Materials Science Forum Vols. 294-296 (1999) pp. 585-588

Kinetics of the Bi Segregation at Grain Boundaries in Polycrystalline Cu

L.-S. Chang[1], E. Rabkin[2], B.B. Straumal[1,3], B. Baretzky[1] and W. Gust[1]

[1] Max-Planck-Institut für Metallforschung and Institut für Metallkunde, Seestr. 92, D-70174 Stuttgart, Germany

[2] TECHNION-Israel Institute of Technology, Department of Materials Engineering, IL-32000 Haifa, Israel

[3] Institute of Solid State Physics, Chernogolovka, Moscow District, RU-142432 Russia

Keywords: Grain Boundaries, Segregation Kinetics, Dislocation-Pipe Diffusion

Abstract

The kinetics of Bi segregation at grain boundaries (**GBs**) in polycrystalline Cu-25 at.ppm and Cu-50 at.ppm Bi alloys has been investigated at different temperatures. In the two-phase region of the Cu–Bi phase diagram the kinetics of the Bi segregation can be described by a model of enhanced diffusion along dislocations, while in the single-phase region it obeys the classical McLean model. This enhanced pipe diffusion can be explained by the precipitation of a Bi-rich liquid phase along the dislocations in the two-phase region. From this dislocation-pipe model a linear relationship between Bi segregation and annealing time was derived.

Introduction

The thermodynamics of GB segregation in the Cu–Bi system has been investigated in a number of works (e.g. [1–4]), however, the kinetic aspects of segregation were rarely addressed [5, 6]. In other systems some attempts have been made to explain the segregation kinetics in the framework of volume diffusion [7, 8] and dislocation-pipe models [9, 10]. However, the fundamental understanding with regard to the applicability of the different kinetic models is still lacking. Moreover, the question about the phase state (single phase or two phases) of the specimens has been widely ignored.

Recently, the bulk solidus line at the Cu-rich side in the Cu–Bi phase diagram has been determined [11] and a GB solidus line has been suggested [4]. These lines provide the knowledge about the state of the bulk and of the GBs in dilute Cu–Bi alloys. Besides, the extraction of Bi from the bulk to the surface of the Cu–Bi alloys has been revealed and investigated with the help of scanning force microscopy and Auger electron spectroscopy (AES) [12]. It was supposed that the enhanced diffusion of Bi atoms occurs along the dislocation lines. It is very plausible that the same process contributes also to the Bi enrichment at GBs. In this work the kinetics of the Bi segregation at GBs in Cu has been investigated in order to clarify the applicability of the different kinetic models.

Experiment and Results

Cast polycrystalline Cu containing 25 and 50 at. ppm Bi was cut into pieces of 3×3×15 mm³. In order to investigate the kinetics of Bi segregation at GBs in the single-phase and two-phase region the temperatures of 850 and 600°C were chosen according to the Cu–Bi phase diagram [11]. All specimens were homogenized at 1000°C for 24 h. In order to be able to measure the initial value of the Bi enrichment a further homogenization was performed at 850°C for the specimens annealed at 600°C. No second homogenization was performed for specimens annealed at 850°C. The homogenized specimens were annealed at 850 and 600°C for different time. The details of the heat treatment are listed in **Table 1**. After annealing the specimens were quenched in water in order to preserve the Bi enrichment at GBs. Then the Bi concentration in the GB was measured by means of AES on *in situ* fractured specimens. Further experimental details may be found in Ref. [13].

Table 1 The details of heat treatment.

Bulk conc.	1st Homogenization		2nd Homogenization		Annealing	
at. ppm Bi	T,°C	t, ks	T,°C	t, ks	T,°C	t, ks
25.....	1000	86.4	–	–	850	0.9/1.8/3.6/10.8/14.4/86.4
	1000	86.4	850	604.8	600	0.3/0.6/0.9/1.8/3.6/86.4/172.8/864
50.....	1000	86.4	850	604.8	600	0.3/0.9/86.4/172.8/2592

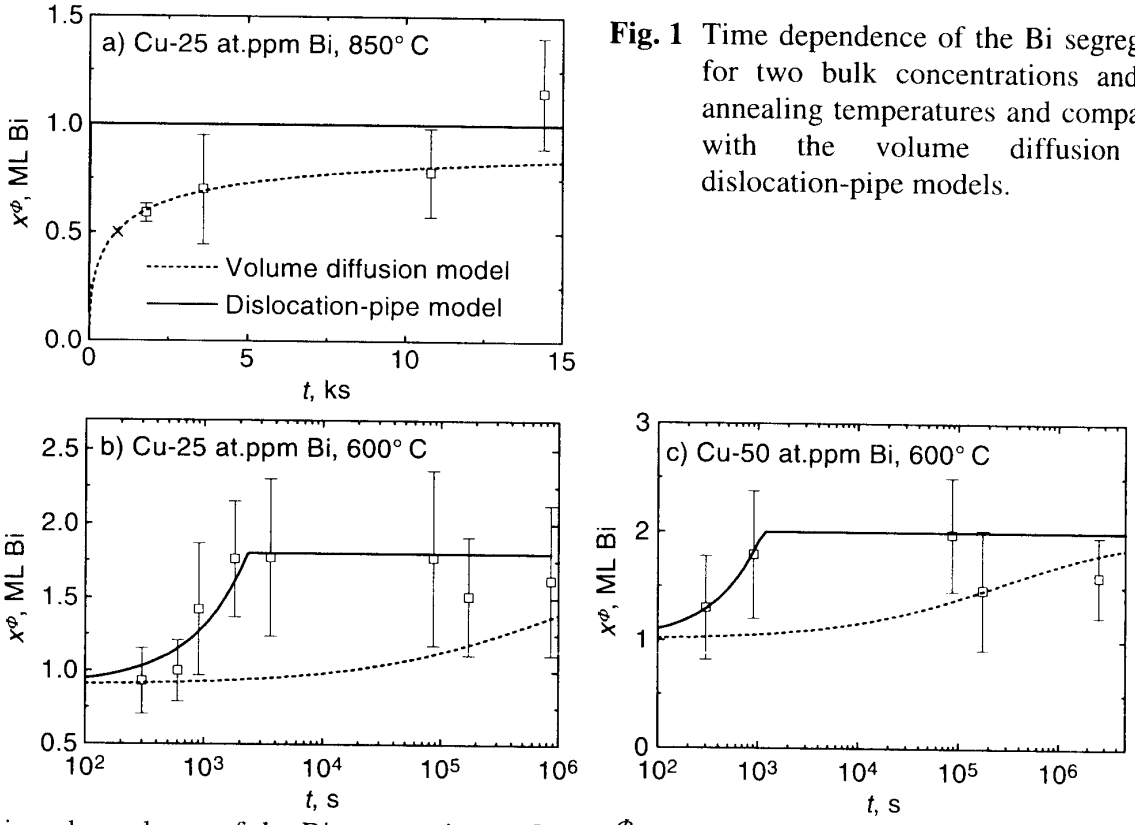

Fig. 1 Time dependence of the Bi segregation for two bulk concentrations and two annealing temperatures and comparison with the volume diffusion and dislocation-pipe models.

The time dependence of the Bi segregation at GBs (x^{Φ}) is shown in **Figs. 1a-c**. The square symbols designate the Bi segregation averaged over 15-20 GBs in one polycrystalline specimen. The error bars are determined from the distribution of the Bi enrichment. The cross indicates that a specimen could not be broken. The Bi concentration is given in monolayers (MLs). One ML is defined in this work as 9.3 atoms/nm². The threshold value of the Bi enrichment for embrittlement is about 0.5 ML, therefore, the cross was set to 0.5 ML. The equilibrium Bi enrichment at GBs in Cu–25 at. ppm Bi was achieved in this work after annealing for 4 h (14.4 ks) at 850°C (**Fig. 1a**) and after 0.5 h (1.8 ks) at 600°C (**Fig. 1b**). For Cu–50 at. ppm Bi the annealing time for saturation was 0.25 h (900 s) at 600°C (**Fig. 1c**).

Discussion

For the interpretation of our data we firstly used the volume diffusion model of McLean [7]. The McLean equation can be written as followed

$$\frac{x^{\Phi}(t)-x^{\Phi}(0)}{x^{\Phi}(\infty)-x^{\Phi}(0)}=1-\exp\left(\frac{4Dt}{s^2\delta^2}\right)\operatorname{erfc}\left(\frac{2\sqrt{Dt}}{s\delta}\right) \quad (1)$$

where $x^{\Phi}(t)$, D, δ and s are the Bi concentration at GBs for the annealing time t, the volume diffusion coefficient, the GB thickness and the Bi segregation factor ($s = x^{\Phi}(\infty)/x^{B}$ where x^{B} is the bulk concentration), respectively. The results are drawn as dashed lines in **Figs. 1a-c**. It is clearly seen that only for Cu–25 at. ppm Bi at 850°C (**Fig. 1a**) the model fits to the experimental data. In this case the specimens are in the single-phase region (Cu-rich solid solution) of the Cu–Bi phase

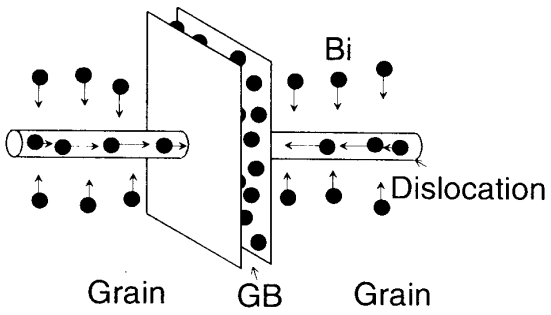

Fig. 2 Schematic view of the dislocation-pipe model.

diagram. Cu–25at. ppm Bi alloys contain so little Bi at GBs after an annealing at 1000°C for 24 h that the GB is not brittle. Therefore $x^{\Phi}(0)$ was set to zero in **Fig 1a**.

To address the discrepancy between the experimental data and the volume diffusion model, we developed a new dislocation-pipe model. A schematic view illustrating the principles of this model is shown in **Fig. 2**. To simplify the model we assume: a) The dislocation-pipe diffusion coefficient ($D^{\perp}$) is much larger than the volume diffusion coefficient. The same assumption has been made by Arabczyk et al. [8] with $D^{\perp}/D \approx 10^5$. b) The bulk flux of Bi atoms into the dislocation is equal to that along the dislocation to the GB. c) The effective diffusion zone around the dislocation is much smaller than the distance between dislocations. d) The dislocation-pipe diffusion is stopped after reaching the previously measured saturation value of the Bi enrichment at GBs [4]. From these assumptions it can be seen that the rate determining process is the volume diffusion of Bi in solid Cu, not the dislocation-pipe diffusion. Starting from the cylindrical Fick's diffusion equation and with some further simplifications we obtain

$$\begin{aligned} x^{\Phi}(t) - x^{\Phi}(0) &= \frac{\rho^{\perp} x^{B} dDt}{\alpha\delta} && t < t_{sat} \\ x^{\Phi}(t) &= x^{\Phi}(\infty) && t \geq t_{sat} \end{aligned} \tag{2}$$

where $\rho^{\perp}$, d and t_{sat} are the dislocation density (= $10^{11}/m^2$), grain size (= 500 μm) and the time for Bi saturation at GBs, respectively. α is a numerical constant between 2 and 4. A detailed description of the derivation of Eq. (2) can be found in Ref. [13]. The results from Eq. (2) are drawn as solid lines. These solid lines agree well with experimental data in **Figs. 1b** and **c** for the specimens which are in the two-phase region (Cu-rich solid solution + liquid) of the phase diagram except that in **Fig. 1a**.

The kinetics of the Bi enrichment at GBs in both regions of the phase diagram cannot be described by only one model. However, the parameters used in the two models are the same in both regions of the phase diagram: The volume diffusion coefficient has been explicitly determined and has the same value in both models. The specimens in both regions have similar grain size and dislocation density due to the same homogenization treatment. However, in the two-phase region of the phase diagram the precipitation of a Bi-rich liquid phase along dislocation lines is possible. This can explain the applicability of these two models in different regions. The Bi enrichment in dislocations enhances the atom flux along the dislocation to such an extent that the assumptions of the dislocation-pipe model become satisfied. According to this model the dislocation diffusivity can be estimated as follows

$$D^{\perp} r_0^2 = (D^{\perp} r_0^2)_0 \exp(-\frac{Q^{\perp}}{RT}) \tag{3}$$

where $(D^{\perp} r_0^2)_0 = 3.47\times10^{-22}$ m^4/s is the pre-exponential factor, $Q^{\perp} = 94.4$ kJ/mol is the activation energy, r_0 is the dislocation core radius, R is the gas constant and T is the absolute temperature.

In the framework of the suggested concept the time needed for approaching the equilibrium GB segregation level can be estimated. This can be done with the help of a temperature-time-enrichment

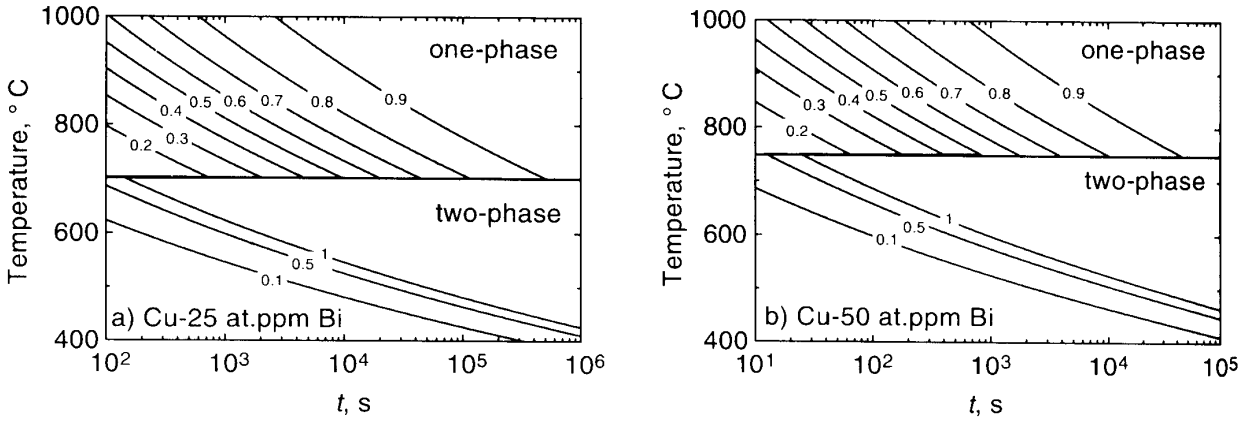

Fig. 3 Temperature-time-enrichment diagram. The number on the lines indicates the Bi enrichment as fraction of the saturated value $\{= [x^{\Phi}(t)-x^{\Phi}(0)]/[x^{\Phi}(\infty)-x^{\Phi}(0)]\}$.

(TTE) diagram. **Figure 3** shows the TTE diagrams for Cu–25 at. ppm Bi and Cu–50 at. ppm Bi. To calculate these diagrams the volume diffusion model and the dislocation-pipe model are used for the single-phase and two-phase regions, respectively. Each curve in the diagram is a contour curve with a constant enrichment level. The number on the lines indicates the Bi enrichment as fraction of the saturated value. The horizontal line in the middle of the diagram shows the bulk solidus temperature which can possibly be regarded as the dislocation solidus temperature, too. This line indicates the frontier between two different kinetic mechanisms: volume diffusion (above) and dislocation-pipe diffusion (below). Consequently, the kinetics in the two-phase region may be even faster than that in the single-phase region, although the annealing temperature in the latter case is higher.

Conclusions

The kinetics of the Bi segregation at GBs in polycrystalline Cu can be described by the volume diffusion model and the dislocation-pipe model in the single-phase and two-phase regions of the Cu–Bi phase diagram, respectively. The enhanced dislocation-pipe diffusion is explained by the precipitation of Bi-rich liquid phase along dislocation lines. Accordingly, the dislocation diffusion coefficient is estimated and a TTE diagram is constructed.

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (contract Gu 258/12-1) and partially supported by the Russian Foundation for Basic Research (grant 97-02-16830), NATO Linkage Grant HTECH.LG.970342 and INCO-COPERNICUS Network PL97-8078.

References

[1] A. Joshi and D.F. Stein, *J. Inst. Metals* **99** (1971), p. 178.
[2] E.D. Hondros and D. McLean, *Phil. Mag.* **29** (1974), p. 711.
[3] M. Menyhard, B. Blum and C.J. McMahon Jr., *Acta metall.* **37** (1989), p. 549.
[4] L.-S. Chang, E. Rabkin, B.B. Straumal, S. Hofmann, B. Baretzky and W. Gust, *Defect Diff. Forum* **156** (1998), p. 135.
[5] W.C. Johnson, A. Joshi and D.F. Stein, *Metall. Trans. A* **7** (1976), p. 949.
[6] A. Fraczkiewicz and M. Biscondi, *J. Physique* **46** (1985), p. C4-497.
[7] D. McLean, *Grain Boundaries in Metals*, Oxford, Clarendon Press (1957), p. 116.
[8] E.D. Hondros and M.P. Seah, *Inter. Metals Rev.* **22** (1977), p. 262.
[9] W. Arabczyk, M. Militzer, H.-J. Müssig and J. Wieting, *Surf. Sci.* **198** (1988), p. 167.
[10] M. Militzer, Y.N. Ivashchenko, A.V. Krajnikov, P. Lejcek, J. Wieting and S.A. Firstov, *Surf. Sci.* **261** (1992), p. 267.
[11] L.-S. Chang, B.B. Straumal, E. Rabkin, W. Gust and F. Sommer, *J. Phase Equilibria* **18** (1997), p. 128.
[12] L.-S. Chang, E. Rabkin, B. Baretzky and W. Gust, *Scripta mater.* **38** (1998), p. 1033.
[13] L.-S. Chang, Ph.D. thesis, *University of Stuttgart* (1998), p. 50.