High-Pressure Influence on the Kinetics of Grain Boundary Segregation in the Cu–Bi System

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Abstract. The effect of pressure on the kinetics of grain boundary (GB) segregation in the Cu–50 at. ppm Bi alloy has been studied. It was found by means of Auger electron spectroscopy that at a temperature of 1173 K the segregation level decreases from 2 to 1.5 monolayer as the pressure increases from 0.01 to 1.2 GPa. This behavior was explained by considering the physical parameters controlling kinetics and thermodynamics of GB segregation. A simplified model based on dislocation pipe diffusion, proposed previously and discussed in more details in this work, was used to calculate the non-equilibrium GB segregation during cooling under high pressure. The pressure effect on bulk diffusion is responsible for the suppression of GB segregation, while the pressure effect on the phase stability in Cu–Bi alloys provides a negligible contribution on GB segregation in the pressure range studied.

Introduction

The influence of high pressure on such interfacial phenomena as grain boundary (GB) wetting, GB diffusion and GB migration has attracted a great deal of attention in the recent decade [1-6]. The pressure effect on GB energy and GB wetting were successfully interpreted in terms of GB free volume: the GB energy increases with pressure proportionally to the GB free volume. On the other hand, the effect of pressure on GB migration or diffusion was interpreted in terms of activation volume V_D for these processes, with PV_D being the increase of activation energy of these processes with pressure.

However, less is known about the pressure effect on GB segregation. As a matter of fact, the results of studies of the pressure effect on diffusion can be fully understood only if the effect of pressure on segregation is known. This is because in a standard diffusion experiment the product of segregation factor s, GB thickness δ, and GB diffusion coefficient D_{gb} is measured. Therefore, a strong effect of pressure on s may influence the rate of matter transport along GBs. For instance, it was shown that pressure induced enhancement of segregation of In to GBs in Cu bicrystals may fully compensate the decrease of In GB diffusion rate which would be expected for a vacancy diffusion mechanism [6]. Therefore, the studies of pressure effect on GB segregation are important for understanding the mechanisms of GB diffusion. It has to be pointed out here that these results may have implications for diffusion under stress in general, since internal stresses in the range of 1 GPa are not uncommon in materials under real working conditions.

It has been shown that under certain circumstances the Bi enrichment of Cu GBs can be described in terms of prewetting model [7]. It was shown that so-called GB prewetting phase transition explains well the thermodynamic and kinetic behavior of GB enrichment. It has been shown that the

equilibrium Bi amount at GBs in both normal segregated and "prewetted" states is negligibly affected by pressure [8]. In this article, we focus on the detailed interpretation of pressure influence on the diffusion of Bi in Cu which furthermore influences the GB enrichment.

Theoretical Background

Contrary to the conventional segregation studies, where the samples are quenched to low temperature to retain the segregation level during analytical investigations, the influence of the relatively slow cooling must be considered at high pressure experiments. Due to the technical limitation of high pressure apparatus the cooling rate in a high pressure experiment can not be higher than $1.5 \, \mathrm{K \, s^{-1}}$. An additional amount of enrichment during cooling from high temperature is to be expected. Therefore, the kinetics of the GB segregation reported in [9] is of a great importance for further analysis. If the pressure drop after the high pressure treatment is not fast enough, the influence of pressure on the kinetics of GB segregation must be taken into consideration. In the kinetic theories, the volume diffusion is the rate-determining process. The pressure influence on the volume diffusion has often been investigated and there are many data about it [10]. The theory of pressure influence on the bulk diffusion will only be represented briefly, for more details see the Refs [11, 12]. The rapid kinetics of GB segregation in the Cu–Bi system can be explained by the model of dislocation-pipe diffusion. The second Fick's law for the bulk diffusion around a dislocation can be written in the cylindrical coordinate r in the following form:

$$\frac{\partial x}{\partial t} = D\left(\frac{\partial^2 x}{\partial r^2} + \frac{1}{r}\frac{\partial x}{\partial r}\right), \tag{1}$$

where x, t and D are the concentration of Bi, annealing time and bulk diffusion coefficient, respectively. It can be Laplace-transformed into

$$\frac{\partial^2 \overline{x}}{\partial r^2} + \frac{1}{r}\frac{\partial \overline{x}}{\partial r} - \frac{p}{D}\overline{x} = \frac{-x_b}{D}, \tag{2}$$

where $\overline{x} = \int_0^\infty \exp(-pt)x\,dt$ and x_b is the bulk concentration far from the dislocation line.

The solution of this differential equation is

$$\overline{x} = \frac{x_b}{p}\left[1 - \frac{K_0\left(r\sqrt{p/D}\right)}{K_0\left(r_0\sqrt{p/D}\right)}\right], \tag{3}$$

where K_0 is the modified Bessel function in the second type of the zero order [13] and r_0 is the core radius of a dislocation under the boundary conditions $\overline{x}(r = \infty) = \dfrac{x_b}{p}$ and $\overline{x}(r = 0) = 0$.

The concentration around a dislocation at the distance r can be deduced from the inversion theorem as

$$x = \frac{2x_b}{p}\int_0^\infty \exp\left(-Dtu^2\right)\frac{Y_0(ur)J_0(ur_0) - Y_0(ur_0)J_0(ur)}{J_0^2(ur_0) + Y_0^2(ur_0)}\frac{du}{u}, \tag{4}$$

where J_0 is the Bessel function in the first type of the zero order and Y_0 is the Neumann's Bessel function in the second type of the zero order.

An important quantity is the atom flux which arrives at the dislocation line. According to the first Fick's law, it can be written as

$$J = -D\frac{\partial x}{\partial r}\bigg|_{r=r_0} = \frac{4x_b D}{r_0 \pi^2}\int_0^\infty \exp(-Dtu^2)\frac{du}{u\left[J_0^2(ur_0)+Y_0^2(ur_0)\right]}. \tag{5}$$

As $Dt/r_0^2 \gg 1$, this equation can be simplified as following [14]

$$J = \frac{2x_b D}{r_0}\sum_{n=1}^\infty \frac{r^{n-1}}{\left[\ln\left(4Dt/r_0^2\right)-2\gamma\right]}, \tag{6}$$

where γ is the Euler constant ($\gamma = 0.5772$). After further simplification one obtains

$$J = \frac{2x_b D}{r_0 \ln\left(4Dt/r_0^2\right)}. \tag{7}$$

Total number of atoms diffusing into dislocations in the vicinity of a GB in a certain time t is then

$$\Delta N = \pi r_0 L n_d \int_0^t J dt' = 2\pi L n_d x_b D \int_0^t \frac{dt'}{\ln\left(4Dt/r_0^2\right)}, \tag{8}$$

where L is the dislocation length and n_d is the dislocation number. The logarithm integral in the equation (8) is the li function [15]

$$\mathrm{li}(x) = \int_0^x \frac{dv}{\ln v}. \tag{9}$$

The equation (8) becomes

$$\Delta N = \frac{\pi}{2}L n_d x_b r_0^2 \mathrm{li}\left(\frac{4Dt}{r_0^2}\right). \tag{10}$$

On the other hand the total amount of atoms supplied into the GB is

$$\Delta N = A_{gb}\delta\left[x_{gb}(t)-x_{gb}(0)\right]. \tag{11}$$

Equating the expressions (10) and (11) results in

$$x_{gb}(t)-x_{gb}(0) = \frac{\pi L \rho_d x_b r_0^2}{2\delta}\mathrm{li}\left(\frac{4Dt}{r_0^2}\right), \tag{12}$$

where ρ_d and δ is the dislocation density and GB width. The li function which is numerically calculated is plotted in Fig. 1. It can be clearly seen that the li function changes almost linearly with x. Denoting the corresponding linear slope as m transfroms Eq. (12) into

$$x_{gb}(t)-x_{gb}(0) = \frac{2\pi m L \rho_d x_b Dt}{\delta}. \tag{13}$$

Based on this linear relationship, the additional enrichment at the GB in the sample cooled down with a constant cooling rate can be written as

$$\Delta x_{gb} = \frac{\rho_d L}{2s\delta R_c}\int_{T_P}^{T_A} DdT, \tag{14}$$

where s is the enrichment factor, R_c is the cooling rate, T_P is the temperature of high pressure treatment, T_A is the ambient temperature. The bulk diffusion coefficient D changes as follows

$$D(P) = D_0 \exp(-\frac{Q + PV_D}{RT})$$

$$(15)$$

where V_D is the activation volume, D_0 is the pre-exponential term and R, T have their usual meanings. Since pressure changes slow in comparison with atmosphere cooling, P is time-dependent. The bulk diffusion of In in solid Cu slows down with increasing pressure due to the positive activation volume [5]. A similar pressure effect on the bulk diffusion of Bi in solid Cu is to be expected because In and Bi atoms are larger than Cu atoms. This points out that the additional GB enrichment during cooling increases with increasing pressure.

Experimental Procedure

The Cu–50 at.ppm Bi alloy was prepared for the high pressure treatment. The alloy was cast in a vacuum remelter from 4N pure raw materials. The as-received alloy was initially homogenized at 1273 K for 24 hours. It must mention that the alloy was not deformed for preventing the formation of low energy twins and fine grain textures. 3×3×10 mm specimens slowly cut by diamond saw were put into a copper mold. The mold was installed in the oven of a high pressure facility. The temperature of specimens was measured with three thermocouples located at different places of the mold. The temperature difference between these places is smaller than 2 K during the treatment. The high pressure chamber was exhausted by a vacuum pump after that the specimens were put in. So long as the vacuum reached 1.3×10^{-3} Pa, argon gas was let into the high pressure vessel. Afterwards, the gas compressor began to work. Heating started at the same time. As long as the pressure in the oven reached 400 MPa, the oil pressure pump began to work. The temperature and pressure were continuously increased till they reached the pre-set values. The specimens were isothermally and isobarically treated for a certain time. The specimens were then cooled down in the oven.

The important parameters in the high pressure treatment are the temperature, pressure, time, cooling rate and pressure relieving rate. The heating rate and pressurizing rate are not important because the specimens were treated long enough to approach the equilibrium. The experimental parameters used in the high pressure treatment are given in Table 1. The lowest pressure which can be maintained in the high pressure apparatus with a reasonable stability of pressure and temperature is 0.01 GPa.

The specimens were investigated by means of Auger electron spectroscopy (AES) to determine the Bi amount at grain boundaries. All specimens were slowly cut to make a 0.8 mm deep notches at each side for easing the *in situ* fracture in the AES apparatus. The AES analysis was carried out in a PHI 600 Scanning Auger Multiprobe. The primary energy of the incident electron beam was 10 keV. The intensity of emitted Auger electrons was measured by means of a cylindrical mirror analyzer. The characteristic peaks of Cu and Bi were obtained from the differentiated intensity-energy spectrum of the 5N pure elements for quantification. Before the analysis the surfaces of these element samples were sputtered by an ion gun in the AES apparatus until they were free from impurities like C, O and S. In this work, the peak-to-peak height of three signals (Cu: 60 and 920 eV, Bi: 101 eV) was measured to determine the thickness and composition of the segregation layer semi-quantitatively. The ratio of the 101 eV Bi intensity to the 60 eV and 920 eV Cu intensity in pure elements was 0.396 and 0.292, respectively. The specimens were cooled down in contact with liquid nitrogen in AES, before being fractured by a hammer. Ten to twenty surfaces which exhibited the mode of intergranular fracture were studied in each specimen and two points on each surface were analyzed. The Auger electron spectrum was recorded in the energy range of 30-1000 eV. The thickness of the segregation layer is given in the unit of monolayer (ML) in this work. One monolayer of pure Bi contains 9.3 atoms/nm^2.

Table 1   Experimental parameters

Temperature [K]	Pressure [GPa]	Time [hr]	Cooling rate [K/s]	Relieving rate [MPa/s]
973	0.01	6	−1.05	–
973	0.3	6	−1.28	−0.18
973	0.6	6	−1.33	−0.34
973	0.9	6	−1.21	−0.38
973	1.2	6	−1.25	−0.44
1173	0.01	1.5	−1.32	–
1173	0.3	1.5	−1.30	−0.17
1173	0.6	1.5	−1.28	−0.26
1173	0.9	1.5	−1.34	−0.35
1173	1.2	1.5	−1.33	−0.74
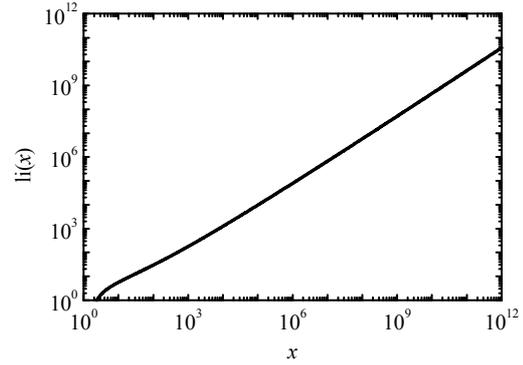
Fig. 1. Numerically calculated $li(x)$ function
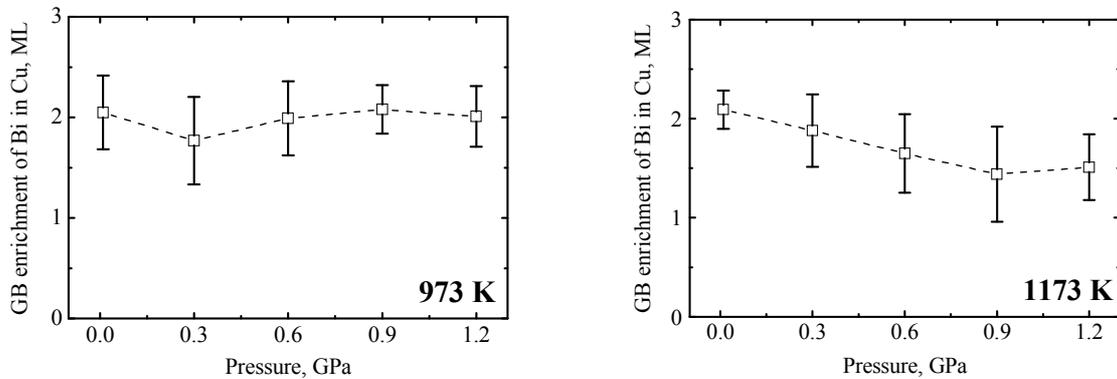
Fig. 2. Grain boundary enrichment in dependence of pressure for Cu–50 at.ppm Bi. The error bars represent the distribution of GB enrichment at various GBs in a polycrystal

Results and Discussion

The pressure dependence of the GB enrichment of Bi in the Cu–50 at.ppm Bi alloys at 973 and 1173 K is shown in Fig. 2. The squares represent the average values of GB enrichment in the unit of ML after the high pressure treatment and the error bars are the standard deviation of experimental data which indicate the distribution of Bi enrichment at various GBs. The enrichment level remains close to 2 ML at 973 K. On the contrary, the GB enrichment decreases from 2 ML down to 1.5 ML at 1173 K when pressure increases from 0.01 to 0.9 GPa, as can be seen in Fig. 2. These phenomena will be explained in the subsequent paragraphs.

It has been shown in the previous work that the equilibrium value of GB enrichment for the polycrystalline Cu–50 at.ppm Bi alloy is ca. 2 and 1 ML at 973 and 1173K, respectively. While the stability of GB phases both in the segregation and prewetting states varies only slightly with changing pressure below several GPa, the GB enrichment of 2 ML in the Cu–50 at.ppm Bi alloy high-pressure treated at 973 K with subsequent oven cooling is the same as in the water quenched samples. This is reasonable because the 2 ML is the saturated value of GB enrichment for the alloy annealed at any temperature below 973 K. The saturation of Bi in GBs inhibits any further enrichment of Bi diffusing along dislocations during cooling. Nevertherless, we used Eq. (14) to calculate the additional amount of Bi which may arrive at an unsaturated GB via dislocation pipes during cooling and plotted it as a function of pressure at the cooling rate of −1.3 K/s in Fig. 3. All parameters used in the calculation are given in Table 2.

To explain the decrease of Bi enrichment with increasing pressure at 1173 K, some additional assumptions should be made. The kinetic model of GB segregation via dislocation pipe diffusion is only valid in the case of high Bi segregation at the dislocation pipes. This restricts the application of this kinetic model in the region in which there is a positive thermodynamic driving force for precipitation of the Bi-rich liquid phase, i.e. in the two-phase region. As a result, instead of the temperature of high pressure treatment, the solidus temperature should be introduced as the starting temperature in Eq. (14). The solidus temperature of the Cu–50 at.ppm Bi alloy is 1033 K. Secondly, as mentioned before, the total Bi enrichment can not exceed the saturated value which is 2 ML.

The additional Bi enrichment due to slow cooling calculated for Cu–50 at.ppm Bi alloy high pressure treated at 1173 K is plotted as a function of pressure in Fig. 3(b). It can be clearly seen that the curve can be fitted by a decaying exponent:

$$\Delta x_{gb} = 3.43 \exp(-\frac{P}{0.40}) \tag{17}$$

The total Bi enrichment which is the sum of the equilibrium value 1 ML at 1173 K and the additional value shown in Fig. 3 is plotted as a function of pressure in Fig. 4. One can combine the experimental data of Fig. 2 with the results of calculations shown in Fig. 4 keeping in mind that the total GB enrichment can not exceed the saturated value 2ML. The resulting Fig. 5 demonstrates a good agreement between the experimental data and predictions of our model.
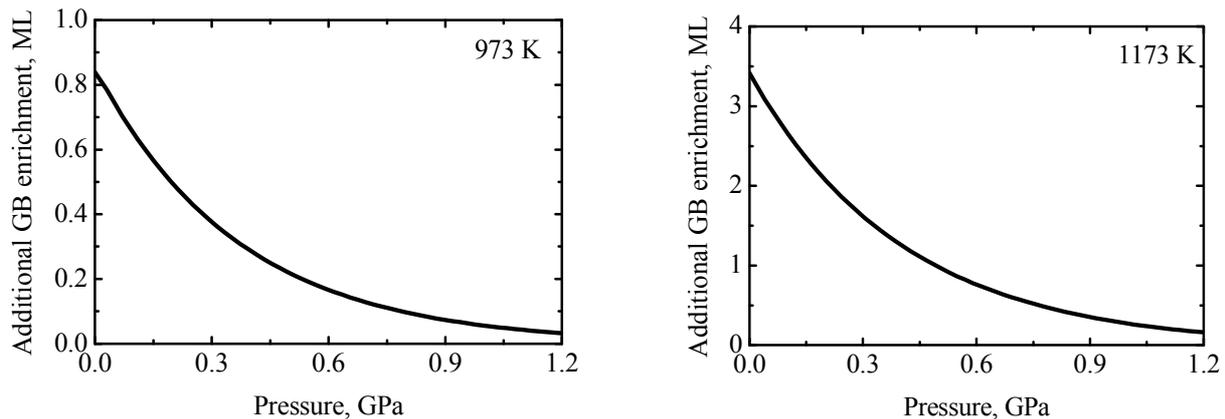
Fig. 3   Calculated additional Bi enrichment at GBs during cooling after the high pressure treatment
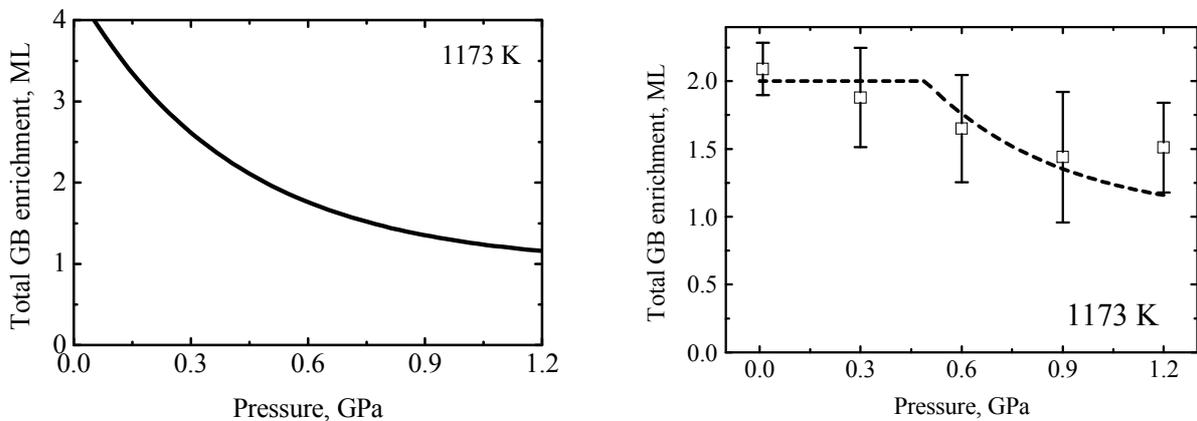
Fig. 4. Calculated total GB enrichment of the Cu–50 at.ppm Bi alloy in term of pressure

Fig. 5. Total GB enrichment shown in Fig. 3 for 1173 K (points) and Fig. 4 (dashed line)

Table 2 The parameters used in the calculation

Parameters	Values
Bulk diffusion coefficient of Bi in solid Cu (D)	$D_0 = 7.66 \times 10^{-5}$ m^2/s, $Q = 178.1$ kJ/mole
Activation volume for bulk diffusion of Bi in Cu (V_D)	20.2 cm^3
Grain boundary width (δ)	0.978 nm
Dislocation length (L)	500 μm
Dislocation density (ρ_d)	10^7 cm^{-2}

Conclusion

The influence of high pressure on the GB enrichment of Bi in the Cu–50 at. ppm Bi alloy annealed at 973 and 1173 K was investigated. At 1173 K the enrichment decreases with increasing pressure from 2 ML at 0.01 GPa down to 1.5 ML at 1.2 GPa, while it remains approximately constant at 2 ML at the temperature of 973 K and all pressures studied. This behavior was interpreted in terms of a kinetic model that takes into account the accelerated diffusion of Bi along the dislocation pipes. The model predicts that an additional amount of Bi that arrives at the GBs during slow cooling after high pressure annealing at 1173 K decreases with increasing pressure, in full accordance with the experimental data.

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