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# A. B. Straumal, B. S. Bokstein, A. L. Petelin, B. B. Straumal, B. Baretzky, A. O. Rodin & A. N. Nekrasov

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- A. B. Straumal · B. S. Bokstein · A. L. Petelin ·
- B. B. Straumal · B. Baretzky · A. O. Rodin ·

A. N. Nekrasov

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Abstract The transition from incomplete to complete grain boundary (GB) wetting has been studied in the (Cu) + L region of the Cu–In phase diagram in the broad interval of In concentrations from 4 to 22 wt% In. The number of completely wetted GBs increases with increasing temperature and In content. With increasing amount of the melt the GBs with non-zero contact angle become apparently completely wetted. A geometrical model describing the influence of the amount of the liquid phase on the mean contact angle and the portion of completely wetted GBs has been developed. Using this model, the values of the temperatures of the start  $T_{\rm wmin} = 715$  °C and the end of the GB wetting transition  $T_{\rm wmax} = 986$  °C in the Cu–In system were determined.

A. B. Straumal · B. S. Bokstein · A. L. Petelin ·
B. B. Straumal (⊠) · A. O. Rodin
Moscow Institute of Steel and Alloys,
National University of Science and Technology,
Leninsky Prosp. 4, Moscow 119991, Russia
e-mail: straumal@issp.ac.ru; straumal@mf.mpg.de

A. B. Straumal · B. B. Straumal Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka 142432, Russia

B. B. Straumal · B. Baretzky
Karlsruher Institut f
ür Technologie (KIT),
Institut f
ür Nanotechnologie, Hermann-von-Helmholtz-Platz 1,
76344 Eggenstein-Leopoldshafen, Germany

A. N. Nekrasov Institute of Experimental Mineralogy, Russian Academy of Sciences, Moscow District, Chernogolovka 142432, Russia

### Introduction

If a two- or multicomponent polycrystal is partially melted, i.e., if the temperature is between the solidus temperature  $T_{\rm S}$ and the liquidus temperature  $T_{\rm L}$ , then the distribution of the liquid phase between solid grains depends on the wetting conditions of grain boundaries (GBs) [1, 2 and references therein]. This wetting phenomenon is particularly important in liquid phase sintering or the description of melt infiltration into rocks [3-5]. The GB is completely wetted if the contact angle  $\theta$  between GB and melt is zero  $\theta = 0^{\circ}$ . In this case, the GB separating the grains is completely substituted by the liquid phase. The GB is incompletely wetted if the contact angle between GB and melt is finite  $\theta > 0^{\circ}$ . In this case, the GB can exist in the equilibrium contact with the liquid phase. The most accurate measurement of a dihedral contact angle  $\theta$  is possible in the experiments with bicrystals [1, 2]. In this case,  $\theta$  is measured in the section perpendicular to the flat individual GB and to the straight contact line between the GB and the liquid phase. In polycrystals, the correct measurement of  $\theta$  is much more complicated. If a GB contains lenticular liquid droplets, they are formed by two spherical solid/liquid interfaces. The correct  $\theta$  value appears only in the section containing the common axis of both spherical solid/liquid interfaces. It can be measured either using transmission electron microscopy (TEM) [6] or by careful three-dimensional analysis of the droplet shape [7, 8]. Even if all GBs have the same energy and the same dihedral angle with the liquid phase, the conventional metallographic (or ceramographic, or petrographic) section would cross the lenticular particles in a random way. This would result in a certain scatter of measured  $\theta$  values around the true values of the dihedral contact angle.

The transition from incomplete to complete GB wetting proceeds at a certain  $T_w$  if the energy of two solid-liquid

interfaces  $2\sigma_{SL}$  becomes lower than the GB energy  $\sigma_{GB} > 2\sigma_{SL}$ . Cahn [9] and Ebner and Saam [10] first showed that the (reversible) transition from incomplete to complete wetting can proceed with increasing temperature, and that it is a true surface phase transformation. The GB wetting temperatures,  $T_w$ , depend both on GB energy and solid–liquid interfacial energy which, in turn, depend on the crystallography of these interfaces [11–13]. The transition from incomplete to complete GB wetting starts at a certain minimum temperature  $T_{wmin}$  which corresponds to



Fig. 1 Part of the Cu–In phase diagram [11] showing the points of annealings (*circles*)

the combination of maximum  $\sigma_{GB}$  and minimum  $\sigma_{SL}$ . The transition from incomplete to complete GB wetting finishes at a maximum temperature  $T_{wmax}$  which corresponds to the combination of minimum  $\sigma_{GB}$  and maximum  $\sigma_{SL}$ . The fraction of completely wetted GBs increases from 0 to 100 % as the temperature increases from  $T_{wmin}$  to  $T_{wmax}$ . However, according to the lever rule, the amount of liquid phase increases as well as the temperature increases from  $T_S$  to  $T_L$ . If the amount of the liquid phase is large, melted layers would separate the solid grains even if the contact angle  $\theta > 0^\circ$ . We can call this phenomenon *apparently complete GB wetting*.

The dependence of microstructure of semi-solid polycrystals on the amount of liquid phase has been discussed for many years. Beere [14] demonstrated that the gaseous or liquid phase in GB triple junctions forms a continuous network if its volume fraction is above a certain threshold value. The threshold volume fraction varies with dihedral angle and increases with increasing  $\theta$  [14, 15]. For example, for a dihedral angle of 15° already 2 % of liquid phase is enough to connect all quadruple points by liquid channels (in a quadruple point four grains contact each other and three triple junctions cross). For the microstructure of liquidphase sintered materials, a quantity known as the contiguity parameter has been defined [16, 17]. This is a quantitative measure of interphase contact, and is defined as the fraction of internal surface area of a phase shared with grains of the same phase in a two-phase microstructure. In liquid-phase sintering, these contacts serve a useful role in providing rigidity to a sintered compact, thereby controlling shape distortion. The contiguity depends strongly on the volume fraction of the solid phase and the dihedral angle; it increases with both parameters. At low dihedral angles, the contiguity increases rapidly as the volume fraction of the solid phase approaches unity [16]. Jurewicz and Watson [18] defined the



Fig. 2 SEM micrographs of a Cu-8 wt% In sample annealed at 952 °C and b Cu-12 wt% In sample annealed at 892 °C



Fig. 3 a Temperature dependence of the mean contact angle for the five Cu–In alloys studied. Histograms for the frequency distribution of contact angles at 772  $^{\circ}$ C for the **b** Cu–12 wt% In and **c** Cu–16 wt% In alloys

so-called equilibrium melt fraction which represents a minimum interfacial energy state when the melt is distributed uniformly along triple junctions in a partly melted polycrystal. The equilibrium melt fraction decreases with increasing  $\theta$ . For example, it is only 2 % for  $\theta = 40^{\circ}$  [18]. The  $\theta$  value also influences the early stages of liquid-phase sintering when individual grains "swim" in a melt and form the first contact necks [19].

The apparently complete GB wetting phenomenon will increase the percentage  $P_{\rm app}$  of completely wetted GBs over and above the equilibrium value  $P_{\rm equ}$ . The goal of this study is the experimental investigation of apparently complete GB wetting. For this purpose, we chose to study Cu–In alloys because it is known that the GB wetting phase transition exists in this system [20].

### Experimental

The Cu–In alloys with 4, 8, 12, 16, and 22 wt% In were prepared from high-purity components (5N8 Cu and 5N6 In) by the vacuum induction melting and casting into 10-mm diameter rods. The 2-mm thick slices were also cut

from these ingots and sealed into evacuated silica ampoules with a residual pressure of approximately  $4 \times 10^{-4}$  Pa at room temperature. Samples were annealed at temperatures between 712 and 992 °C for 2 h, and then quenched in water. The accuracy of the annealing temperature was



Fig. 4 Temperature dependence of the fraction of completely wetted Cu GBs *P* for the five Cu–In alloys studied



Fig. 5 Scheme for the distribution of a liquid phase in a GB segment with a length d between two triple junctions. Other variables are explained in text

 $\pm 2$  °C. The annealing points were in the two-phase (Cu) + L area of the Cu–In phase diagram (circles in Fig. 1) [21]. (The term (Cu) here represents the face-centered cubic solid solution phase based on Cu). After quenching, samples were 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 optical microscopy and scanning electron microscopy (SEM). The SEM investigations were carried out in a Tescan Vega TS5130 MM microscope equipped with a LINK energy-dispersive spectrometer produced by Oxford Instruments. Light microscopy was performed using a Neophot-32 light microscope equipped with a 10 Mpix Canon Digital Rebel XT camera. A quantitative analysis of the wetting transition was performed adopting the following criterion: every boundary between (Cu) grains was considered to be completely wetted only when a layer of In-rich film had covered the whole GB (Fig. 2a); if such a layer appeared to be interrupted, the GB was regarded as incompletely wetted (Fig. 2b). The contact angles  $\theta$  were measured simultaneously to the determination of complete or incomplete wetting. For the GBs completely covered by a liquid phase, the  $\theta = 0^{\circ}$  value was assigned. At least 100 GBs were analyzed at each temperature. Typical micrographs obtained by SEM are shown in Fig. 2.



Fig. 6 Scheme showing the evolution of the distribution of melt in GBs with increasing amount of a liquid phase for non-zero contact angle (from completely dry to completely wet GB)

### **Results and discussion**

In Fig. 2, the SEM micrographs of (a) Cu-8 wt% In sample annealed at 952 °C and (b) Cu-12 wt% In sample annealed at 892 °C are shown. Almost all GBs in Fig. 2a are completely wetted ( $\theta = 0^{\circ}$ ). In Fig. 2b, the incompletely wetted GBs  $(\theta > 0^{\circ})$  are also visible. The temperature dependence of the mean contact angle is shown in Fig. 3 for the five Cu-In alloys studied. The mean contact angle decreases with increasing temperature. However, the dependences for different alloys do not coincide with each other. The increase of In content leads to a decrease in the mean contact angle. Figure 4 shows the temperature dependence of the fraction of completely wetted Cu GBs P for the five Cu-In alloys studied. In this case, too, the dependences for different alloys do not coincide with each other. The increase of In content leads to an increase in the fraction of completely wetted Cu GBs P. It is obvious that the value of the contact angle  $\theta$  for a certain GB at a certain temperature is determined only by the energy of the GB  $\sigma_{GB}$  and the energy of two solid/liquid interphase boundaries  $2\sigma_{\rm SL}$  via the relationship  $2\sigma_{\rm SL} \cos(\theta/2) = \sigma_{\rm GB}$ . This is because the compositions and chemical potentials of (Cu) solid solution and liquid phase L are constant at constant temperature and are determined by the solidus and liquidus points at the ends of the tie-line for that temperature. They do not depend on the amount of the liquid phase. Why, nevertheless, we observe the differences in Figs. 3 and 4?

In Fig. 5, a scheme is shown for the distribution of liquid phase in a GB segment with a length *d* between two triple junctions. It is known that the triple junctions become completely wetted and filled by the melt at lower temperatures in comparison with GBs [14–16, 22, 23]. The GB in Fig. 5 is incompletely wetted by the melt and the contact angle  $\theta$  is around 40°. The shape of the melted pool in a triple junction can be approximated by one equilateral central triangle and three isosceles peripheral triangles each with base 2*a* and a height *t*. The distance between the base of one of the isosceles peripheral triangles and the center of the middle equilateral triangle is *r*. The length of the GB portion that remains dry is *x*. The full area of the liquid phase in the triple junction in this scheme is

$$S_{\text{sum}L} = 6a \times t + 2\sqrt{3} \times a^2. \tag{1}$$

t depends on a as

$$t = a \times ctg(\theta/2). \tag{2}$$

Therefore,

$$S_{\text{sum}L} = 6a^2 \times ctg\left(\frac{\theta}{2}\right) + 2\sqrt{3} \times a^2.$$
 (3)

This means that the area of the liquid phase depends only on a and the contact angle  $\theta$ . In other words, even if the contact

angle is non-zero (incomplete wetting), the melted pools from neighboring triple junctions can meet in the middle of a GB if the amount of the liquid phase increases. The length d of the remaining "dry" GB diminishes with increasing a. Moreover, at lower contact angle  $\theta$ , d decreases faster with increasing a. Figure 6a presents a scheme showing how the distribution of melt in GBs changes with increasing amount of liquid phase for non-zero contact angle. The evolution from completely dry to completely wet GBs is shown. It can be seen from this diagram that, with increasing amount of melt, the *apparently complete GB wetting* phenomenon should appear in a material. The apparently completely wetted GBs are characterized by a non-zero contact angle but, nevertheless, are filled with the liquid phase.

This fact is illustrated by the histograms for the frequency distribution of dihedral contact angles for the same temperature 772 °C but for the alloys with different In content and, therefore, different amounts of the melt (Fig. 3b, c). Both the distributions contain the high amount of completely wetted GBs. They are described as having zero dihedral contact angle  $\theta = 0^\circ$ . Both the frequency distributions of remained contact angles are asymmetrical, and the median values of contact angle  $\theta_{med}$  for those second peaks are also different for two alloys ( $\theta_{med} = 27^\circ$ in the Cu–12 wt% In alloy, Fig. 3b, and  $\theta_{med} = 50^\circ$  in the



Fig. 7 a Dependence of the relative amount of liquid phase needed for the linkup of the liquid pools in a hexagonal grain on the contact angle. **b** Corrected temperature dependence of the amount of completely wetted GBs

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Fig. 8 a Part of the Cu-In phase diagram. The narrow shaded area along solidus line shows the temperatures and concentrations where the true values of the mean contact angle and the amount of completely wetted GBs can be measured. In the broad shaded area along the liquidus line all GBs are apparently wetted. Above the tie-line at 986 °C all GBs are completely wetted. Below the tie-line at 715 °C all GBs are incompletely wetted. b SEM micrographs of Cu-16 wt% In, 712 °C (incomplete GB wetting); c Cu-12 wt% In, 772 °C (incomplete GB wetting); d Cu-4 wt% In, 992 °C (complete GB wetting); e Cu-22 wt% In, 752 °C (individual solid grains "swim" in the melt); f Cu-12 wt% In, 892 °C (microstructure is strongly influenced by the phenomenon of apparently complete GB wetting); g Cu-16 wt% In, 792 °C (above the tie-line at 986 °C, all GBs are completely wetted); h Cu-22 wt% In, 712 °C (below the tie-line at 715 °C, all GBs are incompletely wetted)



Cu–16 wt% In alloy, Fig. 3b). Moreover, the small contact angles in the class  $0^{\circ}-5^{\circ}$  are completely absent in the Cu–12 wt% In alloy (Fig. 3b). The class  $5^{\circ}-10^{\circ}$  is almost empty. In the Cu–16 wt% In alloy (Fig. 3c), already four classes  $(0^{\circ}-5^{\circ}, 5^{\circ}-10^{\circ}, 10^{\circ}-15^{\circ}, and 15^{\circ}-20^{\circ})$  are empty. The class  $20^{\circ}-25^{\circ}$  contains only few GBs. It means that the apparently completely wetted GBs "sweep out" the GBs with small contact angle from the distribution. The remained frequency distributions of the dihedral contact angles are also influenced by the apparently complete wetting of the short GBs with low length *d*.

The relative amount of a liquid phase needed for the linkup of the liquid pools in the hexagonal grain shown in Fig. 6a is

$$\frac{S_L}{S_{\text{sum}}} = \frac{\sqrt{3}ctg\frac{\theta}{2} + 1}{3ctg^2\frac{\theta}{2} + 2\sqrt{3}ctg\frac{\theta}{2} + 1}.$$
(4)

This dependence is shown in Fig. 7. It permits us to estimate the critical amount of a liquid phase required for apparently complete wetting. Below this value the measured mean contact angle and fraction of completely wetted GBs *P* are almost unaffected by the phenomenon of apparent wetting. This means that only the experimental points for low amounts of liquid phase from Figs. 3 and 4 can be used to characterize the true mean contact angle. The corrected temperature dependence of the amount of completely wetted GBs is shown in Fig. 7b. This permits us to determine the true values of  $T_{\rm wmin} = 715$  °C and  $T_{\rm wmax} = 986$  °C.

The main parameter responsible for the spread of wetting temperatures between  $T_{\rm wmin}$  and  $T_{\rm wmax}$  is the GB anisotropy [24]. Indeed, the anisotropy of the solid–liquid interfacial energy is much lower (within a few % for metallic systems) than that of grain boundaries [25 and references therein]. In principle, the GB character distribution may also change with temperature [26-28]. This can occur if the starting polycrystal is annealed for a sufficiently long time to cause the grain growth. However, in our case the disks of each alloy were cut from the same ascast sample and immediately annealed in the (Cu) + L area of the Cu-In phase diagram. This means that the GB character distribution (GBCD) in the disks of each alloy should be rather similar. However, the GBCD could be different in the alloys with different indium contents. It has to be emphasized that the energy distribution of the same GB array can also change with temperature, in particular, due to the faceting-roughening transitions in the coincidence and near-coincidence boundaries [11, 29].

The narrow shaded area in the (Cu) + L region of the Cu– In phase diagram near to the solidus line shows the temperatures and concentrations where the true values of the mean contact angle and the fraction of completely wetted GBs can be measured (Fig. 8a). The corresponding microstructures are shown in Fig. 8b-d. In the broad shaded area adjacent to the liquidus line all GBs are apparently wetted. This is because the amount of liquid phase is high according to the lever rule, and the individual solid grains "swim" in the melt (Fig. 8e). Between the shaded reliability area at the solidus line and the shaded liquid-pool area at the liquidus line the microstructure is strongly influenced by the phenomenon of apparently complete GB wetting (see the microstructure in Fig. 8f). Above the tie-line at  $T_{\text{wmax}} = 986 \text{ }^{\circ}\text{C}$  all GBs are completely wetted (Fig. 8g). Below the tie-line at  $T_{\rm wmin} = 715$  °C all GBs are incompletely wetted (Fig. 8h), and the apparently complete GB wetting is almost negligible. In Fig. 8b, c, e (as well as in Fig. 2), the ex-liquid phase in some GBs displays a kind of "dendrites." We explained recently [30] that at highest temperatures, when all or almost all high-angle GBs are wetted, the liquid phase starts to wet the low-angle GBs (dislocation walls) and to penetrate into the bulk along these cell boundaries.

In this article, we have considered the phenomenon of apparently complete GB wetting by a liquid phase. However, the wetting phase can also be solid [31–34] or even amorphous [35, 36]. Nevertheless, all conclusions derived in this study would be valid also for the GB wetting by a solid phase. The only important difference is that in this case the equilibration time is much longer than in the case of liquid phase GB wetting [31–34].

### Conclusions

- 1. The amount of liquid phase influences the morphology of a partially melted polycrystal with completely and incompletely wetted GBs.
- 2. On increasing the amount of liquid phase, the incompletely wetted GBs become apparently completely wetted.
- 3. The structural model of a polycrystalline sample with GB wetted by the second liquid phase is developed. This model permits us to estimate the correct values of contact angles.
- 4. Using this model, corrected values for the temperatures of the start  $T_{\text{wmin}} = 715 \text{ °C}$  and the end of the GB wetting transition  $T_{\text{wmax}} = 986 \text{ °C}$  were defined.
- The collected data permit us to determine the areas of dominance of the two wetting structure formation factors in the two phase (Cu) + L region of the Cu–In phase diagram.

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