, 170]. The only difference with GB wetting by a liquid phase is that the kinetics is very slow. For example, in order to observe the transformation of a continuous GB layer of an (Al) phase between two (Zn) grains into a chain of lenticular particles, one needs to wait a couple of months instead of a couple of minutes (in case of a liquid phase in GBs). The portion of (Zn)/(Zn) GBs completely wetted by the (Al) fcc solid phase increases with increasing temperature from zero at $T_{ws} = 290^\circ\text{C}$ up to about 30% at $T_e = 381^\circ\text{C}$.

Similar GB phase transformation, namely the wetting of (Al)/(Al) GBs by a layer of second solid phase (Zn), takes place in the (Al') + (Zn) two phase area below the temperature of monotectoid decomposition $T_{mon} = 277^\circ\text{C}$ (see Fig. 1a) [150, 169, 171]. In this case the portion of (Al)/(Al) GBs completely wetted by a continuous layer of second solid phase (Zn) increases with decreasing temperature. It starts at $T_{wsmin} = 205^\circ\text{C}$. Unfortunately, the equilibration process takes place only very slow below 200°C , and we can only roughly estimate the temperature $T_{wsmax} = 125^\circ\text{C}$ where all (Al)/(Al) GBs become completely wetted by the (Zn) layer. Therefore, we used the HPT treatment in order to produce the non-equilibrium vacancies and to accelerate the processes in the (Al') + (Zn) alloys [172, 173]. As a result we observed the phenomenon of the so-called pseudopartial (or pseudoincomplete) GB wetting in the Al–Zn alloys after HPT [113, 174, 175]. In case of pseudopartial GB wetting, the non-zero contact angle between (Al)/(Al) GBs and (Zn) particles coexist with few nm thin Zn-rich layer in the (Al)/(Al) GBs. About 30% of all (Al)/(Al) GBs contain such IFGs [113]. We remember that the presence of thin liquid-like layers in GBs above GB solidus line leads to the high superplasticity of UFG polycrystals [109–119]. Similarly, the presence of thin solid Zn-rich layers in the solid Al–Zn UFG polycrystals also leads to their high ductility [109–114, 176]. The observation of pseudopartial GB wetting is not astonishing. We saw above that the GB wetting by the liquid phase in Al–Zn system can be either of first or second order [29]. According to the theoretical predictions, if the line of the first-order

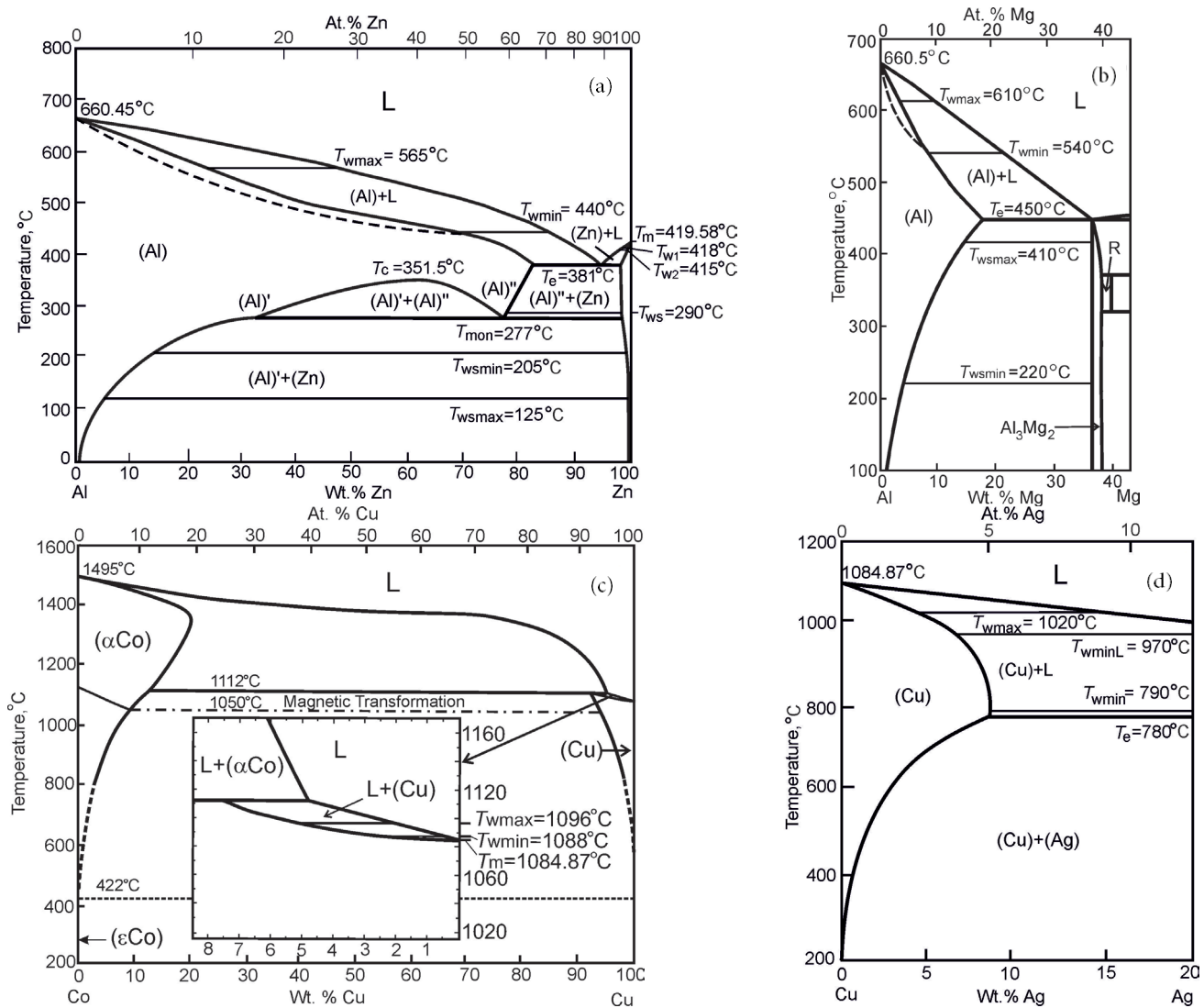


Fig. 1. The phase diagrams with lines of bulk phase transitions (thick lines) [151] and those of GB wetting phase transitions (thin solid lines) as well as GB prewetting and premelting (thin dotted lines) for the systems Al–Zn [29, 68, 88, 109 – 119, 166 – 175] (a), Al–Mg [150, 190] (b), Cu–Co [32, 154, 167, 191 – 193] (c), and Cu–Ag [151, 194] (d).

wetting transformation (from partial to complete wetting) divides into two lines, one of first and one of second order, between them appears the area of pseudopartial GB wetting [177 – 189]. In the (Al) + Al_3Mg_2 two-phase area of the Al–Mg binary phase diagram the transition from partial to complete wetting of (Al)/(Al) GBs by the second solid phase Al_3Mg_2 takes place [150, 190]. $T_{\text{wsmin}} = 220^\circ\text{C}$ all (Al)/(Al) GBs are incompletely wetted by the Al_3Mg_2 layers. Differently to the Al–Zn alloys, the percentage of completely wetted (Al)/(Al) GBs increases with increasing temperature and reaches 100% at $T_{\text{wsmax}} = 410^\circ\text{C}$.

4. Wetting-related GB phase transformations in Cu–Co and Cu–Ag alloys

The Cu–Co phase diagram contains the peritectic transition in the Cu-rich alloys. It means that in the two-phase solid + liquid area of the phase diagram the Co content in the solid solution is higher than that in the melt. Nevertheless, it has been observed that this Co-poor melt can completely wet the (Cu)/(Cu) GBs in the Cu-rich solution [32]. Moreover,

the DSC data permitted us to construct the line of GB solidus or GB premelting line (dotted line in Fig. 1c) just below the bulk solidus line [167]. In works of Zhevnenko et al. the creep of the Cu–Co solid solutions has been studied in details close to the bulk solidus [154, 191 – 193]. They observed the sudden break in the temperature dependences of creep rate even lower than our new DSC points (crosses in Fig. 1c). Such behavior can also be explained by the GB complexions transition.

The Cu–Ag phase diagram (Fig. 1d) is eutectic similar to the Al–Zn one. The Ag-rich melt can completely wet the (Cu)/(Cu) grain boundaries. The transition from partial to complete GB wetting of high-angle GBs (Cu)/(Cu) starts by increasing temperature at $T_{\text{wmin}} = 790^\circ\text{C}$ [194]. It is just above the eutectic temperature $T_e = 779^\circ\text{C}$ [151]. The transition from partial to complete GB wetting finishes at $T_{\text{wmax}} = 1020^\circ\text{C}$ [194]. Moreover, we observed that the low-angle GBs (they have lower energy than the high-angle GBs) become completely wetted above $T_{\text{wmax}} = 1020^\circ\text{C}$. First low-angle GBs (L) start to be completely wetted at $T_{\text{wminL}} = 970^\circ\text{C}$ [194]. These temperatures of GB wetting phase transitions

are shown in the Cu–Ag phase diagram (Fig. 1d) by the respective horizontal tie-lines (thin solid lines) in the (Cu) + L two-phase area.

The GB segregation in Cu–Ag was the topic of numerous modeling works. Thus, the model [195] predicts the transition from monolayer to multilayer segregation or even to thick premelting GB layer [196–198]. The authors of [72] investigated numerically a series of first-order layering transitions associated with grain-boundary segregation in a lattice-gas model of a binary alloy, in particular for the Cu–Ag alloys. Similar to [196–198] are the Monte-Carlo simulations of the [001]-axis symmetric tilt $\Sigma 5$ (310) GB in Cu–Ag alloys. The mean-field theory (effective Ising model) predicted the first order monolayer-to-multilayer phase transition in the first layers near the GB plane, which can be viewed as a generalized Fowler-Guggenheim transition [199, 200]. This transition can follow by the formation of rather thick prewetting GB layer [201]. The first-principles calculations for the $\Sigma 5$ (310) [001] symmetric tilt GB in Cu with Bi, Na, and Ag substitutional impurities explained why Bi causes embrittlement of Cu GBs and Ag does not [202].

5. Conclusions

Thus, we observed that the variety of GB wetting-related phase transformations is quite broad. They can strongly influence the properties of grain boundaries and those of polycrystals as a whole. This influence increases with decreasing grain size and becomes critical in nanograined materials. This short review did not include all “hot topics” in the area of GB phase transformations. In particular, we should discuss the problem of premelting phase transition in pure Al and Cu. Namely, is the grain boundary premelting transition in pure metal possible below the bulk melting point? In other words, should the grain boundary solidus line always terminate at the bulk melting point of the pure component? The GB wetting in Al–Ga system and the controversy surrounding it also remains for the next review paper. In addition to the wetting-related ones, other GB phase transformations can take place. For example, recent review of GB faceting-roughening can be found in Ref. [93].

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