

Hot isostatic pressing of Cu–Bi polycrystals with liquid-like grain boundary layers

Li-Shin Chang ^{a,*}, B. Straumal ^b, E. Rabkin ^c, W. Lojkowski ^d, W. Gust ^e

^a Department of Material Engineering, National Chung Hsing University, 40227 Taichung, Taiwan

^b Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow 142432, Russia

^c Department of Materials Engineering, TECHNION–Israel Institute of Technology, 32000 Haifa, Israel

^d Institute of High Pressure Physics, Polish Academy of Sciences, Sokolowska 29, 01-142 Warsaw, Poland

^e Institute of Physical Metallurgy, University of Stuttgart, Heisenbergstr. 3, D-70569 Stuttgart, Germany

Received 3 April 2006; received in revised form 21 August 2006; accepted 21 August 2006

Available online 31 October 2006

Abstract

The grain boundary segregation in an Cu–50 at.ppm Bi alloy annealed at two temperatures and under various hydrostatic pressures in a hot isostatic pressing apparatus was investigated by means of Auger electron spectroscopy. It was found that high pressures have only little effect on grain boundary segregation. At a temperature of 973 K the segregation level remained approximately constant at 2 monolayers of Bi for all pressures studied. Some decrease of the grain boundary segregation with increasing pressure was observed at 1173 K. It was also demonstrated that the segregation level in the alloy treated at 0.01 GPa depended on the sample cooling rate after annealing. The observed pressure dependence of Bi segregation to the grain boundaries was interpreted in terms of non-equilibrium segregation during specimen cooling.

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Keywords: Grain boundary segregation; Cu–Bi alloy; Hot isostatic pressing; Auger electron spectroscopy

1. Introduction

Hot isostatic pressing (HIP) is an important technology that permits the densification of parts during casting, sintering, welding and joining. HIP can be considerably accelerated in the presence of small amounts of a liquid phase, which wets the powder particles surface and/or interfaces between grains in polycrystals [1–3]. It has recently been shown that thin layers of an equilibrium liquid-like phase may be present at the grain boundaries (GBs) in metallic alloys [4–6]. Such liquid-like GB layers can be stable even without the presence of a “true” bulk liquid phase in a polycrystal [4–6]. In particular, the liquid-like GB layers possess a very high diffusivity, comparable to that of a bulk

melt [5,7]. The liquid-like GB layers in the single-phase “solid-solution” area of a bulk phase diagram may exist only if the liquid phase completely wets all GBs in the neighboring two-phase “liquid + solid” area (Fig. 1). In this case, the tie-line of the GB wetting phase transition continues as the GB solidus line into the single-phase solid solution area (Fig. 1).

It has been established in a previous study [4] that Bi segregation at the GBs in Cu–Bi polycrystals increased discontinuously with increasing bulk Bi concentration. This abrupt increase in the amount of Bi segregated at GBs occurred at lower Bi concentrations (Fig. 1, thin retrograde line in the (Cu) area) than those corresponding to the bulk solidus line (Fig. 1, thick retrograde line). This phenomenon was associated with a pre-wetting phase transformation at the GBs. At the composition or temperature corresponding to this pre-wetting transformation, the GBs are covered with a thin, quasi-liquid layer of the Bi-rich phase. This

* Corresponding author. Tel.: +886 4 22840500x406; fax: +886 4 22852433.

E-mail address: lschang@dragon.nchu.edu.tw (L.-S. Chang).

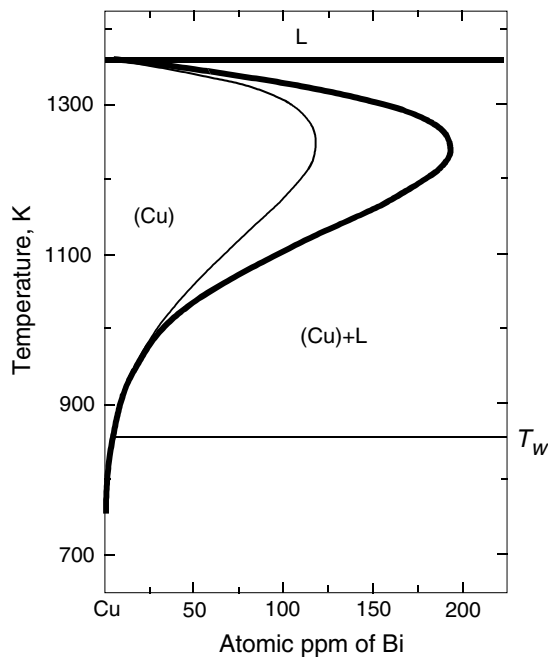


Fig. 1. The Cu-rich part of a Cu–Bi bulk phase diagram with GB lines obtained in previous works [5,6,8,11,17,19,22]. Thick lines are bulk liquidus (nearly horizontal) and solidus (retrograde). Three areas are shown: single-phase “liquid” area L, single-phase “solid solution” area (Cu) and two-phase “solid + liquid” area (Cu) + L. Thin lines are the GB solidus (retrograde) and GB wetting tie-line at T_w (horizontal). The liquid phase completely wets all high-angle GBs in Cu above T_w in the (Cu) + L area. The GB wetting tie-line in the (Cu) + L area has a continuation in the “solid solution” area (Cu). This continuation is a retrograde GB solidus. The GB solidus starts at the intersection between wetting tie-line and bulk solidus and finishes in the Cu melting point. Between GB solidus (thin line) and bulk solidus (thick line) GBs are covered by a thin layer of the liquid-like phase.

layer thickness is equivalent to the segregation of two monolayers (MLs) of Bi, and is nearly temperature-independent. However, the GB segregation of Bi in Cu–Bi alloys containing less Bi is just about one ML or less. The temperature dependence of this “single-layer” segregation can be described by a classical McLean model [4]. In particular, the GB concentration of Bi monotonously decreases with increasing temperature. An abrupt change of GB segregation from two to one ML occurs whenever the GB pre-wetting line or the GB solidus line is crossed by changing the temperature or composition. In addition to the abrupt changes of GB diffusivity and GB segregation, crossing of the GB solidus line also leads to discontinuous changes in GB strength [4,8,9], GB mobility [10] and the electrical resistivity of a polycrystal [11].

High pressure may strongly affect the stability of the liquid-like Bi-rich segregation layers at the GBs in Cu–Bi alloys. Particularly, the melt has a higher specific volume in comparison with the solid phase. Therefore, high pressure may upset the GB wetting conditions, as observed for (Fe–Si)–Zn alloys [2,12]. If the GB wetting conditions are not fulfilled, then the GB liquid-like layer is not stable. As a result, the GB diffusion coefficient decreases from the

values characteristic for the liquid phase to the values corresponding to normal GB diffusion [2,12]. Some further examples of a high-pressure effect on GB diffusion and segregation include the decrease of GB diffusivity of Zn in Al [13] and of Co in Zr [14] with increasing pressure, and the suppression of Bi segregation to GBs in ZnO–Bi₂O₃ [15]. Therefore, the unusually high GB diffusivity is connected to the pressure-dependent GB equilibrium. This unique combination produces a HIP behavior of a system with liquid-like GB layers that is far from trivial and needs careful investigation.

It should also be noted that the GB segregation is especially important during high-pressure studies. This is because most of the high-pressure apparatus do not allow a rapid heating or cooling of macroscopic samples; a typical cooling rate is in the range 1–2 K/s. The non-equilibrium segregation effects that do not manifest themselves during conventional sample processing (annealing followed by quenching in water) can therefore come into play in these high-pressure studies. In most kinetic segregation theories the volume diffusion is the rate-determining process. The effect of high pressure on the volume diffusion is well documented [16] and the reader is referred to the detailed reviews of the subject in Refs. [16,17].

2. Experimental procedure

The details of the sample preparation for the Cu–50 at.ppm Bi alloy can be found in Ref. [18]. Specimens of 3 mm × 3 mm × 10 mm in size were placed in a copper container. The container was installed in the furnace of a high-pressure apparatus. The specimen temperature was measured with three thermocouples located at different locations in the container. The difference in temperature between these locations was less than 2 K during heat treatment.

Fig. 2b shows the cross-section of the high-pressure apparatus. After the specimen container was placed in the apparatus, the piston was set to position A and the high-pressure chamber was evacuated by the rotary oil and diffusion vacuum pumps. After the vacuum reached 10^{-3} Pa, the piston moved to the position B and the high-pressure chamber was filled with Ar gas, which was compressed as the furnace heated. After the Ar pressure in the chamber reached 400 MPa, the oil pressure pump pushed the piston further to the right (position C), thus further increasing the chamber pressure. The temperature and pressure were continuously increased until they reached the pre-set values. After the high-temperature, high-pressure annealing, the furnace was switched off and the specimens were cooled within the furnace as the Ar pressure was lowered.

Typical time dependencies of temperature and pressure are shown in Fig. 3. The important parameters are the steady-state temperature (T_0) and pressure (P_0) of the experiment, the annealing time (t_0), the cooling rate (\dot{T}) and the rate of pressure decrease (\dot{P}). The rates of temperature and pressure increase in the beginning of the

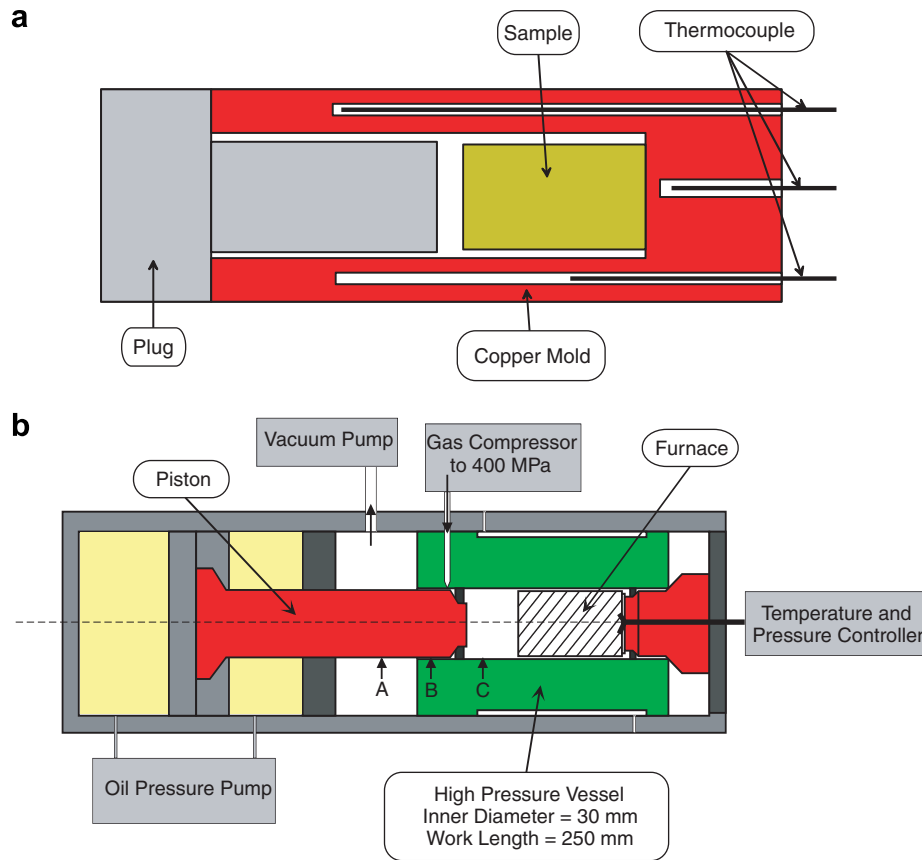


Fig. 2. Cross-sections of the specimens holding container (a) and of the high-pressure apparatus (b).

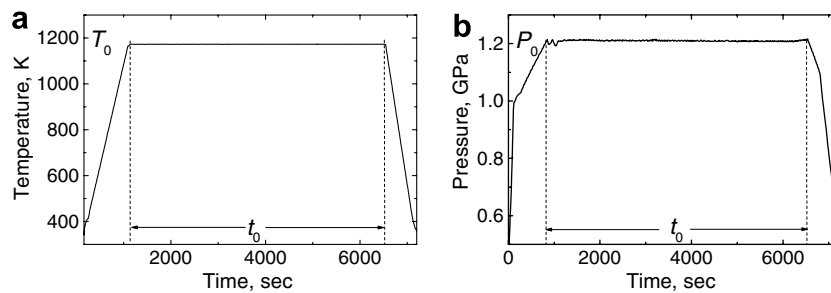


Fig. 3. Typical time dependences of temperature (a) and of pressure (b).

experiment are less important because the specimens were annealed long enough to achieve thermodynamic equilibrium. The experimental parameters are listed in Table 1. The lowest Ar pressure at which the high-pressure apparatus can be operated with reasonable pressure and temperature stability is 0.01 GPa.

The annealed specimens were investigated by means of a 10 keV Auger electron multiprobe (PHI 600) to determine the amount of Bi segregated at the GBs. The specimens were broken in situ after cooling with liquid nitrogen. Because of the large initial grain size in the Cu specimens (in the range of 500 μm), it was possible to localize the Auger electron spectroscopy (AES) measurements at the fractured surfaces of individual GBs. From 5 to 15 individual fractured GBs were analyzed in each specimen, and two spots for each fracture surface were analyzed. The amount

Table 1
The parameters of high-pressure experiments

	T_0 (K)	P_0 (GPa)	t_0 (h)	\dot{T} (K/s)	\dot{P} (MPa/s)
1	1173	0.01	1.5	-1.32	-
2	1173	0.3	1.5	-1.30	-0.17
3	1173	0.6	1.5	-1.28	-0.26
4	1173	0.9	1.5	-1.34	-0.35
5	1173	1.2	1.5	-1.33	-0.74
6	973	0.01	6	-1.05	-
7	973	0.3	6	-1.28	-0.18
8	973	0.6	6	-1.33	-0.34
9	973	0.9	6	-1.21	-0.38
10	973	1.2	6	-1.25	-0.44
11	1073	0.01	3	-1.12	-
12	1273	0.01	0.5	-1.23	-
13	1323	0.01	0.5	-1.21	-

t_0 , \dot{T} and \dot{P} are the annealing time at high temperature, cooling rate and the rate of pressure decrease at the cooling stage, respectively.

of Bi segregation was evaluated from the peak-to-peak heights of the Cu and Bi signals in the electron spectrum in the range 30–1000 eV. For more information about the AES measurements the reader is referred to a previous publication [18].

3. Results

The pressure dependence of the averaged Gibbsian excess of Bi at the GBs in Cu–50 at.ppm Bi at 973 and 1173 K is shown in Fig. 4. The error bars in this figure represent the standard deviation of experimental data, which indicates the distribution of enrichment at various GBs. Figs. 4a and b show that the pressure has only a slight effect on GB segregation. There is a trend for GB segregation to decrease with increasing pressure at 1173 K (Fig. 4b).

The temperature dependence of the averaged Gibbsian excess of Bi at the GBs in Cu–50 at.ppm Bi annealed at 0.01 GPa and cooled with a rate of $\dot{T} = 1.25$ K/s is shown in Fig. 5a. For comparison, the corresponding data for specimens annealed at various temperatures in vacuum (evacuated silica ampoules) and quenched in water ($\dot{T} \approx 500$ K/s) are shown in Fig. 5b. While the Gibbsian excess of Bi stays constant at about 2 MLs for all temperatures in Fig. 5a, Fig. 5b shows an abrupt drop in GB enrichment with increasing temperature. It is very unlikely that the pressure of 0.01 GPa has any significant effect on

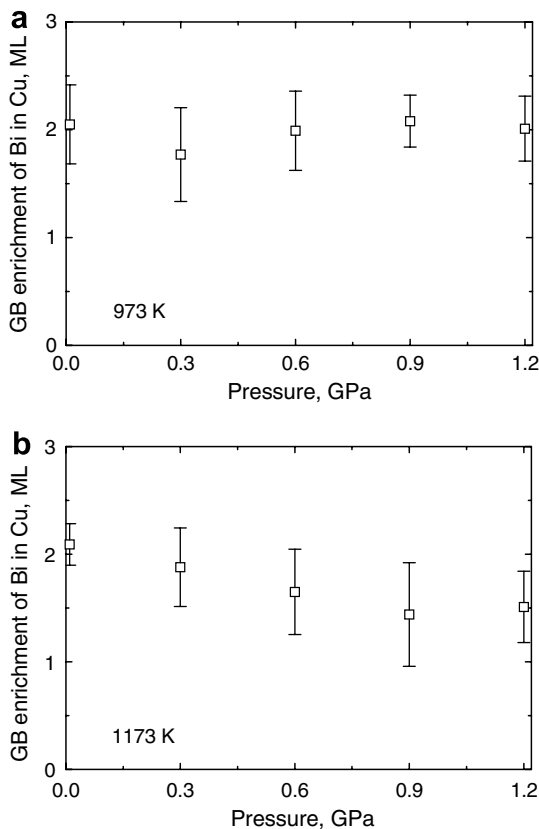


Fig. 4. The pressure dependence of Bi excess at the GBs in Cu–50 at.ppm Bi at 973 K (a) and 1173 K (b).

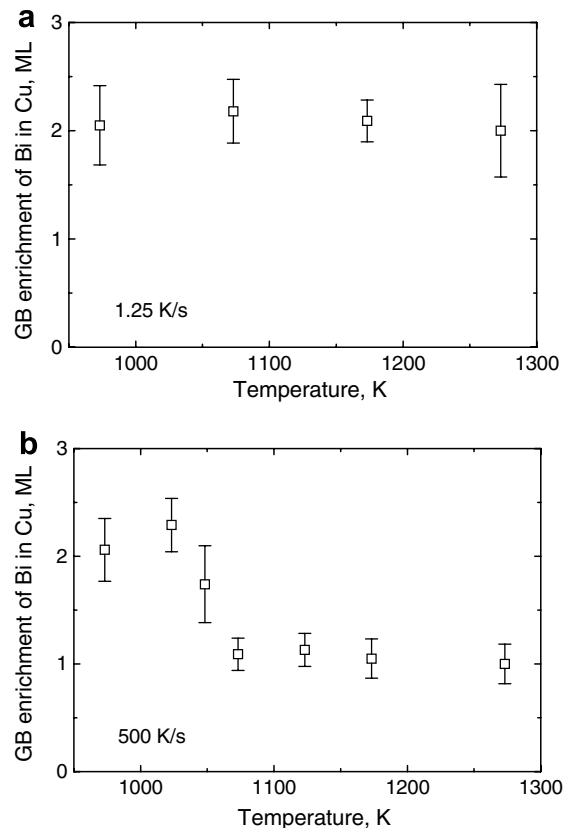


Fig. 5. The temperature dependence of Bi excess at the GBs in Cu–50 at.ppm Bi alloy for different cooling rates: (a) cooling in the high-pressure apparatus (1.25 K/s) and (b) quenching into water (500 K/s).

equilibrium GB segregation of Bi. One can conclude, therefore, that the difference in cooling rates is the main factor determining the difference in segregation behavior observed after annealing in a high-pressure apparatus (Fig. 5a) and after quenching from a conventional furnace (Fig. 5b).

4. Discussion

4.1. Theoretical background

4.1.1. Influence of high pressure on the stability of phases

The equations describing the two-phase equilibrium at normal pressure can be modified for high pressures by taking into account an additional contribution caused by pressure in the Gibbs free energy. The Gibbs energy of an element i can be written as [19]:

$$G_i^0 = G_i^{0,\text{chem}} + G_i^{\text{press}}, \quad (1a)$$

$$G_i^{\text{press}} = \frac{V_0 \exp(\int \alpha dT)}{\beta(n-1)} \left[(1 + n\beta P)^{1-\frac{1}{n}} - 1 \right], \quad (1b)$$

where V_0 , P , α and β are the atomic volume at 0 K, the hydrostatic pressure, the thermal expansion coefficient and the compressibility, respectively. The parameter n is a natural number. For $n \gg 1$ Eq. (1) can be simplified into $G_i^{\text{press}} = PV$, where V is the effective atomic volume:

$$V = V_0 \exp \left(\int \alpha \, dT \right), \quad (2)$$

where

$$\alpha = \alpha_0 + \alpha_1 T + \alpha_2 T^2 - \frac{\alpha_3}{T^2}.$$

Because most of the physical properties of the GB phase are unknown, the corresponding V is normally considered as a variable. In the approximation of a regular solution model, the Gibbs energy of GB segregation under hydrostatic pressure can be represented as:

$$\Delta G^{\text{seg}} = \Delta G^0 + P\Delta V - \Omega^V + \Omega^\Phi \quad (3a)$$

with

$$\Delta V = V_i^\Phi - V_i^V - V_m^\Phi + V_m^V, \quad (3b)$$

where ΔV is the segregation volume [20,21]. Here the subscripts i and m refer to the solute and solvent atoms, respectively. The superscripts Φ and V refer to the GB and bulk phases, respectively. The parameter ΔG_0 is the corresponding difference of the standard Gibbs energies of the components,

$$\Delta G^0 = G_i^{0\Phi} - G_i^{0V} - G_m^{0\Phi} + G_m^{0V}$$

and the Ω parameters represent the interaction energies in the framework of a regular solution model. If the interchange energies in the grain boundary and volume phases are pressure-independent, then the segregation isotherm describing the pressure effect on GB segregation can be derived as

$$\frac{x^\Phi(P)}{1 - x^\Phi(P)} = \frac{x^\Phi(0)}{1 - x^\Phi(0)} \exp \left(-\frac{P\Delta V}{RT} \right), \quad (4)$$

where $x^\Phi(P)$ is the concentration of the element i in GBs at pressure P . According to Eq. (4) the segregation amount in the system with oversized segregating atoms and low GB concentration of segregating atoms increases with increasing pressure. However, the situation is less clear for the systems close to GB saturation, since the segregating solute atoms can consume most of the GB free volume that was available for accommodating the excess size of these atoms.

4.1.2. Dynamic segregation during cooling

In a recent work [22] the unusually fast kinetics of grain boundary segregation in the Cu–Bi system for Bi concentrations above the GB solidus line has been attributed to dislocation pipe diffusion. Since this diffusion is much faster than volume diffusion, some additional amount of solute atoms above the equilibrium segregation level at the heat treatment temperature can segregate to GBs during slow cooling. Based on the linear relationship derived previously [22], the increase in solute concentration at the GB due to slow cooling with a constant cooling rate can be written as

$$\Delta x^\Phi = \frac{\rho^d x^b d}{2\delta \dot{T}} \int_{T_0}^{T_A} D \, dT, \quad (5)$$

where T_A , T_0 , ρ^d , x^b , d and δ are the annealing temperature, the room temperature, the dislocation density, the bulk concentration of Bi, the grain size and the grain boundary width, respectively. D is the volume diffusion coefficient of the solute atoms in the matrix. It is this diffusion coefficient that enters Eq. (5) because the slow process of bulk solute diffusion toward the dislocations is the “bottleneck” controlling the overall segregation kinetics.

During the high-pressure studies the situation is further complicated by the fact that the high pressure after heat treatment is decreased as the sample cools. Therefore, the pressure dependence of the volume diffusion coefficient should be accounted for. The volume diffusion coefficient changes with pressure as

$$D(P) = D_0 \exp \left(-\frac{Q + PV_D}{RT} \right), \quad (6)$$

where V_D is the activation volume. The release of pressure occurs simultaneously with cooling according to

$$P = P_0 + (T_0 - T) \frac{\dot{P}}{\dot{T}}. \quad (7)$$

The activation volume of bulk diffusion for vacancy diffusion mechanism is [16]

$$V_D = V_F - V_B + V_M, \quad (8)$$

where $V_F - V_B$ is the formation volume of a vacancy/impurity atom pair and V_M is the activation volume for the exchange between the vacancy and impurity atoms. Although no quantitative data are available regarding the activation volume for the bulk diffusion of Bi in Cu, it can be safely assumed that it is positive; the diffusion coefficient decreases with increasing pressure. This is always the case for substitutional diffusion in face-centered cubic metals [16]. The gradual release of pressure during cooling of the high-pressure cell means that cooling process takes place under high hydrostatic pressures that slow down the bulk diffusion. This decreases the additional, non-equilibrium segregation caused by slow cooling.

Contrary to volume diffusion, much less is known about the effect of pressure on GBs and dislocation pipe diffusion. The scarce data available in the literature [20,21,23] indicate that the activation volume for GB diffusion is lower than that for volume diffusion, probably because there is more free volume in the GBs and, therefore, more relaxation around the vacancies there. In a previous work [22], we assumed that the dislocation pipe diffusion is so fast that it does not limit the supply of Bi atoms to the GBs. In the absence of detailed information on the pressure effect on dislocation pipe diffusion we will assume that this hypothesis is also valid for heat treatments under high pressures.

The total amount of segregated atoms at GBs is the sum of the equilibrium amount at the annealing temperature and the amount arriving at GBs during cooling (Eqs. (4) and (5)):

$$x^\Phi = x^\Phi(P, T_0) + \frac{\rho^d x^{bd}}{2\delta T} \int_{T_0}^{T_A} D(P) dT. \quad (9)$$

It should be noted that the total amount of segregated atoms cannot exceed the equilibrium value at room temperature.

4.2. Stability of the volume phases

The atomic volume at 0 K and the coefficient of thermal expansion are necessary for estimating the pressure influence on the stability of phases (Eq. (1)). Because there

are no data about the atomic volume of liquid Bi and Cu at 0 K, the values of the atomic volume of solid Bi and Cu at 0 K are used. The parameters used to calculate the Cu–Bi phase diagram are listed in Table 2 [24]. The solidus and liquidus lines calculated are drawn in Fig. 6. Both lines shift towards higher Bi concentrations as pressure increases, which means that at higher pressures the liquid phase is less stable than the solid solution. The retrograde solidus line shifts about 4×10^{-3} at.%/GPa. Under our assumption of equal atomic volumes of the solid and liquid phases at 0 K, the higher thermal expansion coefficient of the liquid phase is responsible for its lower stability.

Table 2
Parameters used to estimate the relative stability of phases in the Cu–Bi alloys

Element (phase)	V_0 (cm ³ /mol)	α_0 ($\times 10^{-6}$ K ⁻¹)	α_1 ($\times 10^{-8}$ K ⁻²)	α_2 ($\times 10^{-11}$ K ⁻³)	α_3 (K)
Bi (S)	21.3245	10.0000	1.4656	-1.8780	0.00399
Bi (L)	21.3245	4.4034	0	0	0
Bi (Φ)	21.3245	20.0000	2.9312	-3.7560	0.00798
Cu (S)	7.0922	8.9679	2.4527	-1.0471	0.00630
Cu (L)	7.0922	33.3750	0	0	0
Cu (Φ)	7.0922	17.9358	4.9054	-2.0942	0.01260

S, L and Φ stand for the bulk solid, bulk liquid and ordered (solid) GB phases, respectively. V_0 is the atomic volume at 0 K and the coefficients α_i are defined by Eq. (2).

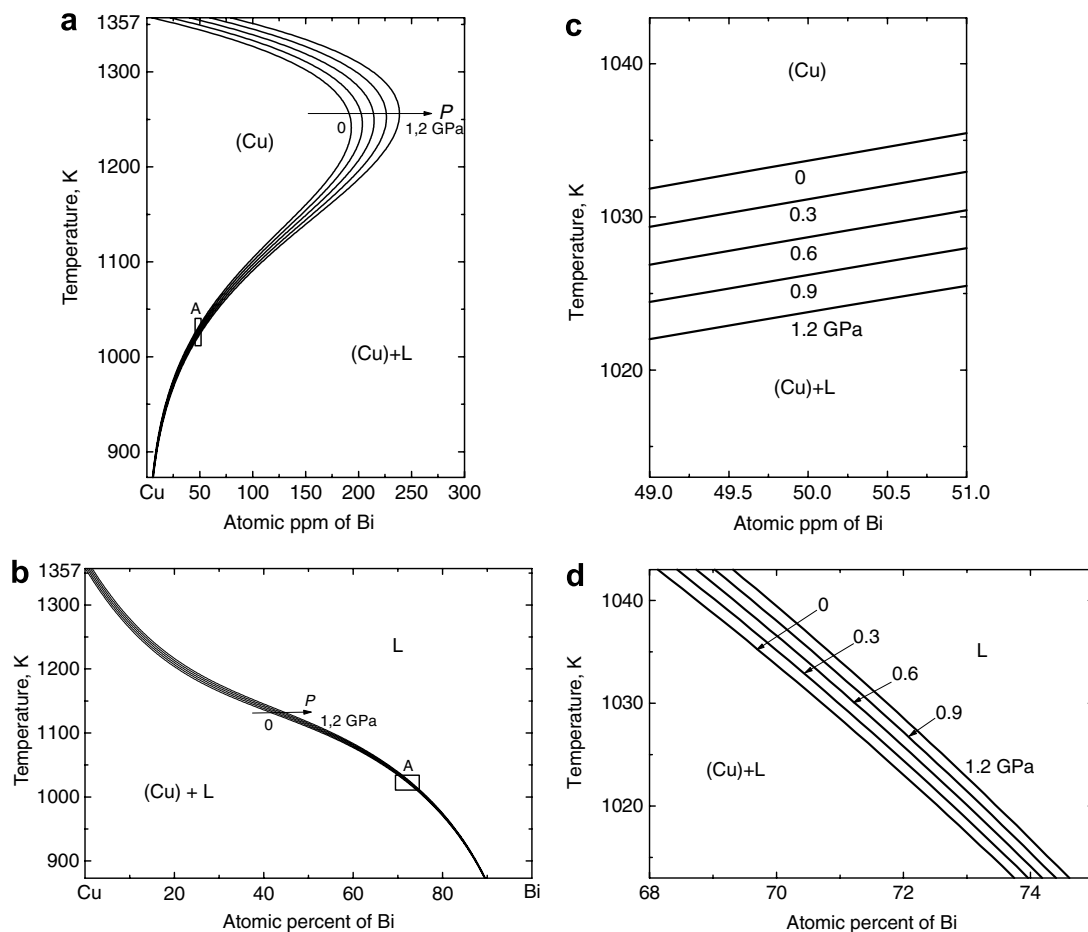


Fig. 6. Calculated solidus (a) and liquidus lines (b) of the Cu–Bi bulk phase diagrams at different pressures, and (c) enlarged views of the area A from (a) and (d) enlarged views of the area A from (b).

Fig. 6c represents an enlarged diagram of area A from Fig. 6a. At a given Bi concentration, the solidus line shifts toward lower temperatures with increasing pressure. The change in solidus temperature for Cu–50 at.ppm Bi is about 10 K/GPa. Fig. 6d shows an enlarged diagram of area A from Fig. 6b. The liquidus line shift with pressure is slight (1 at.%/GPa). This indicates that the high pressure has little effect on the concentration of the liquid phase and, probably, on the properties of the quasi-liquid phase at the GBs.

4.3. Stability of the GB phases

According to the pre-wetting segregation model developed in our earlier work [4], the GB segregation of Bi in Cu–Bi alloys can be described in terms of an equilibrium between the solid and quasi-liquid GB phases. In full analogy with the bulk phases, the stability of these GB phases depends on the effective atomic volumes (Eq. (3b)). In the absence of any reliable experimental data, we made the simplest assumption that at 0 K the atomic volume of the GB quasi-liquid phase is the same as that of the bulk liquid phase, and the atomic volume of the GB solid phase is the same as that of the bulk solid phase. Certainly, the latter assumption ignores the free volume of the GB, however, this volume is negligible with respect to the difference of atomic volumes of the Cu-based solid phase and Bi-rich liquid phase. Fortunately, in an elegant work of Gleiter and co-workers the thermal expansion coefficient of the GB phase was experimentally measured [25]. We adopted the value of $4 \times 10^{-5} \text{ K}^{-1}$ for our calculations, which is larger than the thermal expansion coefficient of the bulk solid phase by a factor of 2.

The temperature dependence of GB enrichment for Cu–50 at.ppm Bi calculated according to the model of pre-wetting phase transition is shown in Fig. 7. It can be seen from this figure that the amount of Bi segregated at GBs at 973 and 1173 K is pressure-independent. The only significant effect caused by high pressures is the shift of GB solidus temperature.

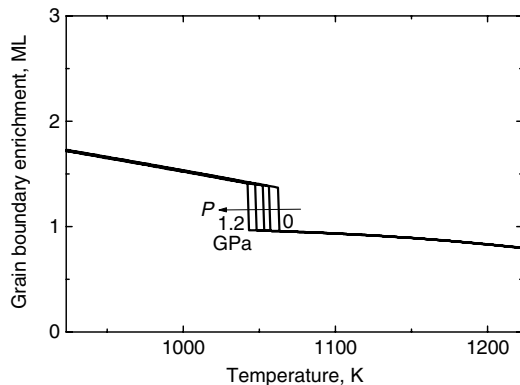


Fig. 7. The calculated temperature dependencies of Bi excess at the GBs in Cu–50 at.ppm Bi alloy at various pressures.

The calculated results (Fig. 7) showing that the GB enrichment at 973 K is pressure-independent explains the experimental data in Fig. 4a. Indeed, the segregation level at 973 K amounts to about 2 MLs, which is a saturation level for high-energy random GBs [4]. Being saturated with Bi, the GBs do not adsorb any additional Bi atoms during cooling. On the contrary, the predictions of our model disagree with the decrease of GB enrichment with increasing pressure experimentally observed at 1173 K (see Fig. 4b). The results of the segregation experiments with the different cooling rates (see Fig. 5) hint at the reason for this disagreement. In the following section we will discuss the additional, non-equilibrium GB segregation occurring during slow cooling with and without applied hydrostatic pressure.

4.4. Influence of the cooling rate in vacuum

We will first discuss the effect of slow cooling on the observed GB segregation for annealing without applied high pressure. In a previous work [22], we have shown that while the bulk diffusion of Bi is a factor that controls the kinetics of GB segregation in the single-phase region of the Cu–Bi phase diagram (and, correspondingly, the McLean model is valid), a much faster diffusion of Bi along disordered quasi-liquid dislocation cores controls the kinetics of GB segregation in the two-phase region. Our further analysis is based on these findings of Ref. [22]. In addition, we will assume that the cooling rate is time-independent.

Fig. 8 shows the additional, non-equilibrium amount of segregated Bi calculated according to Eq. (5) as a function of the annealing temperature (T_A) for different cooling rates (indicated near the corresponding curves). Each curve exhibits a sudden slope change at the bulk solidus temperature of 1033 K (dashed line). According to our previous work, this is the temperature at which the pre-wetting phase transformation along the dislocations cores occurs. Because the kinetics of GB segregation in the two-phase region is much faster than that in the single-phase

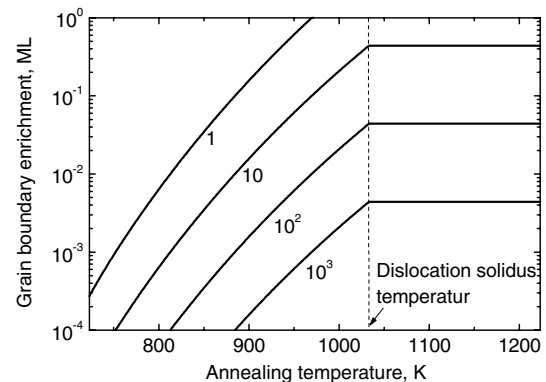


Fig. 8. The dependence of the additional, non-equilibrium amount of Bi segregated at the GBs during cooling on annealing temperature.

region, a major contribution to the amount of Bi segregated at the GBs during cooling comes from the Bi atoms transported to the GBs at temperatures just below the bulk solidus temperature. Therefore, the additional, non-equilibrium amount of Bi segregated at GBs remains almost unchanged (1 ML) when a specimen is annealed in the single-phase region (above solidus temperature) and then slowly cooled.

If, however, the specimen is annealed within the two-phase region, an additional amount of segregated Bi decreases with decreasing annealing temperature, since Bi atoms diffuse slower at lower temperatures. The additional amount of segregated Bi falls below 0.1 ML for cooling rates faster than 50 K/s. This estimate demonstrates that quenching samples into water (ca. 500 K/s) produces cooling rates that are fast enough to maintain the equilibrium segregation established at high temperatures. Therefore, the data of Fig. 5b can be considered as equilibrium Bi segregation levels at the GBs at 1173 K.

The total calculated (equilibrium and non-equilibrium) amount of Bi segregated at GBs in the Cu–50 at.ppm Bi alloy for several different cooling rates is shown in Fig. 9. For a cooling rate higher than 10 K/s, an abrupt change in segregation can be observed, while for the cooling rate of 1 K/s, the total amount of segregated Bi remains at 2 MLs and no abrupt changes occur. This is in agreement with the experimental data of Fig. 5a corresponding to a cooling rate of 1.25 K/s.

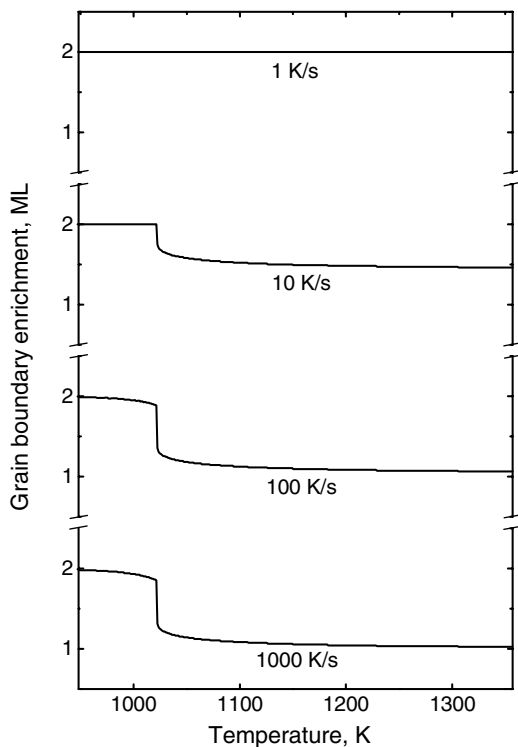


Fig. 9. The calculated temperature dependencies of Bi excess at the GBs in Cu–50 at.ppm Bi alloy for various cooling rates without applied pressure.

4.5. Influence of the cooling rate at high pressure

In the previous section, we discussed the effect of cooling rate on the observed GB segregation after annealing in vacuum or without applied high pressure. Applying a high pressure during both annealing and cooling changes the results of the previous paragraph, firstly, by shifting the solidus temperature, and secondly, by changing the bulk diffusion coefficient of Bi in Eq. (5). Both effects should be taken into account while calculating the total amount of Bi segregated at GBs in the Cu–50 at.ppm Bi alloy as a function of annealing temperature and pressure.

Because the activation volume for Bi bulk diffusion in solid Cu is unknown, it will be considered as a fitting parameter to fit the experimental data in Fig. 4b. The best fit was achieved with an activation volume of 20.2 cm³/mol. This value is closer to the atomic volume of Bi at 0 K than to the atomic volume of Cu (see Table 2). Roughly speaking, the activation volume for bulk diffusion can be split into a vacancy formation volume and an activation volume for the vacancy–impurity exchange. While the former should be slightly lower than the atomic volume of Cu, the latter can be quite large because of the difficulties in moving the oversized Bi atom in the Cu lattice. Fig. 10 presents the additional, non-equilibrium amount of segregated Bi calculated for annealing at different temperatures and pressures. This non-equilibrium addition decreases with increasing pressure. In the two-phase region, it increases with increasing annealing temperature, while no changes occur in the single-phase region because of the low bulk diffusion rate. The solidus temperature shift caused by high pressure is not large enough to produce a noticeable effect on the amount of segregated Bi. The effect of high pressure on bulk diffusion is the main reason for the decrease in GB segregation.

The total amount of Bi segregated at the GBs is the sum of the equilibrium segregation $x^{\Phi}(P, T_0)$, which, according to our estimates, is hardly affected by high pressure, and

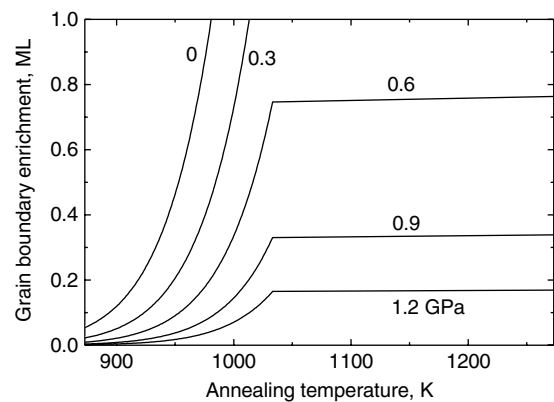


Fig. 10. The dependence of the additional, non-equilibrium amount of Bi segregated at the GBs during cooling on annealing temperature for different annealing pressures. The corresponding values of \hat{T} and \hat{P} are given in Table 1.

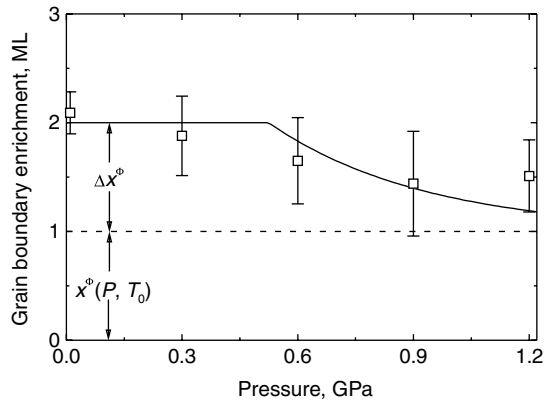


Fig. 11. Comparison of the calculated pressure dependence of Bi excess at the GBs in Cu–50 at.ppm Bi alloy after annealing at 1173 K with the corresponding experimental data. $x^{\phi}(P, T_0)$ and Δx^{ϕ} represent the equilibrium and non-equilibrium contributions to the total amount of Bi segregated at the GBs, respectively.

the additional, non-equilibrium amount (Δx^{ϕ}) adsorbed at the GBs during cooling. The calculated total Gibbsian excess of segregated Bi at the GBs in the Cu–50 at.ppm Bi samples annealed at 1173 K and under different pressures is shown in Fig. 11 along with the corresponding experimental data. The agreement between the experimental data and our model is satisfactory.

5. Conclusions

We studied the effect of high hydrostatic pressures on the segregation of Bi at GBs in a Cu–50 at.ppm Bi alloy annealed at 973 and 1173 K. The following conclusions can be drawn from our study:

1. It was found that the overall effect of pressure on the grain boundary segregation of Bi in Cu is weak. At 973 K the amount of segregated Bi was about 2 MLs for all pressures studied. At 1173 K the increase in pressure led to a weak decrease of the amount of segregated Bi from 2 MLs at 0.01 GPa down to 1.5 MLs at 1.2 GPa.
2. The Cu–Bi alloy heat treated at 0.01 GPa and cooled at a rate of 1.25 K/s in the high-pressure apparatus exhibited the segregation amount of 2 MLs for all annealing temperatures, while the Cu–Bi alloy annealed in vacuum and quenched into water showed an abrupt change in the temperature dependence of the Bi segregation at about 1043 K.
3. Model calculations of the dependence of GB segregation on annealing pressure were performed. It was shown that the applied high pressure affects the GB segregation indirectly, through the effect of pressure on the relative stability of bulk and GB phases, the slow cooling rate in the high-pressure apparatus and the effect of pressure on the bulk diffusion of Bi in Cu. The slow cooling rate was shown to be the most important factor affecting the

GB segregation, followed by the pressure effect on bulk diffusion. Good agreement between the experimental results and predictions of the model was achieved.

4. It was also shown that quenching the samples into water after high-temperature annealing provided a cooling rate high enough to keep the equilibrium segregation level at the GBs in Cu–Bi alloys.

Acknowledgments

These investigations were partly supported by the National Scientific Council of Taiwan (contract NSC 94-2218-E-005-015) and Russian Foundation for Basic Research (contract 05-03-90578). E.R. thanks the Israel Science Foundation for partial support of this study (Grant No. 794/04). W.L. thanks the Institute of High Pressure Physics, PAS for support of his work.

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