Pergamon

Scripta Materialia, Vol. 37, No. 6, pp. 729-735, 1997
Elsevier Science Ltd

1359-6462/97 $17.00 + .00

PII S1359-6462(97)00171-1

TEMPERATURE DEPENDENCE OF THE GRAIN BOUNDARY SEGREGATION OF Bi IN Cu POLYCRYSTALS

L.–S. Chang, E. Rabkin, B. Straumal, P. Lejček*, S. Hofmann** and W. Gust
Max-Plank-Institut für Metallforschung and Institut für Metallkunde,
Seestr. 75, D-70174 Stuttgart, Germany
*Institute of Physics , Academy of Sciences, Na Slovance 2, CZ–18040 Prague 8, Czech Republic
**Also at: National Research Institute of Metals, 1–2–1 Sengen, Tsukuba, Ibaraki 305, Japan

(Received January 24, 1997)
(Accepted April 6, 1997)

Introduction

The phenomenon of grain boundary (**GB**) segregation is of a great practical importance and constantly attracts the attention of materials scientists [1,2]. The equilibrium thermodynamics provides a quantitative basis for the description of the temperature and concentration dependence of the impurity adsorption at the GBs. Depending on the simplified model adapted for the solid solution at the GB, two different types of segregation behaviour are possible: the Fowler type for the regular solution with a strong demixing tendency and the McLean type for the ideal solution in the GB. In the former case the impurity adsorption at the GB changes rapidly in a narrow range of temperature or bulk concentration, while in the latter case a smooth decrease of the impurity adsorption with increasing temperature occurs.

The type of the Bi segregation at the GBs in Cu is still uncertain. A reasonable agreement was found between the McLean model and the experimental segregation data obtained by analytical electron microscopy (**AEM**) [3] and Auger electron spectroscopy (**AES**) [4] with the close values of the segregation energies of 66 and 67 kJ/mol, respectively. Contrariwise, Menyhard *et al.* [5] showed in their AES studies that the Bi segregation in Cu polycrystals exhibits the Fowler type behaviour. However, there is no disagreement between the results of [3,4] and [5] because the bulk Bi compositions in the Cu–Bi alloys studied were different. The maximum segregation amounts measured in these works were also different, especially, the maximum value found in [4] was almost twice as large as that from [3].

Recently, the solubility of Bi in solid Cu, which is one of the most important parameters for the understanding of the segregation phenomena, was determined by Chang *et al.* [6] (Fig. 1). No relationship can be found between the segregation data from the previous studies [3–5] and the solidus line. In [3] the Bi concentration (2.7 at. ppm) was too small to reach the thermodynamic equilibrium at low temperatures. A possible low–temperature jump in the temperature dependence of the GB adsorption of Bi could not be detected in such conditions. On the contrary, in [4] a high–temperature jump might be overlooked because the highest annealing temperature was merely 650°C. A more systematic work

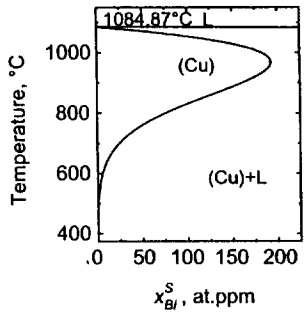

Figure 1. Solidus line on the Cu side of the Cu–Bi phase diagram; L = liquid.

was carried out in [5] in which the jump of Bi segregation in Cu was reported for the first time. But the proposed GB phase transition seemed to be not so convincing due to the uncertainty of the bulk Bi concentration (see also [7]), the lack of high–temperature segregation data and the misapplication of the Fowler model for one monolayer to interpret a multilayer segregation. The aim of this study is to verify the existence of an anomalous change of the Bi segregation on the GBs in Cu polycrystals with an accurately determined bulk Bi composition.

Experimental Procedure

The polycrystalline Cu cylinders containing 25 at. ppm Bi were prepared by vacuum induction melting followed by casting. Bar specimens (15 × 3 × 3 mm) were cut from these as–received cylinders for AES studies. The specimens were encapsulated and homogenized in vacuum at 900°C for 24 hours. The grain size was about 100 μm. The specimens were then vacuum annealed at temperatures between 500 and 1000°C for different times estimated from the volume diffusion coefficient of Bi atoms in solid Cu [8]. The details of the heat–treatment are listed in Table 1. Such a large temperature range was chosen to avoid any oversight of a possible segregation transition. A notch (ca. 0.8 mm) was cut at each side of the bars by a diamond saw with a slow cutting speed. Finally, the specimens were cleaned with acetone by an ultrasonic vibrator.

A 10 keV Auger electron multiprobe was used to determine the amount of Bi on the fractured surface. The specimens were broken *in situ* after they were cooled down in contact with liquid N_2 in the AES chamber. Depending on the behaviour of the rupture, 5–15 fracture surfaces exhibiting an intergranular fracture were chosen for the investigation and two points from each surface were analysed. The Bi segregation amount is evaluated from the peak-to-peak heights of the Cu and Bi signals in the electron spectrum introduced into the characteristic equation in the model of a pure Bi thin film [9] in which the Bi atoms have the same average atomic volume as that in pure standard Bi. A depth profile was determined by the sputtering with argon ions on some surfaces in order to compare the thickness of the Bi segregation layers estimated from spectrum with that from the depth profile.

TABLE 1
Details of the Annealing Conditions

T(°C)	400	500	550	600	650	675	700	710	720	750	800	850	900	950	1000
time	20 d	10 d	10 d	2 d	2 d	25 h	4 h	4 h	4 h	4 h	4 h	4 h	1 h	1 h	30 min

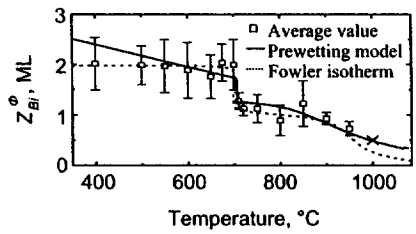

Figure 2. Bi grain boundary segregation as a function of annealing temperature; x: not brittle.

Results and Discussion

The amount of the Bi adsorption on GBs in monolayers (ML) at different annealing temperatures is presented in Fig. 2. Each square point indicates the average value from all analysed data from the fracture surfaces in a specimen, and the error bars show the standard deviations. One can see that there are two levels of the adsorption. At temperatures below 710°C the adsorption stays at 2 ML and at 710°C it suddenly drops down to 1.25 ML. At temperatures above 710°C the average value of Bi adsorption decreases with increasing temperature. Such a kind of "jump" of the GB adsorption is similar with that observed by Menyhard *et al.* [5]. According to their analysis the saturated Bi segregation level is 1–1.2 ML on the fracture surface before the jump, that means, the saturated level for grain boundaries is 2–2.4 ML before the jump. This is in agreement with our results. On the other hand, their specimens showed a ductile fracture at 720°C while in our work the specimens were embrittled till 900°C. The difference may be in the treatment of specimens. Our specimens were neither cold nor hot worked after casting, in contrast to the severe deformation in their work. Such a deformation may result in a texture full with twins. The fraction of high energy GBs in the sample, which are always impurity-favourable, was reduced. Therefore, at temperatures above the jump temperature the specimens may be ductile because of the unembrittled twin boundaries. Otherwise, at lower temperatures the twin boundaries may be also segregated with Bi atoms. The segregation on twins is prominent after that the specimen is deformed [10].

The jump in the temperature dependence of Bi segregation between 700 and 710°C could be mathematically described with the classic Fowler isotherm for two layers. We assumed that there are two different layers with different types of segregation sites. Each layer exhibits its own segregation energy but the interaction energies between the Cu and Bi atoms in these two layers are the same. For

TABLE 2
Parameters for the Description of the Cu–Bi Binary System

Phase	Model	Parameter
Solid (S).....	Regular	$\Omega^S = 112 \times 10^5 - 35 \times T$ J/mol
Liquid (L).....	Self–associate	$n = 1.4$
		$W = 210 \times 10^4 - 8 \times T$ J/mol
GB (Φ).....	Fowler	$\Omega^{\Phi} = 5.5 \times 10^4 - 34 \times T$ J/mol
		$\Delta G^{seg} = -96$ kJ/mol .....1st layer
		$\Delta G^{seg} = -66$ kJ/mol .....2nd layer
	Prewetting	$\Omega^{\Phi} = 5.5 \times 10^4 - 34 \times T$ J/mol
		$\Omega^{I} = 19$ kJ/mol
		$\Delta\gamma\omega = 55$ kJ/mol

the first and second layer the relation between the Bi concentration in the GBs (x_{Bi}^{Φ}) and in the bulk (x_{Bi}^{S}) can be written as followed

$$\frac{x_{Bi}^{\Phi'}}{1-x_{Bi}^{\Phi'}} = \frac{x_{Bi}^{S}}{1-x_{Bi}^{S}} \exp\left(\frac{\Delta G'}{RT}\right) \tag{1}$$

$$\frac{x_{Bi}^{\Phi''}}{1-x_{Bi}^{\Phi''}} = \frac{x_{Bi}^{S}}{1-x_{Bi}^{S}} \exp\left(\frac{\Delta G''}{RT}\right) \tag{2}$$

and the total segregation amount (Z_{Bi}^{Φ}) measured is the sum of the two layers

$$Z_{Bi}^{\Phi} = x_{Bi}^{\Phi'} + x_{Bi}^{\Phi''} \tag{3}$$

while ΔG is presented as

$$\Delta G = -\Delta G^{seg} + 2\Omega^{\Phi} x_{Bi}^{\Phi} - 2\Omega^{S} x_{Bi}^{S} \tag{4}$$

where ΔG^{seg} is the segregation energy, Ω^{Φ} and Ω^{S} are the interaction energies in the GB phase and in the solid phase, respectively. Ω^{Φ} and Ω^{S} depend linearly on the temperature as derived by Chang *et al.* [6]. The fitting curve with the segregation data is plotted in Fig. 2 as a dashed line. All optimized parameters are listed in Table 2. The segregation energy of the second layer (-66 kJ/mol) and the interaction energy in GB phase at the jump temperature (21.9 kJ/mol) are similar to that from [5]: -58.6 and 20.9 kJ/mol, respectively. Surprisingly, the segregation energy of the first layer (-96 kJ/mol) is comparable with that calculated from computer simulation using pair potentials by Sutton and Vitek [11] and using the embedded atom method by Vitek *et al.* [12]. This invalidates the skeptical viewpoint from Wetzel and Machlin [13] that the lattice energy functions used may yield too high values for the segregation energy. The first monolayer which was actually the object simulated in [12] gives the main contribution to the Bi segregation due to its high segregation energy. And the sudden change results from the properties of the second layer whose segregation energy is reduced because of smaller free spaces for the Bi atoms. However, the discontinuous change of GB segregation was not predicted in computer simulations of Vitek *et al.* [12]. Their result showed that the Bi segregation obeys the McLean equation.

A New Prewetting Model

Based on the Cu–Bi phase diagram [6] the solidus temperature of a Cu–25 at. ppm Bi alloy is approx. 700°C. It is identical with the jump temperature of Bi segregation within the experimental error. In spite of the fact that the Bi segregation in a Cu–25 at. ppm Bi alloy is properly described by using the classic Fowler isotherm, this coincidence cannot be explained in the framework of the Fowler isotherm. It shows that the liquid phase plays some role in the segregation behaviour. Accordingly, a "prewetting model" is developed to explain this coincidence. The similarity between the GB segregation and the prewetting phenomenon described by Cahn was firstly pointed out in [14]. Instead of a second layer of the GB phase assumed in the Fowler isotherm, two monolayers of a quasi–liquid phase straddling the Bi–rich monolayer are supposed to occur in the two–phase area of the Cu–Bi phase diagram. This quasi–liquid phase reduces the excess chemical energy associated with the Bi–rich first

layer, while in bulk Cu solid solution the excess Gibbs energy associated with such a quasi–liquid phase is comparably large to cause it to be unstable. The prewetting model is illustrated schematically in Fig. 3. The case (a) shows that only a Bi–enriched GB solid phase is presented, while in the case (b) two layers of the quasi–liquid phase are built between the liquid 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. Howe [15] observed recently such a density modulations in the liquid phase close to the solid/liquid interface by the high resolution electron microscopy. Following assumptions were made to simplify the calculation:

(i) The GB phase can be described as a regular solution and its structural energy remains unchanged even after the formation of the quasi–liquid film.
(ii) The quasi–liquid phase can be described with the self–associate model proposed in [16].
(iii) The Gibbs energy of pure elements in the GB phase is that in the solid phase plus the product of the GB energy (γ) by the partial molar area (ω).
(iv) The mole numbers of atoms per unit area (n_s) at the GB(Φ)/solid(S), Φ/liquid(L) and L/S interfaces are the same and the number of the interatomic bonds per atom across each of these three kinds of interfaces divided by the coordination number in the bulk is 0.5.
(v) The interaction energy across the L/S interface is the same as in the solid phase (Ω^S), while the interaction energies across the Φ/S and Φ_L/L interfaces (Ω^I) are equal to each other and do not depend on temperature.

In the case (a) the energy increase per unit area can be written as

$$\Delta G_1 = n_s[\Delta G^{\Phi} h^{\Phi} + \Omega^I (x_{Bi}^{\Phi} - x_{Bi}^{S})^2] \tag{5}$$

and in the case (b) it is

$$\Delta G_2 = n_s\{\Delta G^{\Phi} h^{\Phi} + \Delta G^{L} + \Omega^I (x_{Bi}^{\Phi} - x_{Bi}^{L})^2 + \Omega^S (x_{Bi}^{L} - x_{Bi}^{S})^2]\} \tag{6}$$

where ΔG^{Φ} and ΔG^{L} are the excess Gibbs energies of one monolayer of the GB phase and liquid phase, respectively, h^{Φ} is the thickness of the GB phase which is assumed to be 1.25 ML [17], and x_{Bi}^{L} is the Bi concentration in the quasi–liquid phase. The excess Gibbs energies can be expressed as

$$\Delta G^{L,\Phi} = G^{L,\Phi}(x_{Bi}^{L,\Phi}) - G^{S}(x_{Bi}^{S}) - (x_{Bi}^{L,\Phi} - x_{Bi}^{S}) \cdot \left.\frac{dG^{S}}{dx_{Bi}}\right|_{x_{Bi} = x_{Bi}^{S}} \tag{7}$$

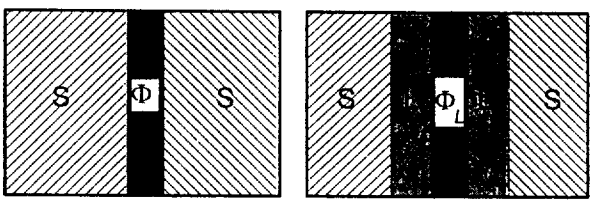

Figure 3. Two possible GB structures in the framework of the prewetting model; S = solid, L = quasi–liquid, Φ and Φ_L are the solid and liquid GB phases, respectively.

where G^S, G^L, G^Φ are the Gibbs energies of the solid, the liquid and the GB phases, respectively. The square–concentration terms derived from [18] in Eqs. (5) and (6) are the chemical energies induced by the difference of the Bi concentrations on both sides of the interface. The square–concentration form for the liquid/solid and liquid/GB interfaces is an approximation due to the regular behaviour of the atomic clusters in the liquid phase.

x_{Bi}^Φ is determined by minimizing ΔG_1 to obtain the most stable state of the GB phase. In the meantime the combination of x_{Bi}^L and x_{Bi}^Φ which minimize the value of ΔG_2 should be found out. From a comparison of the minimized values of ΔG_1 and ΔG_2 the conclusion can be drawn which from two structures, (1) or (2), is stable. If the structure (1) is stable, the segregation amount $Z_{Bi}^\Phi = h^\Phi x_{Bi}^\Phi$. On the contrary, if ΔG_2 is smaller, the quasi–liquid phase is in equilibrium with the GB phase. The segregation amount in this case is the sum of Bi concentrations in the GB phase and the quasi–liquid phase: $Z_{Bi}^\Phi = h^\Phi x_{Bi}^\Phi + 2x_{Bi}^L$. This is reasonable because of the short diffusion length (some atomic diameters) for precipitating of Bi atoms from the quasi–liquid phase during water quench. In carrying out the fitting in the framework of the prewetting model the same value of the interaction energy in the GB phase is used as in the Fowler isotherm. For the interaction energies in the solid and liquid phases the same parameters have been used as in the previous study of the Cu–Bi phase diagram [6]. The difference between the products of the GB energy by the partial molar area of Cu and Bi ($\Delta\gamma\omega$) and Ω' are the optimized variables. The fitting curve derived from the prewetting model is drawn in Fig. 2 as a solid line and all parameters used are listed in Table 2. The value $\Delta\gamma\omega = 55$ kJ/mol is acceptable as comparing with the roughly estimated value of 40 kJ/mol [19].

Finally, it must be stressed that in the prewetting model the coincidence between the temperature of the anomalous change of the segregation with the solidus temperature is physically explained. The existence of such a quasi–liquid phase may result in other anomalous changes of the GB properties, for instance, the faceting–defaceting transition [20, 21] and some erratic changes observed in the measurement of the GB mobility [22] and GB diffusion coefficient [23].

Acknowledgment

This work has been supported by the Deutsche Forschungsgemeinschaft (contracts Gu 258/12–1 and Ho 708/15-1).

References

1. E.D. Hondros and M.P. Seah, Inter. Metals Rev. **22**, 262 (1977).
2. S. Hofmann and P. Lejček, Interface Sci. **3**, 241 (1996).
3. J.R. Michael and D.B. Williams, Met. Trans. A **15**, 99 (1984).
4. A. Fraczkiewicz and M. Biscondi, J. de Phys. **46**, C4-497 (1985).
5. M. Menyhard, B. Blum and C.J. McMahon Jr., Acta metall. **37**, 549 (1989).
6. L.–S. Chang, B.B. Straumal, E. Rabkin, W. Gust and F. Sommer, J. Phase Equilibria., in press (1997).
7. B. Blum, M. Menyhard, D.E. Luzzi and C.J. McMahon, Jr., Scripta metall. **24**, 2169 (1990).
8. H. Mehrer (ed.), Diffusion in Solid Metals and Alloys, Landolt–Börnstein New Series, Springer-Verlag, Berlin, **III/26**, 142 (1990).
9. S. Hofmann, in "Wilson & Wilson's Comprehensive Analytical Chemistry", edited by G. Svehla, Vol. IX, Elsevier, Amsterdam, 89 (1979).
10. D.E. Luzzi, Phil. Mag. Lett. **63**, 281 (1991).
11. A.P. Sutton and V. Vitek, Acta metall. **30**, 2011 (1982).
12. V. Vitek, G.J. Ackland, M. Menyhard and Min Yan, in "Interfaces: Structure and Properties", edited by S. Ranganathan, C.S. Pande, B.B. Rath and D.A. Smith, Trans Tech Publications Ltd., Aedemannsdorf, 3 (1993).
13. J.T. Wetzel and E.S. Machlin, Scripta metall. **17**, 555 (1983).

14. E. Rabkin, Mater. Lett. **25**, 199 (1995).
15. J. Howe, Phil. Mag. A **74**, 761 (1996).
16. R.N. Singh and F. Sommer, Z. Metallk. **83**, 533 (1992).
17. V. Vitek and G.–J. Wang, Surf. Sci. **144**, 110 (1984).
18. Y.W. Lee and H.I. Aaronson, Acta metall. **28**, 539 (1980).
19. L.E. Murr, Interfacial Phenomena in Metals and Alloys, Addison-Wesley Reading, Massachusetts, 82 (1975).
20. T.G. Ference and R.W. Balluffi, Scripta metall. **22**, 1929 (1988).
21. C. Urdaneta, D.E. Luzzi and C.J. McMahon, Jr., Mater. Sci. Forum **126**, 85 (1993).
22. E.L. Maksimova, L.S. Shvindlerman and B.B. Straumal, Acta metall. **36**, 1573 (1988).
23. E.I. Rabkin, L.S. Shvindlerman and B.B. Straumal, J. Less–Common Metals **159**, 43 (1990).