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THERMODYNAMIC ASPECTS OF THE GRAIN BOUNDARY SEGREGATION IN Cu(Bi) ALLOYS

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Abstract—The grain boundary segregation of Bi in dilute polycrystalline Cu–Bi alloys was systematically studied as a function of temperature and composition. The temperature dependencies of the Gibbsian excess of Bi at the grain boundaries exhibited discontinuous changes at the temperatures close to, but different from the bulk solidus temperatures. The observed segregational phase transition was interpreted in terms of prewetting model. © 1999 Acta Metallurgica Inc. Published by Elsevier Science Ltd. All rights reserved.

1. INTRODUCTION

The system Cu(Bi) represents a classical example for the strong segregation of oversized impurity atoms to the grain boundaries (GBs) in dilute alloys and has been the subject of detailed investigations for more than a hundred years [1]. The contemporary understanding of the GB segregation in the Cu(Bi) system is based on the results of Auger electron spectroscopy (AES) [2], energy dispersive X-ray spectroscopy (EDS) in the scanning transmission electron microscope (STEM) [3], high resolution electron microscopy (HREM) [4] and computer simulation [5] studies. These works have shown that:

- The segregation zone at the GB is only a few interatomic distances thick.
- The enrichment ratio is very high and the GB core may be represented as a monolayer of Bi for Bi concentrations in Cu as low as 25–30 at. p.p.m.
- Bi atoms occupy the Cu sites in the GB and decrease the free volume in the GB structure.
- In some cases, a brittle-to-ductile fracture transition is observed during the increase of temperature [6].
- The Gibbsian excess of Bi atoms at the GBs depends on their crystallographic parameters and geometry.

However, until now no proper attention has been paid to the effect of temperature on the GB segre-

gation behaviour of Cu(Bi) alloys. It is a conventional wisdom that a high concentration of low-melting point impurities at the GB may cause a local melting there. The situation in which this local melting occurs at the same conditions as the bulk one corresponds to the perfect wetting of the GB by the liquid phase. The perfect wetting of GBs and free surfaces by the melt is the reason why solids cannot be overheated. If, however, the local melting at the GB occurs at the conditions at which the liquid phase is thermodynamically unstable in the bulk, the phenomenon of prewetting or premelting occurs [7]. Under premelting conditions the formation of a microscopically thin layer of the liquid phase with properties different from those of a bulk liquid is possible. Therefore, the term *quasi-liquid* is more appropriate in this case. The relationship between GB wetting/prewetting and GB segregation was first discovered by Kikuchi and Cahn [8]. Using the cluster variation method they have shown that the GB core becomes more disordered (melted) and its width increases logarithmically with increasing temperature. Though the occupancy of each individual segregation site by the solute atoms decreases with increasing temperature, the value of the Gibbsian excess of impurity atoms increases because of the widening of the GB core. This interesting theoretical prediction has not been verified experimentally until now.

In binary systems the stability of the liquid phase in the bulk is determined by the liquidus and solidus lines of the binary phase diagram. Recently, we have determined the solidus line of the Cu–Bi phase diagram with a high precision [9]. In this paper we will present the results of extensive AES study of the temperature and concentration dependence of

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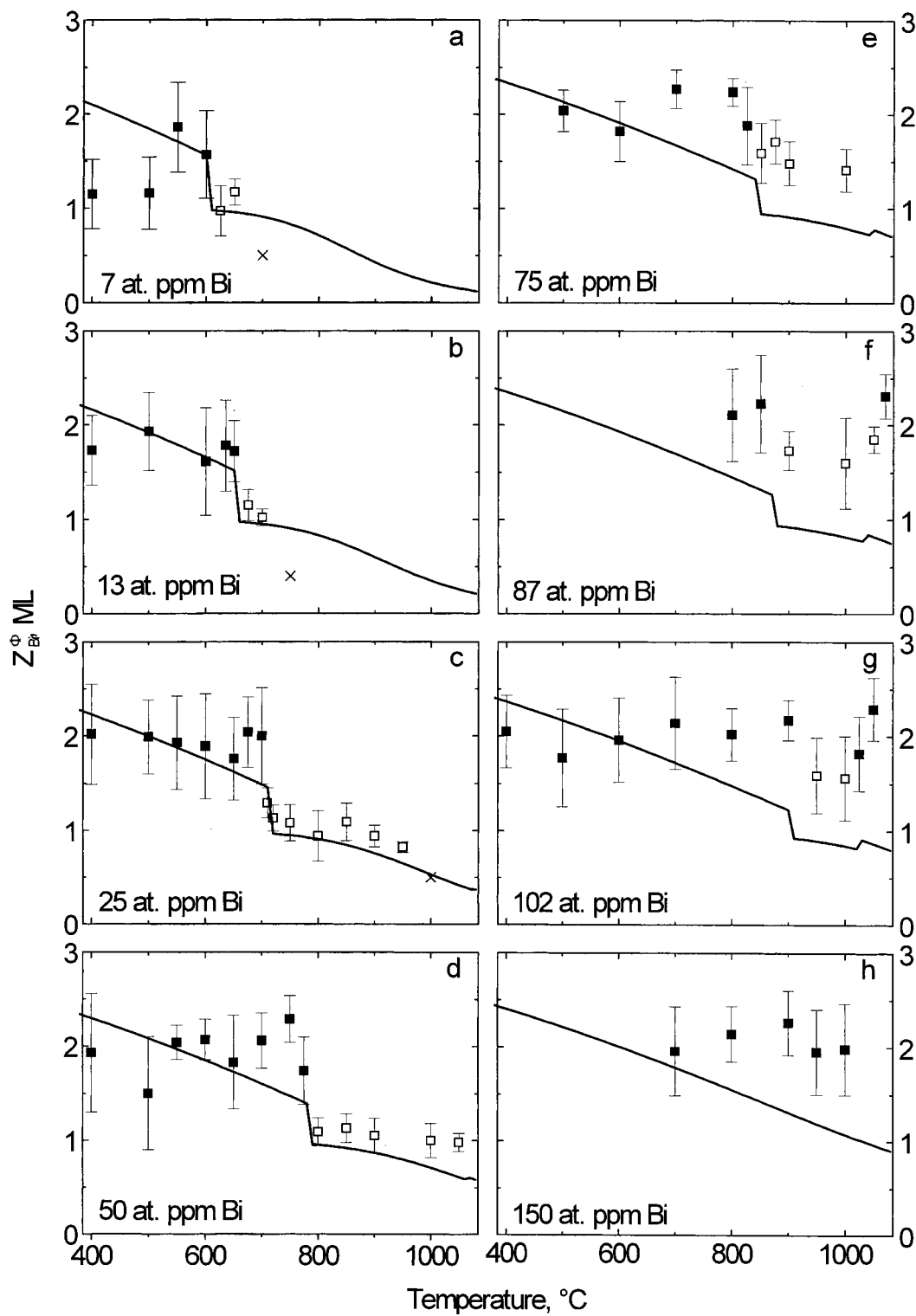‡To whom all correspondence should be addressed.

Fig. 1. Temperature dependence of the GB Gibbsian excess of Bi in Cu(Bi) polycrystals of various compositions, measured by AES. For two low-temperature points in (a) the annealing time was insufficient to establish the thermodynamic equilibrium. The solid line is calculated in the framework of the prewetting model.
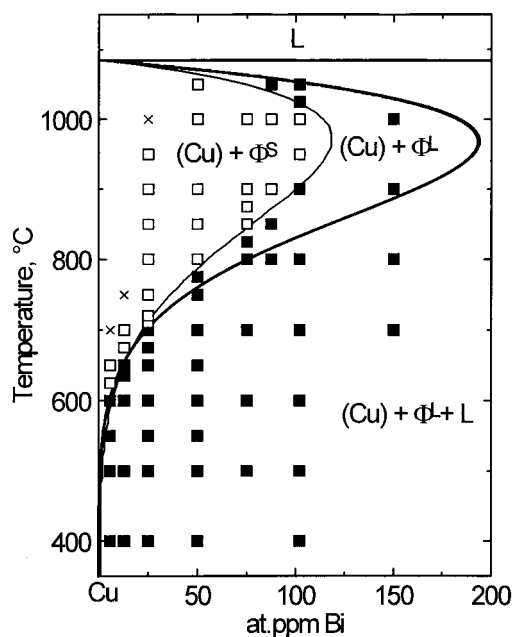
Fig. 2. The GB segregation data from Fig. 1 presented in the bulk Cu–Bi phase diagram. The GB solidus line (thin solid line) is calculated according to equations (2a), (2b) and (3) with the parameters from Table 1.

the GB segregation in the Cu(Bi) system. These results can be properly discussed in terms of the stability of the bulk phases due to the availability of the bulk phase diagram [9].

2. EXPERIMENTAL

Cylindrical Cu(Bi) polycrystals containing 7, 13, 25, 50, 75, 87, 102 and 150 at. p.p.m. Bi were produced from Cu and Bi of 99.999 at.% purity by casting in vacuum. All samples were homogenized for 24 h at 1000°C in evacuated (5×10^{-4} Pa) silica ampoules. After homogenization, the Bi content in the specimens was measured by atom absorption spectroscopy in a Perkin-Elmer spectrometer (model 5000). The specimens were then annealed at temperatures between 400 and 1050°C for various times estimated from the Bi diffusion coefficient in Cu. Details of the heat treatment conditions are given in Ref. [10]. After annealing the specimens were quenched *ex situ* and then fractured *in situ* in the ultra high vacuum chamber of the PHI 600 Scanning Auger Multiprobe at the temperature of liquid nitrogen. The Bi concentration was measured by means of AES at 20–30 sites on the fracture surface. The standard methods of Auger signal processing have been used [10]. In this work we express the Gibbsian excess of Bi atoms at the GBs in monolayers (ML) of Bi. One ML of pure Bi contains 9.3 atoms/nm^2.

3. RESULTS

The temperature dependence of the GB segregation in the Cu(Bi) alloys studied is shown in Fig. 1. Three types of temperature behaviour can be distinguished in this figure:

- Figures 1(a)–(e). The Bi content at the GBs decreases discontinuously during the increase of temperature. At low temperatures, the Gibbsian excess of Bi atoms is approximately 2 ML, decreasing to the value of 1–1.5 ML at some definite temperature which depends on the Bi concentration in the bulk.
- Figures 1(f) and (g). The discontinuous decrease of the Bi content at the GBs during the increase of temperature is accompanied by an increase of the Bi content at the GBs at higher temperatures close to the melting point of Cu. To our knowledge this is the first experimental observation of an increase of the GB Gibbsian excess of the segregating impurity with an increase of the temperature in a binary system.
- Figure 1(h). The Bi content at the GB is approximately constant (2 ML) and does not depend on temperature.

To visualize the discontinuous nature of the GB segregation transition we used filled and open symbols in Fig. 1 for the high- and low-Bi content branches of the respective temperature dependencies. The cross in Figs 1(a)–(c) is used for the samples which exhibited a ductile fracture and on which, therefore, it was impossible to perform the AES measurements. It should be noted that the scanning electron microscopy (SEM) of fractured surfaces has not revealed any GB faceting.

In Fig. 2 the GB segregation data are depicted together with the bulk solidus line (thick solid line) of the Cu–Bi system. The thin solid line is plotted through the points, at which the discontinuous change of the GB Gibbsian excess of Bi occurs. This line represents, therefore, the GB phase transformation line in the phase diagram in the coordinates "temperature–bulk concentration of Bi". Because of the similarity of the GB phase transformation line with the bulk solidus line (both lines have a characteristic retrograde shape), we call the former the *GB solidus line*.

4. DISCUSSION

The absolute value of Gibbsian excess of Bi at low temperatures found in our work (2 ML) is somewhat higher than the values reported in Ref. [6] (1.4 ML) for the Cu–42 at. p.p.m. Bi alloy in the same range of temperatures. This can be connected with the different thermomechanical treatment of the samples: the severe mechanical deformation followed by short annealing at 800°C

used in Ref. [6] probably resulted in a high fraction of singular and vicinal GBs less prone to the GB segregation.

As can be seen from Fig. 2, the GB phase transformation line lies almost entirely (at least for bulk Bi contents higher than 25 at. p.p.m.) in the single-phase area of the bulk phase diagram. Therefore, we are dealing with the true GB phase transformation induced by a segregation process, and not with the precipitation of a second phase at the GB. At the same time, the GB phase transformation line follows closely the bulk solidus line and, therefore, the thermodynamic properties of the bulk phases should somehow enter into the proper thermodynamic description of the GB segregation. Another important feature of the observed segregation behaviour is the increase of the GB Gibbsian excess of Bi with an increase of the temperature at high temperatures [Figs 1(f) and (g)]. This retrograde behaviour cannot be described by any model treating the GB as an assembly of a fixed number of segregation sites with fixed values of the segregation enthalpy. In a previous paper [11] we demonstrated the failure of the classical Fowler–Guggenheim model of GB segregation for the Cu–Bi system and gave the outline of a new prewetting model. From the first glance it would be natural to assume that at the GB solidus line the ordered GB core is replaced by a homogeneous layer of the quasi-liquid phase, in the spirit of the Kikuchi–Cahn model [8]. This description meets, however, serious quantitative difficulties. At high temperatures, the concentration of Bi in the Cu–Bi liquid is low, and one needs to assign a large thickness to the layer of the quasi-liquid phase in order to get the observed value of the GB Gibbsian excess of Bi of 1 ML and more (see Fig. 1). Such a thick (more than 100

interatomic distances thick) layer of a quasi-liquid cannot be stabilized by short-range forces from two solid/liquid interfaces and is, therefore, unstable.

In the prewetting model of the GB segregation we assume that the quasi-liquid layer at the GB is thin but inhomogeneous, the Bi-rich core region still having a structure similar to the structure of the untransformed GB core, but being surrounded by two thin layers of the quasi-liquid phase (Fig. 3). Indeed, a thin layer of a quasi-liquid should be strongly modulated by the adjacent crystals [12], and the structure of the GB core region may be similar to that of the untransformed GB. The driving force for the formation of two quasi-liquid layers surrounding the GB core is the high chemical energy ΔG_{chem} associated with a stepwise change of the Bi concentration at the GB core. According to Lee and Aaronson [13]

$$\Delta G_{chem} = \left(x_{Bi}^{\Phi S} - x_{Bi}^{(Cu)}\right)^2 n_s Z_v \left(\varepsilon_{Cu-Bi}\right.$$

$$\left. - \frac{\varepsilon_{Cu-Cu} + \varepsilon_{Bi-Bi}}{2}\right)$$

$$= \left(x_{Bi}^{\Phi S} - x_{Bi}^{(Cu)}\right)^2 \Omega^I \qquad (1)$$

where $x_{Bi}^{\Phi S}$, $x_{Bi}^{(Cu)}$, n_s and Z_v are the Bi concentration in the GB core and in the bulk, the number of atoms per unit area of the GB core and the coordination number across the GB core, respectively. ε_{A-B} is the energy of the atomic A–B bond and Ω^I defined by equation (1) is the interaction energy across the GB core. The chemical energy is associated with the presence of Cu–Bi bonds across the GB core, which are energetically unfavourable in systems with a high positive enthalpy of mixing. It is this mixing enthalpy which causes the retrograde solubility in the bulk [9, 14]. The system tries to decrease this chemical energy by smearing out the sharp concentration step at the GB core. The energetically easiest way to arrange such a smearing out is the formation of a liquid phase, in which the concentration of Bi is intermediate between the bulk and the Bi-rich GB core. We will quantify the prewetting model under the following assumptions:

- The GB core can be described by the regular solution model and the structural component of its energy stays unchanged even after the formation of the quasi-liquid phase ($\Phi^S = \Phi_1^{QL}$). The interaction energy in the GB phase (Ω^Φ) depends linearly on temperature.
- The quasi-liquid phase Φ_2^{QL} can be described by the thermodynamic functions of the bulk liquid obtained earlier during the optimization of the bulk Cu–Bi phase diagram [9].
- The interaction energy across the $(Cu)/\Phi_2^{QL}$ interface is the same as in the solid phase (Ω^S), while the interaction energies across the $\Phi^S/(Cu)$ and
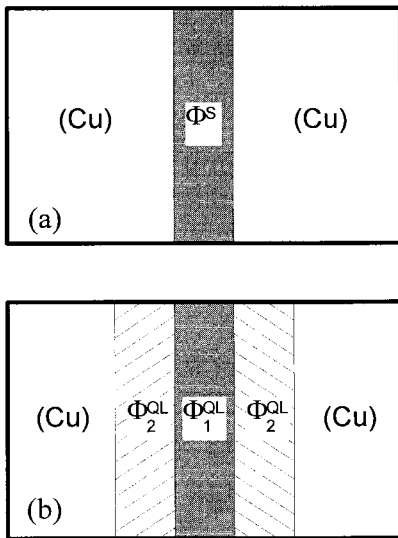

Fig. 3. Two possible GB structures: (a) GB with a Bi-enriched solid core; (b) prewetted GB. QL = quasi-liquid.

Φ_1^{QL}/Φ_2^{QL} interfaces (Ω^I) are equal to each other and depend linearly on temperature.

In the case of Fig. 3(a) the excess Gibbs energy per unit area, ΔG_1, can be written as

$$\Delta G_1 = \Delta G^{\Phi S} h^{\Phi S} + 2\left(x_{Bi}^{\Phi S} - x_{Bi}^{(Cu)}\right)^2 \Omega^I \quad (2a)$$

and for the case of Fig. 3(b)

$$\Delta G_2 = \Delta G^{\Phi S} h^{\Phi S} + \Delta G^L h_2^{\Phi QL} +$$

$$2\left(x_{Bi}^{\Phi S} - x_{Bi}^{\Phi QL}\right)^2 \Omega^I + 2\left(x_{Bi}^{\Phi QL} - x_{Bi}^{(Cu)}\right)^2 \Omega^S/w \quad (2b)$$

where $\Delta G^{\Phi S}$ and ΔG^L are the excess Gibbs energies per unit area of one monolayer of the GB phase and liquid phase, respectively. $x_{Bi}^{\Phi S}$ and $x_{Bi}^{\Phi QL}$ are the Bi concentrations in the GB core surrounded by the quasi-liquid and in the quasi-liquid itself, respectively. $h^{\Phi S}$ and $h_2^{\Phi QL}$ are the thickness of the GB core and of the adjacent quasi-liquid layers, respectively, which are both assumed to be 1 ML. w is the molar area of the alloy which is assumed to be constant throughout the GB region and the bulk. The excess Gibbs energies can be expressed as

$$\Delta G^{L,\Phi S} = G^{L,\Phi S}\left(x_{Bi}^{L,\Phi S}\right) - G^{(Cu)}\left(x_{Bi}^{(Cu)}\right)$$

$$- \left(x_{Bi}^{L,\Phi S} - x_{Bi}^{(Cu)}\right) \frac{dG^{(Cu)}}{dx_{Bi}}\bigg|_{x_{Bi}=x_{Bi}^{(Cu)}} \quad (3)$$

where $G^{(Cu)}$, G^L and $G^{\Phi S}$ are the Gibbs energies of the solid, liquid and GB phases, respectively. The ΔG_1 should be minimized with respect to $x_{Bi}^{\Phi S}$, while the two-dimensional minimization is applied to the function $\Delta G_2(x_{Bi}^{\Phi S}, x_{Bi}^{\Phi QL})$. At the given temperature T and $x_{Bi}^{(Cu)}$ the comparison of the minimized values of ΔG_1 and ΔG_2 provides the conclusion which of the two GB structures [Figs 3(a) or (b)], is stable. A new important parameter emerges during the minimization procedure

$$\Delta G^0 = \left(\bar{G}_{Bi}^{\Phi 0} - \bar{G}_{Bi}^{S0}\right) - \left(\bar{G}_{Cu}^{\Phi 0} - \bar{G}_{Cu}^{S0}\right) \quad (4)$$

where $\bar{G}_{Cu}^{S0}$, $\bar{G}_{Bi}^{S0}$, $\bar{G}_{Cu}^{\Phi 0}$ and $\bar{G}_{Bi}^{\Phi 0}$ are the partial Gibbs energies (chemical potentials) of pure Cu and Bi in the bulk and in the GB phases. ΔG^0 represents the change in the Gibbs energy during the exchange of Bi atoms in the bulk with Cu atoms in the GB (Gibbs energy of segregation in the substitutional solid solution). Therefore, there are a total of five independent variable parameters in the prewetting model: four parameters for Ω^Φ and Ω^I (remember that both of them depend linearly on temperature) and ΔG^0. The results of the optimization are shown in Table 1.

The GB solidus line in Fig. 2 has been calculated from the equation $\Delta G_1 = \Delta G_2$ using the optimized values of parameters. The Gibbsian excess of Bi at the GB, Z_{Bi}^Φ, can be calculated according to $Z_{Bi}^\Phi = h^{\Phi S} x_{Bi}^{\Phi S}$ and $Z_{Bi}^\Phi = h^{\Phi S} x_{Bi}^{\Phi S} + 2h_2^{\Phi QL} x_{Bi}^{\Phi QL}$ for the GB

Table 1. Parameters for the description of the GB segregation in the framework of the prewetting model

ΔG^0 (kJ/mol)	Ω^Φ (J/mol)	$w\Omega^I$ (J/mol)
−55.0	$5.5 \times 10^4 - 34 \times T$	$2.75 \times 10^4 - 18 \times T$

structures in Figs 3(a) and (b), respectively. The solid lines in Fig. 1 represent the temperature dependencies of Z_{Bi}^Φ calculated according to these formulae. For bulk concentrations below 25 at. p.p.m. Bi the model is in a good quantitative agreement with the experimental data. For higher Bi concentrations the model reproduces well the temperatures of the GB phase transition, while there is some quantitative discrepancy in Z_{Bi}^Φ between the theory and experiment, especially at high temperatures. This discrepancy may be associated with the simplifying assumption of the model. For instance, much better agreement can be reached by making the thickness of the GB core, h^Φ, temperature-dependent [10], however, this will cost the introduction of an additional parameter.

It should be noted that the number of parameters we used to optimize the GB behaviour is the same as used previously for the optimization of the bulk Cu–Bi phase diagram [9]. Moreover, all values of parameters obtained here are reasonable. Indeed, for the temperature of 700°C studied by Menyhard *et al.* [6] we get from Table 1 the values $\Delta G^0 = -55$ kJ/mol and $\Omega^\Phi = 21.9$ kJ/mol which are very close to the values suggested in Ref. [6] (−58.6 and 20.9 kJ/mol for the Gibbs energy of segregation and interaction energy, respectively).

In conclusion we would like to note that our new prewetting model, though perhaps oversimplified, captures the major features of the GB segregation behaviour. It provides the natural explanation for the striking similarity between the GB and bulk solidus lines (Fig. 2). Indeed, the major contribution into ΔG_2 (excess Gibbs energy of the prewetted GB) arises from the excess energy of the liquid phase, ΔG^L. The latter is zero at the bulk solidus line and increases rapidly as the deviation of the Bi concentration from the bulk solidus increases. Therefore, the GB solidus *must* closely follow the bulk one. Recently, it was shown that the formation of sharp GB wetting grooves in the solid Cu/liquid Bi system characteristic for a perfect wetting of the GB by the melt is accompanied by a rapid Bi GB diffusion ahead of the groove on long distances [15]. The activation energy for this rapid diffusion was considerably lower than the activation energy for GB diffusion in pure Cu. After quenching, solidified Bi particles of several micrometres in diameter have been also observed at the GBs [16]. Such a rapid diffusion and the redistribution of a large amount of Bi during the short quenching time are consistent with the presence of a quasi-liquid Bi-rich phase at the GBs. We also believe that our prewetting model

will sustain the test by atomistic simulations. Such simulations should be essentially dynamic and the interatomic potential used should reproduce the bulk phase diagram [9] correctly. This is not an easy task because the extremely small solubility of Bi in Cu at low temperatures requires a large number of atoms to be simulated.

5. CONCLUSIONS

From the results of the present study, the following conclusions can be drawn:

1. The AES studies of the GB segregation in polycrystalline Cu(Bi) alloys revealed a segregational GB phase transformation at bulk compositions and temperatures within the single-phase area of the bulk phase diagram.
2. The line plotted through the points of the GB phase transformation in the bulk phase diagram (GB solidus line) exhibits a striking similarity to the bulk solidus line. For the first time it was shown that the Gibbsian excess of Bi atoms at the GBs could increase abruptly with increasing temperature.
3. A prewetting model of the GB segregation has been suggested. In the framework of this model, two thin quasi-liquid layers surrounding the GB core are formed in the Bi-rich GB phase. This leads to the decrease of the chemical excess energy associated with a sharp concentrational discontinuity at the GB. The model gives an excellent description of the GB solidus line and is in a reasonable quantitative agreement with the AES data.

REFERENCES

1. Hampe, W., *Z. Berg-, Hütten- u. Salinenwesen*, 1874, **22**, 93.
2. Joshi, A. and Stein, D. F., *J. Inst. Metals*, 1971, **99**, 178.
3. Michael, J. R. and Williams, D. B., *Metall. Trans. A*, 1984, **15**, 99.
4. Duscher, G., Chisholm, M. F., Alber, U., Pennycook, S. J. and Rühle, M., *Mater. Sci. Forum*, in press.
5. Vitek, V., Ackland, G. J., Menyhard, M. and Yan, M., in *Interfaces: Structure and Properties*, ed. S. Ranganathan, *et al.* Trans Tech Publications, Aedermannsdorf, 1993, p. 3.
6. Menyhard, M., Blum, B. and McMahon Jr, C. J., *Acta metall.*, 1989, **37**, 549.
7. Rabkin, E. I., Straumal, B. B. and Shvindlerman, L. S., *Int. J. Mod. Phys. B*, 1991, **5**, 2989.
8. Kikuchi, R. and Cahn, J. W., *Phys. Rev. B*, 1987, **36**, 418.
9. Chang, L.-S., Straumal, B. B., Rabkin, E., Gust, W. and Sommer, F., *J. Phase Equilibria*, 1997, **18**, 128.
10. Chang, L.-S., Ph.D. thesis, University of Stuttgart, 1998.
11. Chang, L.-S., Rabkin, E., Straumal, B., Lejcek, P., Hofmann, S. and Gust, W., *Scripta mater.*, 1997, **37**, 729.
12. Howe, J., *Phil. Mag. A*, 1996, **74**, 761.
13. Lee, Y. W. and Aaronson, H. I., *Acta metall.*, 1980, **28**, 539.
14. Swalin, R. A., in *Thermodynamics of Solids*. John Wiley, New York, 1972, p. 184.
15. Joseph, B., Barbier, F. and Aucouturier, M., *Mater. Sci. Forum*, 1999, **294–296**, 735.
16. Joseph, B., Barbier, F., Dagoury, G. and Aucouturier, M., *Scripta mater.*, 1998, **39**, 775.