Grain Boundary Segregation in the Cu-Bi System

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ABSTRACT

The grain boundary segregation of Bi in Cu polycrystals containing 6, 13, 25, 50, 75 and 102 at.ppm Bi has been investigated. In all studied alloys at certain temperatures (jump temperatures) abrupt changes of the Bi segregation were observed. Below 25 at.ppm Bi the jump temperatures coincide with the solidus temperatures of the Cu–Bi system, while for higher Bi concentrations they deviate upward from the solidus line. At the Bi concentration of 102 at.ppm the Bi segregation decreases and then increases again with increasing temperature. To explain these effects, the concept of a grain boundary solidus line has been suggested. This line is calculated in the framework of the phenomenological prewetting model. Additionally, it was shown that for a one-monolayer thick segregation film on the grain boundary the classical McLean behaviour should be observed, irrespectively of the interchange energy.

INTRODUCTION

Many studies have confirmed that there are two main models describing the grain boundary (GB) segregation. The Fowler model exhibits an abrupt change of the GB adsorption in a narrow range of the temperature or bulk concentration for a solution with a strong demixing tendency. For the McLean model a smooth decrease of the impurity adsorption with increasing temperature is observed. A suitable description of the segregation of Bi atoms at the GBs in Cu is still obscure because both types of segregation have been observed in this system. Some research groups [1,2] have found that their results were well explained by the McLean model. Although, the Fowler-type behaviour was shown in Cu–50 at.ppm Bi alloys in the temperature range between 700 and 720°C by Menyhard *et al.* [3]. Recently, the GB-segregation of Bi in Cu–25 at.ppm Bi polycrystals was investigated by Chang *et al.* [4] and the solubility of Bi in solid Cu was determined [5]. In their study a complicated behaviour of segregation was observed. A prewetting model of segregation was proposed explaining successfully the coincidence between the jump temperature of the GB segregation and the solidus temperature of Cu–25 at.ppm Bi alloy [5]. However, the relevancy of the Fowler isotherm was not excluded in this case because of the good agreement between the experimental results and the optimized curve. This study examined the GB segregation in Cu–Bi alloys with six different compositions in an attempt to clarify the applicability of these two models.

EXPERIMENTAL AND RESULTS

Polycrystalline Cu cylinders containing 7, 13, 25, 50, 75 and 102 at.ppm Bi were prepared by vacuum induction melting followed by casting. After homogenization at 950°C for 24 hours the

specimens were vacuum annealed at temperatures between 500 and 1050°C for various times estimated from the volume diffusion coefficient of Bi atoms in solid Cu [6]. The details of the preparation of specimens can be found in Ref. [4]. Auger electron spectroscopy (AES) was used to determine the amount of Bi on the fracture surface of specimens which were broken *in situ* in the ultra–high vacuum chamber (with a base pressure lower than 1×10^{-7} Pa) after cooling down in contact with liquid N_2. About a dozen fracture surfaces exhibiting an intergranular fracture were chosen for analysis at each concentration and temperature. The peak-to-peak heights of the Cu and Bi characteristic signals in the electron spectrum, 55 to 60 and 94 to 99 eV respectively, were measured. In order to evaluate the amount of segregation, the segregation layer was assumed to be a pure Bi thin film in which the Bi atoms have the same average atomic volume as that in pure standard Bi. A detailed description of the quantitative analysis of AES data can be found in [7]. The determined value of segregation is the thickness of the segregation layer in the unit of a monolayer (ML). One ML of Bi contains 9.3 atoms/nm^2. The thickness of the Bi segregation layers were determined from the spectrum as well as from the sputter depth profile. The data of the depth profile were interpreted using the sequential layer sputtering model [8]. The thickness of the Bi segregation layer derived with the help of both methods agreed well with each other. Therefore, the pure Bi layer model is a reasonable assumption.

The temperature dependencies of the Bi segregation at the GBs are presented in Fig. 1 for all alloys studied. It can be seen that the average value of the Bi adsorption changes abruptly from approx. 2 ML to a value between 1 and 1.5 ML as the temperature increases. This trend occurred in all alloys studied except for the values of Cu–6 at.ppm Bi alloys below 550°C. The reason for the lower Bi adsorption in Cu–6 at.ppm Bi at 400 and 500°C is that the annealing time is not long enough to approach equilibrium. While only one sudden change can be seen in Fig. 1a to e, the Cu–102 at.ppm Bi alloy exhibited two abrupt changes in the Bi adsorption (see Fig. 1f). Between 900 and 950°C the Bi segregation jumps down from 2 to 1.5 ML, while it changes from 1.5 up to 2 ML between 1000 and 1020°C. The GB segregation data in combination with the recently determined solidus line for the Cu–Bi system are shown in Fig. 2. Open and filled symbols are used for the Bi adsorption below and above 1.5 ML, respectively. At concentrations below 25 at.ppm Bi the jump temperature is close to the solidus line. Above 25 at.ppm Bi the jump temperature deviates from the solidus line. The difference between the jump temperature and the solidus temperature increases with increasing bulk concentration of Bi.

An upward jump with increasing temperature similar to that observed at Cu–102 at.ppm Bi alloys in this work was observed during the study of the GB segregation of In in Ni [9]. It was explained by the non-equilibrium segregation which results from the high vacancy concentration and fast diffusivity of the vacancy–impurity pair at high temperatures. However, the increase of the Bi segregation with increasing temperature cannot be explained by this kind of non-equilibrium segregation in the Cu–Bi system because the estimated segregation amount induced by the vacancy–impurity pair in the water–quenched samples does not exceed 0.01 ML. This is much less than the change of the adsorption value of 0.5 ML found in this work (Fig. 1f).

DISCUSSION

At first the classical Fowler isotherm was used for the description of the anomalous changes of the GB segregation observed experimentally. This isotherm is often employed for the description of the GB segregation in the systems with a high enthalpy of mixing, and such parameters as the segregation Gibbs energy and interchange energy in the GB can be extracted from the fitting procedure. In this discussion all samples are assumed to be in the single-phase state and the Bi content in the solid solution is equal to the bulk Bi concentration.

Optimization with the classical Fowler isotherm

Because the maximum average value of Bi adsorption at the GB is approx. 2 ML, the double-layer model will be considered. The double-layer model is a simplification of the general dependence of the segregation Gibbs energy on the distance across the GB. We suppose that atom sites in each layer are characterized by a fixed segregation Gibbs energy. The schematics in Figs. 3a and b demonstrate
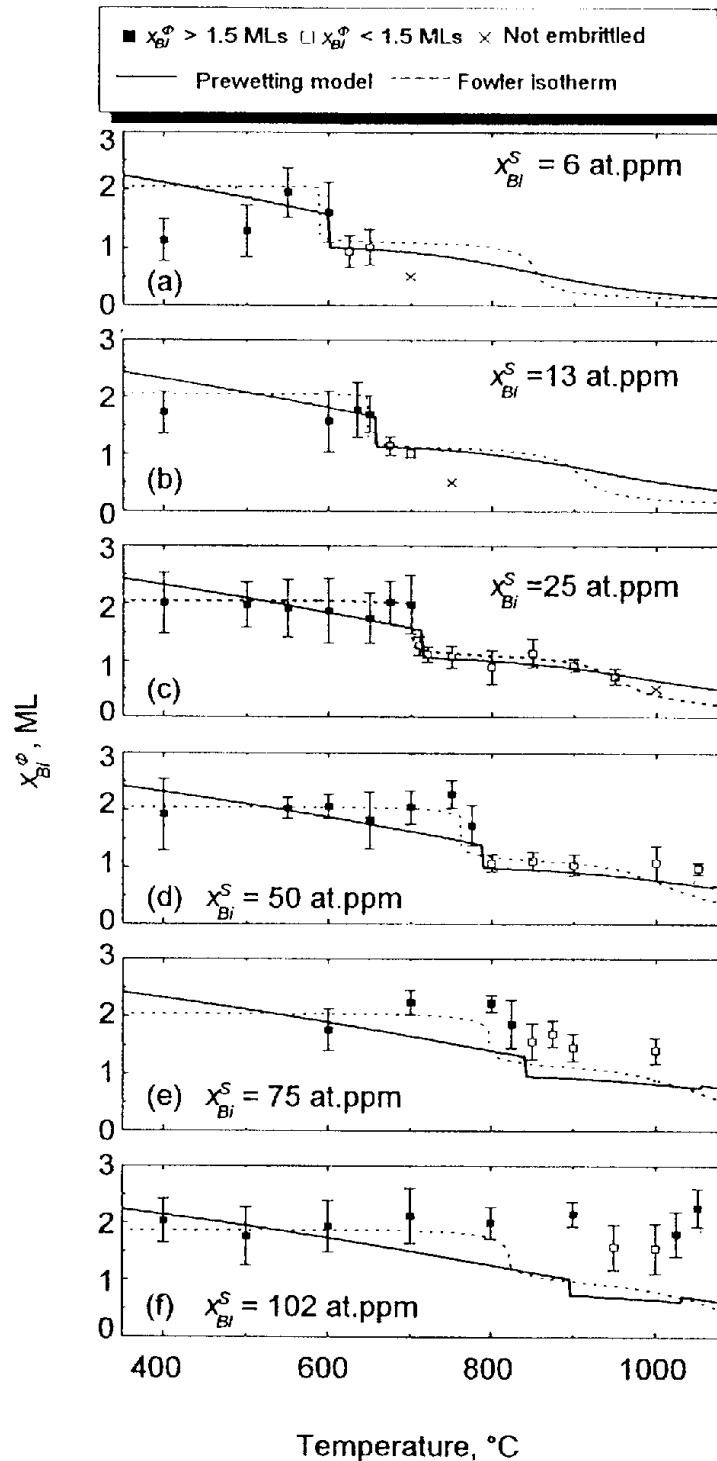

Fig. 1. Temperature dependence of the GB segregation of Bi in Cu–Bi alloys of different compositions.
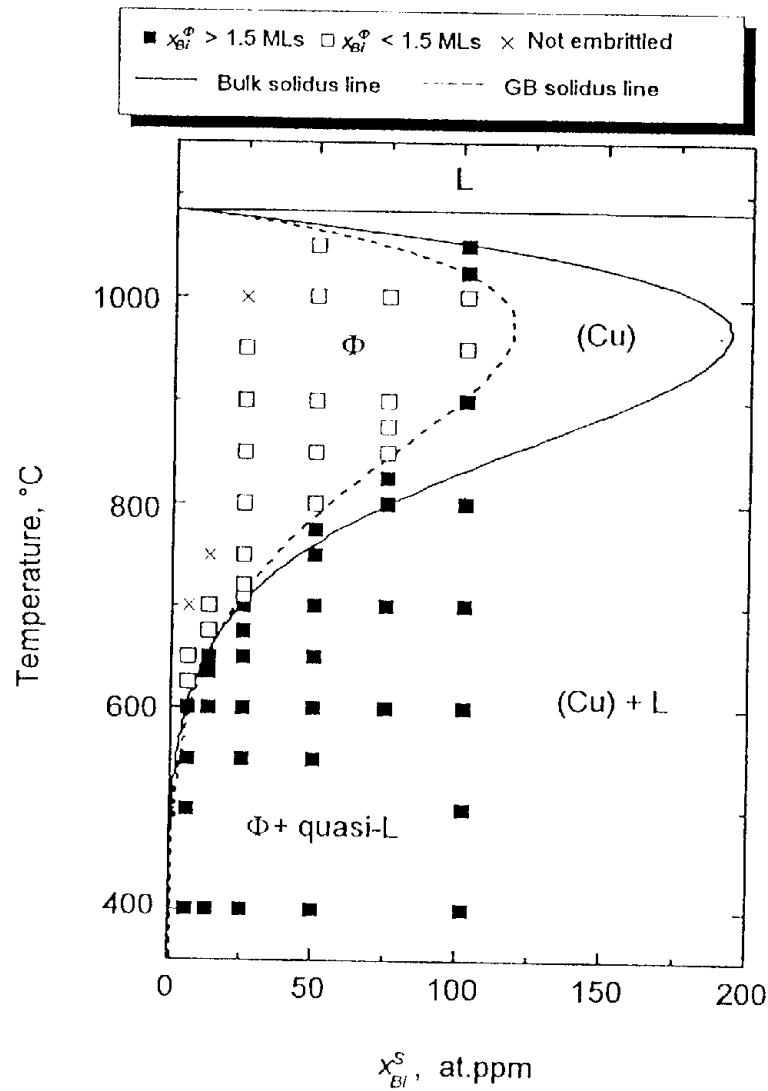
Fig. 2.   Comparison of the segregation data with the solidus line on the Cu-rich side of the Cu–Bi phase diagram.

the difference between the single-layer and double-layer models. The double-layer approximation seems to be reasonable for a "general" GB in which the segregation Gibbs energy varies considerably from site to site [10]. During the fracture in ultra-high vacuum the crack propagates mainly along such general GBs.

The Fowler isotherm can be written in the following form:

$$\frac{x^\Phi}{1-x^\Phi} = \frac{x^S}{1-x^S} \cdot \exp(\frac{\Delta G}{RT})$$

Eq. 1

where

$$\Delta G = -\Delta G^{seg} + 2\Omega^\Phi x^\Phi - 2\Omega^S x^S$$

Eq. 2

R is the gas constant, T is the absolute temperature, ΔG^{seg} is the segregation energy for the first or second layer, and x^Φ, Ω^Φ, x^S and Ω^S are the mole fraction of Bi atoms and the interchange energy in the GB phase (Φ) and in the solid phase (S), respectively. Ω^Φ and Ω^S depend linearly on the temperature and are position independent. Ω can be expressed as

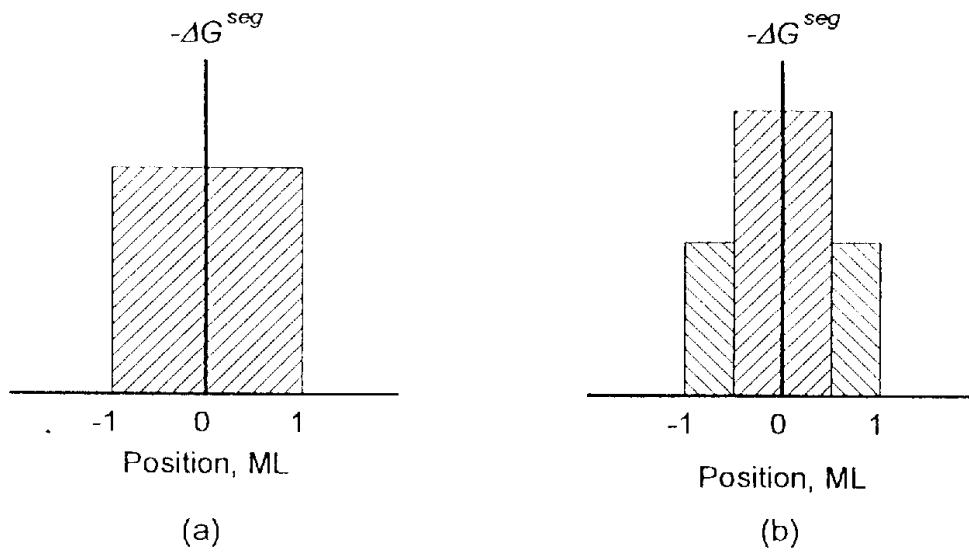$$\Omega = AZ(\varepsilon_{Cu,Bi} - \frac{\varepsilon_{Cu,Cu} + \varepsilon_{Bi,Bi}}{2})$$

Eq. 3

Fig. 3. Schematic representation of the (a) single-layer model and (b) double-layer model of the spatial dependency of the segregation Gibbs energy (ΔG^{seg}).

where A and Z are the Avogadro number and coordination number, respectively. $\varepsilon_{Cu,Bi}$, $\varepsilon_{Cu,Cu}$ and $\varepsilon_{Bi,Bi}$ are corresponding binding energies.

The measured total GB adsorption is the sum of the Bi mole fraction in these two layers. All optimized parameters are listed in Table 1 and the calculated curves are plotted in Fig. 1 as dashed lines. The segregation Gibbs energies for two layers and the interchange energy obtained agree well with those from the literature [3, 11, 12]. However, it can be seen from Fig. 1 that an agreement between the calculated and experimentally observed jump temperatures of the Bi adsorption is obtained merely for Bi concentration below 25 at.ppm . For the concentration above 25 at.ppm Bi

Table 1. Parameters for the description of the Cu–Bi binary system. *n* is the ratio of the cluster sizes of Cu and Bi. *W* is the product of the interchange energy and the size of the Cu cluster.

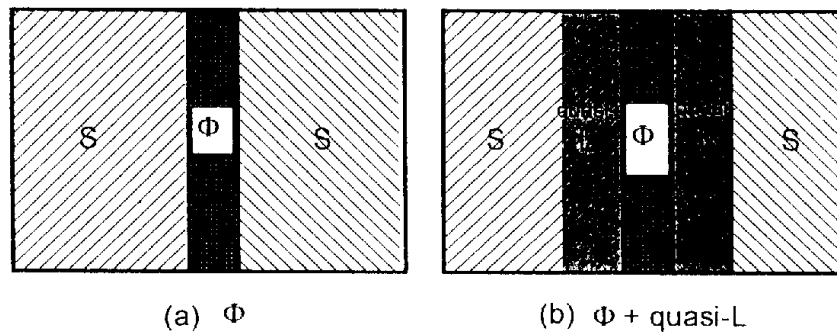| Phase	Model	Parameter
Solid (S)	Regular	$\Omega^S = 1.12 \times 10^5 - 35 \times T$ J/mol
Liquid (L)	Self–associate	$n = 1.4$
		$W = 2.10 \times 10^4 - 8 \times T$ J/mol
GB (Φ)	Fowler	$\Omega^\phi = 5.5 \times 10^4 - 34 \times T$ J/mol
		$\Delta G^{seg} = -9.6 \times 10^4$ J/mol ....1st layer
		$\Delta G^{seg} = -6.6 \times 10^4$ J/mol ....2nd layer
	Prewetting	$\Omega^\phi = 5.5 \times 10^4 - 34 \times T$ J/mol
		$\Omega^I = 2.75 \times 10^4 - 18 \times T$ J/mol
		$\Delta \gamma \omega = 5.5 \times 10^4$ J/mol

(a) Φ   (b) Φ + quasi-L

Fig. 4. Two possible GB structures in the framework of the prewetting model. S = solid, L = liquid and Φ = GB phase.

the discrepancy between these jump temperatures from the model and experiments increases with increasing concentration and the "re-jump" observed at 102 at.ppm Bi cannot be described. In the next section it will be shown that the observed experimental effects can be described in the framework of the GB solidus line concept.

The prewetting model: the grain boundary solidus line

It is shown above that the phenomena of the GB segregation of Bi in Cu observed in this work cannot be physically explained or mathematically described by the classical Fowler segregation isotherm. The coincidence of the solidus temperature and the jump temperature at Bi concentrations below 25 at.ppm indicates that the liquid phase plays some role in the segregation behaviour. The similarity between the GB segregation and the prewetting phenomenon described by Cahn [13] was originally pointed out by Rabkin [14]. Therefore, to explain the observed phenomena a prewetting model was developed in which the interfacial chemical energy was considered.

The interfacial chemical energy associated with the interface between two phases of different compositions arises due to the different (if compared with the bulk) types of neighbourhoods between atoms across the interface. For coherent and semi-coherent interfaces in binary systems the interfacial chemical coherent energy is proportional to the square of the difference in the composition of the two phases. If the Bi-enriched GB in Cu is considered as an individual phase, a high interfacial chemical energy should be associated with the two interfaces "GB phase-bulk" because the segregation layer is almost pure Bi. The system can decrease this energy by smoothing the sharp discontinuity in composition across the interface. This is illustrated schematically in Fig. 4 and the case (a) shows that only one Bi-enriched GB phase is present, while in the case (b) two layers of the quasi-liquid phase are built between the GB phase and Cu crystals. The stability of the GB phase between two layers of a quasi-liquid phase is connected with the strong density modulations in these layers commensurate with the periodicity of two adjacent grains. Such density modulations were recently observed in the liquid phase close to the solid/liquid interface by high resolution electron microscopy [15]. The GB phase is described as a regular solution and the quasi-liquid phase is described as a self-associate solution. The self-associate solution was also used to describe the liquid phase in the Cu–Bi system [4]. The structure of the GB phase does not change after the formation of the quasi-liquid film. The Gibbs energy of elements in the GB phase can be presented as the Gibbs energy in the solid phase plus the product of the surface tension of the GB phase (γ) by the partial molar area (ω) of the elements. The mole numbers of atoms per unit area at the Φ/S, Φ/L and L/S interfaces are assumed to be the same (n_s). The interchange energy across the L/S interface is the

same as in the solid phase (Ω^S), while the interchange energies across the Φ/S and Φ/L interfaces (Ω^I) are equal to each other and depend on the temperature.

In the case shown in Fig. 4a the excess Gibbs energy of the GB per unit area can be written as

$$\Delta G_a = n_s[\Delta G^{\Phi}h^{\Phi} + 2\Omega^I(x^{\Phi} - x^S)^2] \qquad \text{Eq. 4}$$

and in the case shown in Fig. 4b it is

$$\Delta G_b = n_s[\Delta G^{\Phi}h^{\Phi} + 2\Delta G^L h^L + 2\Omega^I(x^{\Phi} - x^L)^2 + 2\Omega^S(x^L - x^S)^2] \qquad \text{Eq. 5}$$

where x^L is the Bi concentration in the quasi-liquid phase, and ΔG^{Φ} and ΔG^L are the excess Gibbs energies of one ML of the GB phase and liquid phase, respectively. h^{Φ} is the thickness of the GB phase and h^L is the thickness of the quasi-liquid phase at one side of the GB phase. Both h^{Φ} and h^L are assumed to be one ML. The excess Gibbs energies can be expressed as

$$\Delta G^{L,\Phi} = G^{L,\Phi}(x^{L,\Phi}) - G^S(x^S) - (x^{L,\Phi} - x^S) \cdot \left.\frac{\partial G^S}{\partial x}\right|_{x^S} \qquad \text{Eq. 6}$$

where G^S, G^L and G^{Φ} are the Gibbs energies of the solid, liquid and GB phases, respectively. The square-concentration terms derived from [16] in Eqs. 4 and 5 are the chemical energies due to the difference of the Bi concentrations on both sides of the interface. The square-concentration form for the L/S and Φ/L interfaces is an approximation because the liquid phase is described in the framework of the self-associate model, but not in the regular solution model. However, the ratio of the cluster size of Cu and Bi (1.4) does not exceed unity very much; therefore, the square-concentration approximation of the chemical energies for L/S and Φ/L interfaces is still reasonable.

ΔG_a is minimized with respect to x^{Φ}, and ΔG_b is minimized with respect to x^L and x^{Φ}, independently. The minimized values of ΔG_a and ΔG_b are compared. The lower value determines the stable structure. If the structure (a) is stable, the segregation amount is x^{Φ}. If, however, ΔG_b is smaller than ΔG_a, the quasi-liquid phase is in equilibrium with the GB phase. The segregation amount in this case is the sum of the Bi concentration in the GB phase (x^{Φ}) and in the quasi-liquid phase ($2x^L$). This is reasonable because of the short diffusion length (some atomic diameters) for precipitating of Bi atoms from the quasi-liquid phase during water quenching. For the prewetting model the same value is used for the interchange energy in the GB phase as for the Fowler isotherm. For the interchange energies in the solid and liquid phases the same parameters have been used as in the previous study of the Cu-Bi phase diagram [5]. The optimized variables are $\Delta \gamma \omega$, Ω^{I0} and k. $\Delta \gamma \omega$ is the difference between the products of the GB energy by the partial molar area of Cu and Bi, Ω^{I0} and k are the parameters which determine the temperature dependence of Ω^I according to the equation $\Omega^I = \Omega^{I0} + kT$.

All thermodynamic parameters used are listed in Table 1. The value Ω^I is close to the interchange energies in the GB as expected, and $\Delta \gamma \omega = 55$ kJ/mol is acceptable because it is comparable with the roughly estimated value of 40 kJ/mol [17]. The temperature dependence of the GB adsorption calculated in the framework of the prewetting model is drawn in Fig. 1 as a solid line. The temperatures at which the discontinuous changes of GB segregation occur in the calculated curves and the experimental results are in a good agreement with each other. The only discrepancy is that the calculated Bi enrichment is lower than obtained in experiments at high Bi bulk concentrations and high temperatures (see Figs. 1e and f). It is expected that a better agreement can be achieved if the temperature and concentration dependence of the thickness of the GB and quasi-liquid phases are taken into account. Because the widening of the quasi-liquid phase may violate the stability of the GB phase, the prewetting model with these temperature and concentration dependence will be modified in future works.

The jump temperature of segregation calculated in the framework of the prewetting model is plotted as a function of the Bi concentration in Fig. 2 as a dashed curve. Figure 2 shows a better overview compared to Fig. 1. Such a line could be supposed as the "*grain boundary solidus line*" and was recently suggested for the Fe–Si–Zn system [18]. On the left side of the GB solidus line only the GB solid solution (Φ) is stable. On the right side of the GB solidus line, the quasi-liquid phase forms in the GB (Φ + quasi-L). Alloys which lie in the two-phase region of the bulk phase diagram contain the quasi-liquid phase in GBs. However, the quasi-liquid phase in the GBs can be stable even in the single-phase area of the bulk phase diagram (between the GB and bulk solidus lines). Apparently, the GB solidus line is very important in practice because numerous properties of materials depend severely on the GB structure. It should be mentioned that, despite the good agreement between the experimental and calculated data, the result obtained by the AES analysis of the fracture surfaces is not a direct proof for the existence of a quasi-liquid phase. However, an *in-situ* observation of the quasi-liquid phase is difficult because of the high vapour pressure of liquid Bi and the surface segregation which are especially important in the thin specimens used in investigations with the transmission electron microscopy. Both effects induce the instability of the quasi-liquid phase.

The McLean behaviour of the regular model for a thin film

One of the parameters used in this work is the interchange energy of Cu and Bi atoms which characterizes the behaviour of the solution. To estimate the interchange energy in the GB phase the enthalpy of mixing of a binary system in the GB phase is derived by the quasi-chemical method in which only the bonding between the nearest neighbours is considered. Let assume that the GB phase is a homogeneous thin film having a thickness of h measured in ML. All atoms in this film have the same co-ordination number (Z) which can be divided into three parts: within the film (Z_l), oriented toward the neighbouring planes (Z_v) and toward the outer environment (Z_o). The co-ordination of an atom at the border of the film is drawn schematically in Fig. 5. When the film is composed of N_i atoms of a pure element, its enthalpy can be expressed as

$$H_i = \frac{N_i Z}{2}\varepsilon_{i,i} + 2n_i Z_o \varepsilon_{i,o} - n_i Z_v \varepsilon_{i,i}$$ Eq. 7

for i as Cu or Bi where $\varepsilon_{i,o}$ is the binding energy between i atoms and outer atoms and $n_i = N_i/h$ is the planar atom density in the film. If the film is composed of N_{Cu} and N_{Bi} atoms, the enthalpy becomes

$$H_{Cu,Bi} = \frac{N_{Cu}N_{Bi}}{N}Z\varepsilon_{Cu,Bi} + \frac{1}{2}\cdot\frac{(N_{Cu})^2}{N}Z\varepsilon_{Cu,Cu} + \frac{1}{2}\cdot\frac{(N_{Bi})^2}{N}Z\varepsilon_{Bi,Bi} + 2n_{Cu}Z_o\varepsilon_{Cu,o} + 2n_{Bi}Z_o\varepsilon_{Bi,o} -$$

$$(\frac{n_{Cu}N_{Bi}}{N}Z_v\varepsilon_{Cu,Bi} + \frac{n_{Bi}N_{Cu}}{N}Z_v\varepsilon_{Cu,Bi} + \frac{n_{Cu}N_{Cu}}{N}Z_v\varepsilon_{Cu,Cu} + \frac{n_{Bi}N_{Bi}}{N}Z_v\varepsilon_{Bi,Bi})$$ Eq. 8

for $N = N_{Cu} + N_{Bi}$. Here $\varepsilon_{Cu,Bi}$, $\varepsilon_{Cu,Cu}$ and $\varepsilon_{Bi,Bi}$ have the same meaning as in Eq. 3 but refer to the thin film.

From Eqs. 7 and 8 the molar enthalpy of mixing in the thin film can be expressed as

$$\Delta H_{mix} = \frac{H_{Cu,Bi} - H_{Cu} - H_{Bi}}{N} = x_{Cu}x_{Bi}(Z - \frac{2Z_v}{h})(\varepsilon_{Cu,Bi} - \frac{\varepsilon_{Cu,Cu} + \varepsilon_{Bi,Bi}}{2})$$ Eq. 9

When $h = 1$ for a one-ML film and $Z_v/Z = 0.25$ ΔH_{mix} can be written as

$$\Delta H_{mix} = \frac{1}{2}x_{Cu}x_{Bi}\Omega = x_{Cu}x_{Bi}\Omega^\Phi$$ Eq. 10

Ω and Ω^Φ can be considered as the "real" interchange energy and the "apparent" interchange energy of the thin film. From Eq. 10 we get that $\Omega^\Phi = \Omega/2$. It is interesting to note that if the real interchange energy in the GB is assumed to be the same as in the bulk at absolute zero (112 kJ/mol), the value of 56 kJ/mol estimated for the apparent interchange energy in the GB is very close to that
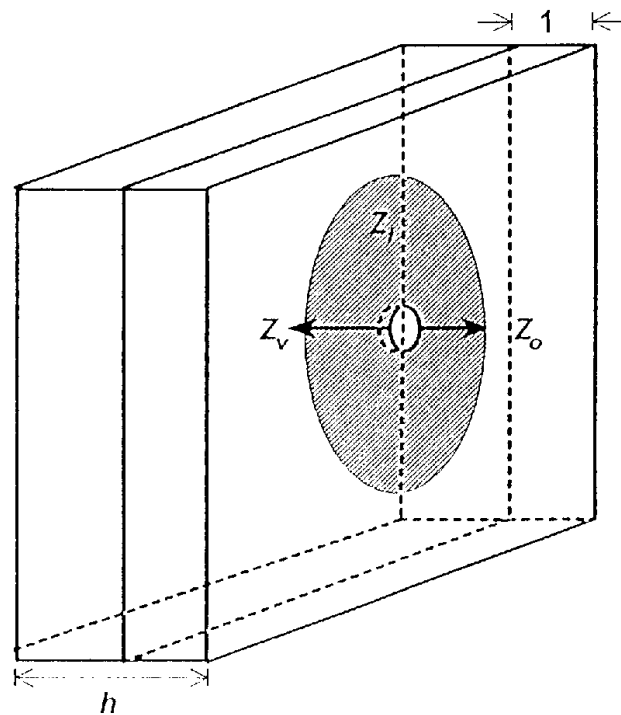
Fig. 5. A schematic presentation of the co-ordination of an atom in the border plane of a thin film with the thickness of *h* ML.

obtained by optimization (55 kJ/mol, see Table 1). A stronger temperature dependence for the GB phase ($k = -34$) than that calculated from the solid phase ($k = -17.5$) indicates that the GB phase may exhibit a higher entropy.

On the other hand, the interchange energy across the interfaces introduced in the interfacial chemical energy can be expressed as

$$\Omega^I = A Z_v (\varepsilon_{Cu,Bi} - \frac{\varepsilon_{Cu,Cu} + \varepsilon_{Bi,Bi}}{2})$$

Eq. 11

With the same condition $Z_v / Z = 0.25$ used above it is found that $\Omega^I - \Omega/4$ or $\Omega^I = \Omega^\Phi / 2$. This is in a good agreement with the optimized parameters.

Minimizing ΔG_a in Eq. 4 with respect to x^Φ, we arrive at the following equation which is very similar to the general segregation equation [19] :

$$\frac{x^\Phi}{1-x^\Phi} = \frac{x^S}{1-x^S} \exp[-\frac{(\Delta y\omega + \Omega^\Phi - \Omega^S) - 2(\Omega^\Phi - 2\Omega^I)x^\Phi}{RT}]$$

Eq. 12

As it was shown above, for a segregation film of 1 ML $\Omega^I = \Omega^\Phi / 2$, and the coefficient of the concentration-dependent term $2(\Omega^\Phi - 2\Omega^I)$ vanished. Equation 12 turns into the Langmuir–McLean adsorption isotherm [20]. This indicates a McLean–type behaviour of the GB segregation even if the interchange energy in the GB layer is high. The latter condition was thought to cause the Fowler–type segregation behaviour. Indeed, no discontinuity on the concentration and temperature dependencies of the GB segregation has been found in the Mo–O [21] and Ni–In [7] systems in which the interchange energy in the bulk is high. According to the classical point of view, these systems should exhibit the Fowler–type segregation behaviour. Our prewetting model provides a reasonable explanation of this point of confusion. However, to clarify the possibility of the existence of the thin GB quasi-liquid films in these systems, further experimental and theoretical efforts are necessary.

CONCLUSIONS

From the present studies the following conclusions can be drawn.

- Discontinuities in the temperature dependencies of the Bi segregation on the GBs in Cu have been observed in six Cu–Bi alloys of different compositions.
- These discontinuities correlate with the bulk solidus line in the Cu–Bi system. The prewetting model of the GB segregation has been suggested since it explains the abrupt change of the Bi adsorption at the GB due to the formation of a thin layer of a Bi-rich quasi-liquid phase.
- The GB solidus line for the Cu–Bi system was suggested. Such a line may play a decisive role in material properties.
- A simple deduction of the enthalpy of mixing for a thin film was made in the framework of the regular solution model to explain the McLean-type behaviour of a one-ML segregation. It is shown that the McLean behaviour of a thin film is independent of the magnitude of interchange energy.

ACKNOWLEDGMENTS

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DISCUSSION

Beke: What is about the role of triple junctions?

Straumal: It is a very interesting question. We plan to start the experimental studies. It is not so easy to predict what will happen. Of course, if grain boundaries are wetted the triple junctions must also be wetted. As I believe the wetting depth must be lower.

Beke: Do you think that the transition is lower?

Straumal: When you study at the beginning you see the liquid located at the triple junctions.

Gupta: You showed us the case when the composition drops with the temperature. There are the systems where liquidus goes up with the temperature. There is a definite difference. Did you study the systems like that? Because sometimes these shifts are defined as A and C types. Actually, A-type is an ordered type, C-type is not. Grain boundary segregation is connected with the A-type of behaviour.

Straumal: It is not easy to answer. But I believe such behaviour is more probable for the diagrams of the type I have shown.

Gupta: That is curious.

Philibert: My question is about the thickness of the liquid film. Is it important whether it is finite or infinite reservoir for this wetting material?

Straumal: It is important only from the experimental point of view, not the thermodynamical. If the energy of two interfaces is lower than the grain boundary energy, you have the wetted grain boundary. But from the experimental point of view you must have a limited reservoir in order to understand whether the angle at the top of the liquid channel is zero or not. If you have a lot of liquid you can simply lose the grain boundary.

Philibert: If you have a limited reservoir you can saturate the liquid with the substrate material. So, this saturation can change quite a lot σ_0 as compared with the infinite reservoir in which should be always σ_0 for a pure tin.

Straumal: We consider actually the limited reservoir, because in our experiments we tried to keep the thermodynamical equilibrium. In that case we must consider solid and liquid in thermodynamical equilibrium. Other case has no sense.

Bokstein: Your tin was a saturated solution initially, wasn't it?

Straumal: At the beginning not, but as a result it was.

Philibert: It depends on the difference of the kinetics of the dissolution of the flat phase and grain boundary. Because you have the general dissolution.

Straumal: Yes, we have the general dissolution, but the penetration will proceed further. We can wait, but the penetration will not be so quick.

Bokstein: What was the thickness of these channels?

Straumal: Few micrometers. You can see them into optical microscope. Look at the photos.

Bokstein: Very nice photos.