

## Reversible “Wetting” of Grain Boundaries by the Second Solid Phase in the Cu–In System

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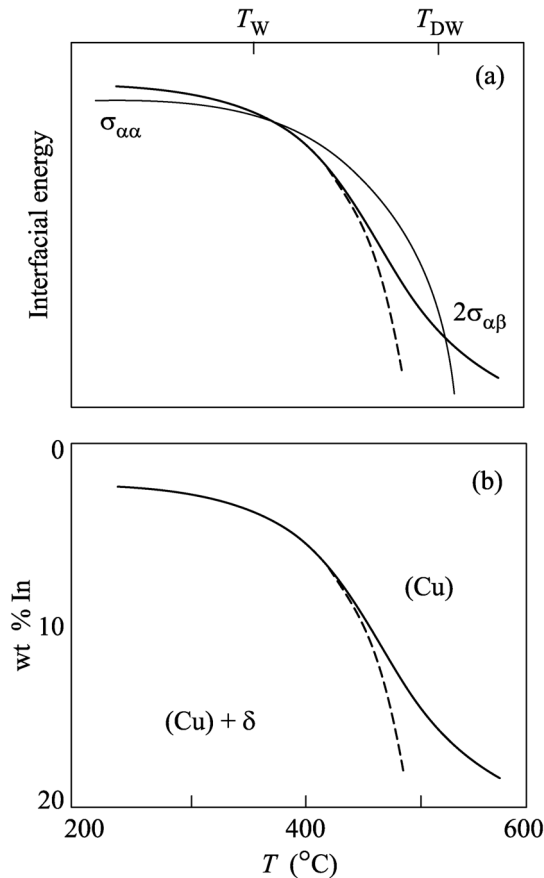
The reversible wetting of grain boundaries by the second solid phase in the copper–indium system has been observed. With an increase in the temperature, the contact angle  $\theta$  between the (Cu)/(Cu) grain boundary in a Cu-based solid solution based and particles of the  $\delta$ -phase ( $\text{Cu}_{70}\text{In}_{30}$ ) decreases gradually. Above  $T_W = 370^\circ\text{C}$ , the first (Cu)/(Cu) grain boundaries completely “wetted” by the  $\delta$  phase appear in Cu–In polycrystals. In other words, the  $\delta$  phase forms continuous layers along grain boundaries and  $\theta = 0$ . At  $440^\circ\text{C}$ , the fraction of completely wetted grain boundaries reaches a maximum (93%), whereas the average contact angle reaches a minimum ( $\theta = 2^\circ$ ). With a further increase in the temperature, the fraction of completely wetted grain boundaries decreases and vanishes again at  $T_{DW} = 520^\circ\text{C}$ . This phenomenon can be explained by an anomalous shape of the solubility limit curve of indium in a solid solution (Cu).

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The wetting of internal interfaces is of great interest not only for numerous applications but also for fundamental science [1, 2]. As early as the 1970s, it was shown that the transition from incomplete wetting to complete wetting is a true phase transition [3, 4]. In such a thermodynamic consideration, the free energy per unit area of an interface plays the same role as the free energy per unit volume in the theory of normal bulk phase transitions. The analysis showed that the temperature dependences of the free energies of two interfaces between the solid and liquid phases and of grain (crystallite) boundaries in principle can intersect each other at a certain temperature (see Fig. 1a). This temperature  $T_W$  is called the wetting phase transition temperature. This phase transition occurs because the free energy of the two interfaces between the solid and liquid phases  $2\sigma_{SL}$  below  $T_W$  is higher than the energy of the grain boundary  $\sigma_{GB}$ . In this case, the liquid phase constitutes lenticular droplets at the grain boundary with a nonzero contact angle  $\theta$  (incomplete wetting). If (above the temperature  $T_W$ ) the energy  $\sigma_{GB}$  of the grain boundary is higher than the energy  $2\sigma_{SL}$  of the two interfaces between the solid and liquid phases,

the existence of the grain boundary in contact with a liquid becomes thermodynamically unfavorable. In this case, the grain boundary should be replaced by a liquid-phase layer. This situation is called complete wetting. The free energy of any interface decreases with an increase in the temperature because of the entropy contribution  $-T\Delta S$ . The energy of the interface between the solid and liquid phases will obviously decrease with an increase in the temperature more rapidly than the energy of the grain boundary between two solid crystallites (since the entropy of the liquid phase is always higher than the entropy of the crystal). The phase transitions of wetting of grain boundaries by a melt were studied in detail both in polycrystals [5–9] and in specially grown bicrystals [10] with individual grain boundaries [11, 12].

The second, wetting, phase can also be solid. In this case, the word “wetting” should not shade the thermodynamic meaning of the phase transition. This meaning remains unchanged: if the energy  $\sigma_{\alpha\alpha}$  of the  $\alpha/\alpha$  grain boundary in the  $\alpha$  phase is lower than the energy  $2\sigma_{\alpha\beta}$  of the two interfaces between the  $\alpha$  and  $\beta$  phases, the  $\alpha/\alpha$  grain boundary can exist in equilibrium con-



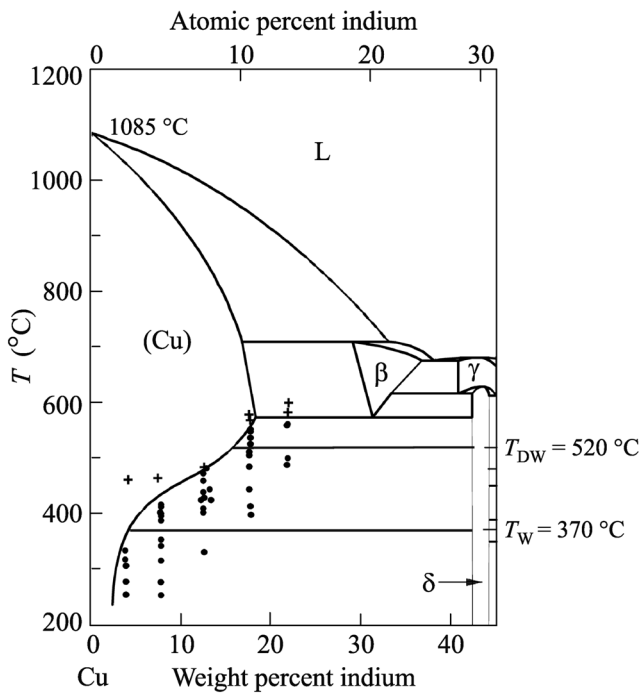
**Fig. 1.** (a) Schematic temperature dependences of the energies of (thin solid line  $\sigma_{\alpha\alpha}(T)$ ) (Cu)/(Cu) grain boundaries and (thick solid line  $2\sigma_{\alpha\beta}(T)$ ) (Cu)/ $\delta$  interfaces. The dashed line is the conventional dependence  $2\sigma_{\alpha\beta}(T)$ . Between the temperatures  $T_W = 370^\circ\text{C}$  and  $T_{DW} = 520^\circ\text{C}$ , (Cu)/(Cu) grain boundaries completely wetted by the  $\delta$  phase are observed in polycrystals. (b) (Solid line) Temperature dependence of the solubility limit of indium in the (Cu) solid solution taken from the phase diagram of Cu–In (Fig. 2). The dashed line is the conventional dependence of the solubility limit of the second component in the solid solution [25].

tact with the  $\beta$  phase. If the energy  $2\sigma_{\alpha\beta}$  is lower than  $\sigma_{\alpha\alpha}$ , the  $\alpha/\alpha$  grain boundary should be replaced by the layer of the second solid phase  $\beta$ . This transition does not thermodynamically differ from wetting by the liquid phase, but it takes much longer time than liquid-phase wetting for kinetic reasons. However, there is an important difference because, if both phases are solid, it is unobvious that the free energy of the interface between the phases decreases with the temperature faster than the free energy of the grain boundary. This means that the mutual position of the curves  $2\sigma_{\alpha\beta}(T)$  and  $\sigma_{\alpha\alpha}(T)$  can be different. In particular, complete wetting can be implemented at a low temperature and can be transferred to incomplete wetting with an increase in the temperature. Furthermore, the curves  $2\sigma_{\alpha\beta}(T)$  and  $\sigma_{\alpha\alpha}(T)$  can intersect each other twice (see

Fig. 1a). In this case, for example, incomplete wetting is replaced by complete wetting at  $T_W$  (subscript W means wetting), then disappears again, and is transformed to incomplete wetting at  $T_{DW}$  (subscript DW means dewetting). “Wetting” of the grain boundary by the second solid phase was theoretically analyzed in detail in [13–17] and was studied experimentally in [18, 19]. In particular, in the aluminum–manganese system, a “usual” order of transformations was observed: incomplete wetting of boundaries in aluminum by the  $\text{Al}_3\text{Mg}_2$  phase at low temperatures and complete wetting at high temperatures [19]. The opposite effect was observed in the aluminum–zinc system: the transition from the incomplete wetting of boundaries in aluminum by solid zinc layers to complete wetting occurred with a decrease rather than with an increase in the temperature [20, 21]. If a second-order phase transition occurs in the bulk of one of the phases (e.g., a transition from the ferromagnetic to paramagnetic state [22] or from the disordered to ordered state [23]), this circumstance additionally affects the relation between the energies of grain boundaries and the interphase energy of interfaces. Additional attraction between magnetic-phase grains separated by a nonmagnetic-phase layer appears in the ferromagnetic state. This circumstance affects the fraction of completely wetted boundaries at the transition through the Curie temperature [20, 24]. Can the double transition from the incomplete wetting of boundaries to complete wetting and back to incomplete wetting be observed without such an additional effect of magnetic transformations?

To answer this question, we studied the wetting of Cu/Cu grain boundaries in the copper–indium system. This system is interesting because the solubility of indium in copper is quite high and reaches 18 wt % [25]. Moreover, the solubility limit curve of indium in solid copper (so called solvus) has a quite complex shape (see Fig. 2 in [25]). This circumstance makes it possible to expect a nonmonotonic transformation of wetting.

In this work, copper alloys with indium concentrations of 4, 7.9, 12.5, 13.5, 17.5, and 22 wt % were studied. They were prepared by means of vacuum induction melting from extremely pure components (99.9995 wt % Cu and 99.9993 wt % In). The resulting ingots with a diameter of 10 mm were cut into 2-mm-thick disks, which were chemically polished and were then sealed into evacuated (a residual pressure of  $4 \times 10^{-4}$  Pa) quartz ampoules. After that, the ampoules were annealed in a muffle furnace at temperatures of 250 to  $590^\circ\text{C}$  for 455–2120 h. After annealing, the samples were quenched in water, ground, polished, and analyzed by means of scanning electron microscopy on a Tescan Vega NS5130MM instrument. Figure 3 shows typical micrographs, where copper and the  $\delta$  phase are dark and light, respectively. The  $\delta$  ( $\text{Cu}_{70}\text{In}_{30}$ ) phase is present both in the bulk of copper

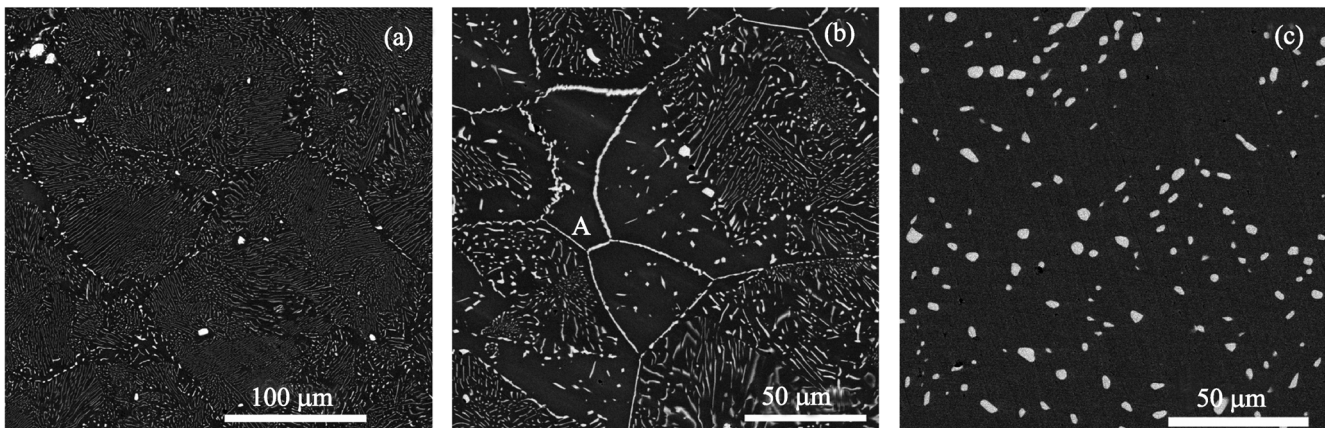


**Fig. 2.** Part of the phase diagram of Cu–In [25]. Points indicate the temperatures and concentrations at which annealings were performed in the two-phase region (Cu)+ $\delta$ . Crosses mark the annealing conditions beyond the two-phase region (Cu)+ $\delta$ . (Cu)/(Cu) grain boundaries completely wetted by continuous  $\delta$ -phase layers are observed in Cu–In polycrystals between tie-lines at  $T_W = 370^\circ\text{C}$  and  $T_{DW} = 520^\circ\text{C}$ .

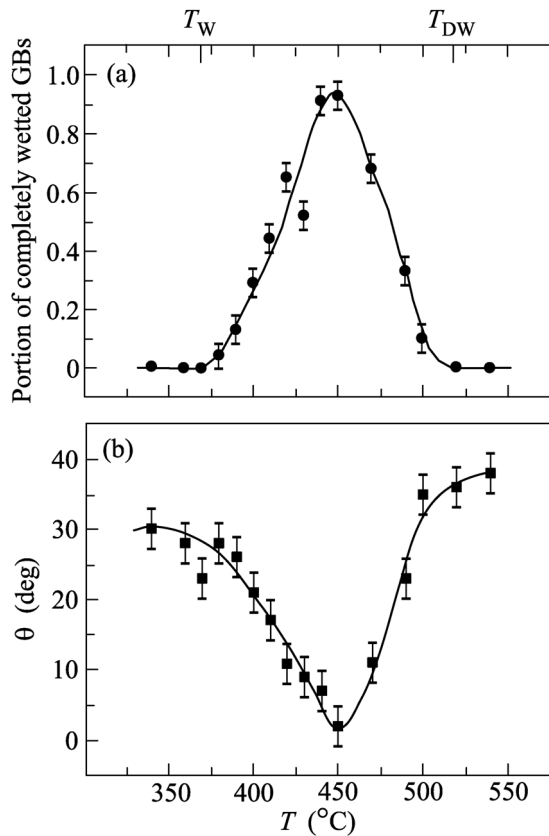
grains in the form of thin plates and at the boundaries of copper grains. Grain boundaries in copper were treated as completely wetted if a thin layer of the  $\delta$  phase completely separated copper grains from each other throughout the entire boundary from one triple junction to another junction (in Fig. 3b, three such

boundaries are marked by symbol A). In the opposite case, the grain boundary was considered as incompletely wetted by the  $\delta$  phase. Contact angles at the points of contact between copper grain boundaries and  $\delta$  phase particles were also determined. If the boundary was completely wetted, the contact angle was taken to be zero. Experimental points corresponding to studied temperatures and concentrations are shown in the phase diagram of the copper–indium system (Fig. 2). The experiment was performed so as to study a region near the solubility limit of indium in copper where the volume fraction of the wetting phase is small. This is because with an increase in the bulk of the wetting phase, so-called apparent wetting appears when the second phase separates the first-phase grains simply because its amount is large rather than because the contact angle is zero [26].

Figure 3 shows three microphotographs obtained after annealings at temperatures of 360, 450, and  $520^\circ\text{C}$ . It is clearly seen that the  $\delta$  phase in the first case (Fig. 3a) forms chains of individual particles at grain boundaries in copper. In other words, grain boundaries in copper are incompletely wetted by the  $\delta$  phase. In the micrograph shown in Fig. 3b, almost all grain boundaries in copper are completely wetted by the  $\delta$  phase. Continuous layers of this phase completely separate copper grains from each other. Thus, an increase in the temperature is accompanied by a transition from the incomplete wetting of grain boundaries in copper by the  $\delta$  phase to complete wetting. With a further increase in the temperature, grain boundaries in copper that are completely wetted by the  $\delta$  phase disappear again (Fig. 3c). Two new lines appear at the temperatures  $T_W = 370^\circ\text{C}$  and  $T_{DW} = 520^\circ\text{C}$  in the phase diagram of the copper–indium system shown in Fig. 2. Below  $T_W = 370^\circ\text{C}$ , completely wetted grain boundaries are absent (see also Fig. 4, which shows the temperature dependences of the fraction of completely wetted boundaries and aver-



**Fig. 3.** Micrographs of Cu–In alloys after long-term annealings at various temperatures for (a) Cu–8 wt % In at  $360^\circ\text{C}$ , (b) Cu–12 wt % In at  $450^\circ\text{C}$ , and (c) Cu–17.5 wt % In at  $520^\circ\text{C}$ .



**Fig. 4.** Temperature dependences of (a) the fraction of (Cu)/(Cu) grain boundaries completely wetted by continuous  $\delta$ -phase layers and (b) the average contact angle  $\theta$ . The temperatures  $T_W = 370^\circ\text{C}$  and  $T_{DW} = 520^\circ\text{C}$  are indicated.

age contact angle). Above  $T_W = 370^\circ\text{C}$ , completely wetted boundaries in copper appear in the samples. Their fraction increases with the temperature and reaches 93% (Fig. 4). The average contact angle decreases simultaneously from  $27^\circ$  to  $2^\circ$ . At  $440^\circ\text{C}$ , the fraction of wetted grain boundaries reaches a maximum (93%), whereas the average contact angle reaches a minimum ( $2^\circ$ ). With a further increase in the temperature, the fraction of completely wetted boundaries begins to decrease, whereas the contact angle begins to increase. At  $T_{DW} = 520^\circ\text{C}$ , the fraction of wetted boundaries vanishes again. Above this temperature, completely wetted boundaries in copper are not observed and the contact angle continues to increase and reaches  $37^\circ$  at  $570^\circ\text{C}$ .

In Fig. 1b, the solid line is the temperature dependence of the solubility limit of indium in the (Cu) solid solution taken from the phase diagram of Cu–In (Fig. 2). The dashed line is the conventional dependence of the solubility limit of the second component in the solid solution as in the great majority of phase diagrams [25]. Above a temperature of about  $400^\circ\text{C}$ , an increase in the solubility limit of indium in copper becomes noticeably slower and the characteristic

“shoulder” appears in the solubility limit curve. Figure 1a shows the schematic temperature dependences of the energies of (Cu)/(Cu) grain boundaries and (Cu)/ $\delta$  interfaces. If the solubility limit curve of indium in copper had a usual shape, the lines  $2\sigma_{\alpha\beta}(T)$  and  $\sigma_{\alpha\alpha}(T)$  would intersect each other only once at the point  $T_W = 370^\circ\text{C}$ . However, the temperature dependence  $2\sigma_{\alpha\beta}(T)$  deviates from the usual behavior (dashed line) and the second intersection of the lines  $2\sigma_{\alpha\beta}(T)$  and  $\sigma_{\alpha\alpha}(T)$  appears at the point  $T_{DW} = 520^\circ\text{C}$ .

To summarize, a double (reversible) phase transition of wetting of grain boundaries by the second solid phase is indeed observed in copper–indium alloys. With an increase in the temperature, incomplete wetting is transformed to complete wetting and, then, again to incomplete wetting. Such transformation was observed for the first time in a system where there are no additional second-order phase transitions in the bulk that can affect the shape of temperature dependences of the free energies of grain boundaries and phase interfaces. This phenomenon has been explained by an anomalous shape of the solubility limit curve of indium in the (Cu) solid solution.

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