

Diffusion-Controlled Liquid Bismuth Induced Intergranular Embrittlement of Copper

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Abstract. The consequences of the contact between liquid bismuth and a copper bicrystal are investigated at 500°C. Atoms of bismuth are shown to penetrate and embrittle the copper grain boundary. Grain boundary concentration profiles of bismuth are obtained on fracture surfaces by both Auger electron spectroscopy and He⁴⁺ Rutherford backscattering spectroscopy. The maximum bismuth intergranular concentration is calculated from experimental data to be about 1.7 monolayers (near the liquid bismuth / solid copper interface). The overall profiles are significantly different from typical erfc profiles and an interpretation is proposed, based on the coupling effect between grain boundary diffusion and non-linear segregation. These results allow us to conclude on the absence of grain boundary wetting for the Cu / Bi system at 500°C.

Introduction

Bismuth intergranular segregation into copper has been the object of numerous works in the past and notably one very complete [1-3] where the authors used AES in-situ fracture at room temperature to reveal Bi presence in grain boundaries of Cu-Bi alloys. For a Cu-25at.ppm Bi alloy, bismuth intergranular concentration was shown to drop suddenly (within only 10°C around 700°C) from as much as 2 monolayers at low temperatures to about 1 monolayer at higher temperatures [1]. The authors proposed a pre-wetting model to describe this so called “segregational phase transition”, but they recognized that this behavior could also be properly described in the framework of the “classic” Fowler segregation isotherm as suggested previously by Menhyard et al. [4] who obtained comparable results. This segregation isotherm can be written as follows [4, 5]:

$$\frac{c_{gb}}{c_{gb}^0 - c_{gb}} = \frac{c_v}{1 - c_v} \cdot \exp \left[- \frac{\Delta G_s + \alpha \cdot \frac{c_{gb}}{c_{gb}^0}}{RT} \right], \quad (1)$$

where c_{gb} is the bismuth intergranular concentration, c_{gb}^0 is the bismuth maximal intergranular concentration, c_v is the bismuth volume concentration, ΔG_s is the free enthalpy of segregation ($\Delta G_s < 0$) and α represents the interaction between bismuth atoms in copper grain boundaries ($\alpha < 0$ in the case of bismuth segregation where attraction takes place [4, 6]). Such an expression is typically used for systems that present a high segregation factor s , making Henry’s isotherm ($c_{gb} = s \cdot c_v$) inappropriate as it concerns only dilute solutions. It is worth to notice that the classical McLean segregation isotherm [7] can be obtained with $\alpha = 0$ in equation (1).

On the other hand, the intergranular embrittlement of copper by bismuth can also be obtained when putting in contact solid copper with liquid bismuth. Vogel and Ratke [8] studied grain boundary grooving of copper bicrystals by liquid bismuth at 400°C. They showed the formation of deep channel-like grooves at the grain boundary intersection. As an interpretation, they developed a model for grain boundary grooving under the influence of grain boundary diffusion, leading to a kinetic law of the penetration depth of the grooves proportional to time^{1/3}. Using the same type of experiments, Joseph et al. [9-11] obtained linear kinetics for bismuth intergranular penetration between 300 and 400°C [10] and proposed a mechanism of liquid bismuth penetration along copper grain boundaries lying on the grain boundary wetting formalism [11] and thus leading to the replacement of copper grain boundaries by a several nanometer thick bismuth-rich liquid phase [9]. Then it appears that both the intergranular concentration and the intergranular penetration kinetics of bismuth into copper are controversial. The aim of the following paper is therefore to state on these two points by acquiring bismuth concentration profiles in copper grain boundaries after a contact with liquid bismuth at 500°C. After that, this will allow us to identify the mechanism responsible for the liquid bismuth induced intergranular embrittlement of copper at this temperature: either grain boundary wetting or grain boundary diffusion [12].

Experimental details

A Cu bicrystal containing a symmetric tilt boundary with a misorientation angle of 50° was prepared by melting and controlled solidification in an horizontal furnace (using a bicrystalline seed on an alumina mould) and cut by spark erosion to get parallelepipeds with an approximate position of the grain boundary at half-length. They were then chemically polished in order to remove residual stresses introduced by spark erosion (avoiding, in that way, any recrystallisation during the subsequent heat treatment). Two equivalent procedures were used to put liquid bismuth in contact with the bicrystalline specimens: direct contact (DC) with Bi-Cu alloy oversaturated with copper in order to avoid any dissolution of copper and vapor contact (VC) where a thin layer of liquid bismuth is deposited by condensation of its vapor (more details on these 2 procedures and their equivalence will be found in [13]). Both of these procedures were done at 500°C for durations selected to lead to incomplete embrittlements of the bicrystals. Then, the specimens were water quenched and in-situ broken by tensile test at room temperature within the main chamber of an AES spectrometer in order to reveal grain boundary composition. The biggest specimens (used for the longest durations) were analyzed by RBS, as it wasn't possible to get in-situ AES ruptures. Fracture surfaces were also analyzed by scanning electron microscopy in order to determine the length of the brittle zone.

Fracture surface analysis

Figure 1 shows a SEM picture of the fracture surface of a copper bicrystalline specimen that has been previously put in contact with liquid bismuth during 1 hour at 500°C. The brittle zone and the ductile core can be clearly distinguished on the fracture surface. We made AES analyses on this fracture surface and used a quantification procedure (fully described in [14]) in order to determine the bismuth coverage. Bismuth concentration profile is shown in figure 2. When observing it, 4 zones can be distinguished in the brittle zone (Br₁ to Br₄). Nevertheless, zones Br₁ to Br₃ present similar aspects on the fracture surface with very limited deformation: even if bismuth intergranular concentration decreases, it remains sufficient to cause the brittle rupture. In zone Br₄, brittle rupture is accompanied by larger deformation and bismuth intergranular concentration falls progressively. Then, bismuth intergranular concentration is not sufficient to be detected by AES and a mixed rupture appears with an increasing percentage of ductility when moving to the core of the sample until reaching pure ductility fracture where bismuth was totally absent.

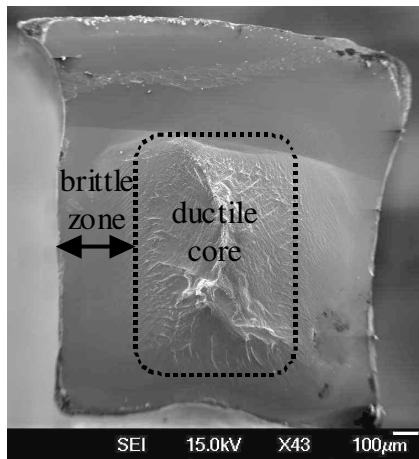


Figure 1: SEM fracture surface of a copper bicrystal (after 1h at 500°C in contact with liquid bismuth)

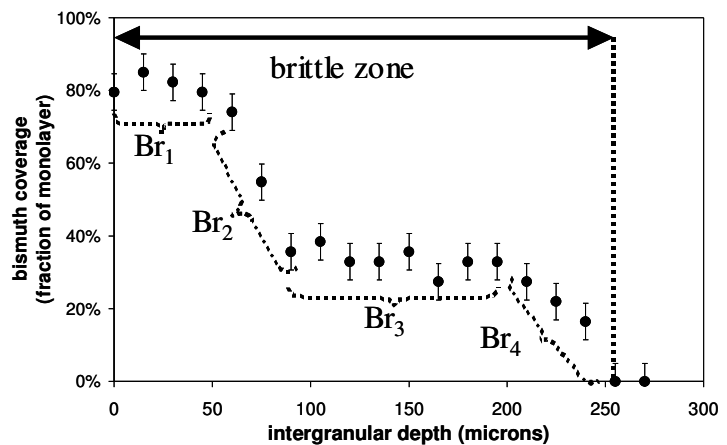


Figure 2: Bi intergranular concentration evolution as calculated after AES quantification [14]

The maximal coverage is 0.85 monolayer (in the zone Br₁). Before the rupture, the maximal bismuth intergranular concentration was hence $2 \times 0.85 = 1.7$ monolayers if we make the assumption that the rupture led to 2 fracture surfaces identically covered by bismuth (assumption verified in [14]). This value has been confirmed by further coupled AES, XPS and RBS analyzes [14]. It is very similar to concentration values obtained after segregation treatments (cf. introduction). Finally, it is not high enough to be the result of grain boundary wetting. It shows clearly that, in the Cu/Bi system, the grain boundary wetting transition is not expected to appear for $T \leq 500^\circ\text{C}$. At 500°C, grain boundary diffusion can therefore be supposed to be the controlling mechanism for bismuth intergranular penetration into copper.

Concentration profile evolution with time

In order to conclude undoubtedly that grain boundary diffusion is the sought mechanism, bismuth intergranular concentration profiles have been investigated for longer durations and are shown in figure 3. It appears that the previously defined Br₁ zone length grows with the square root of time. Further analyzes [13] allowed us to conclude that the total brittle zone length also follows a square root of time evolution (proving that the iso-concentration surfaces follow a square root of time evolution). Following Harrison's classification of grain boundary diffusion kinetic regimes, such a parabolic evolution can only be obtained for the C regime, when the volume diffusion is neglected. However, experimental concentration profiles look evidently different from the classical erfc type concentration profiles obtained for this C regime [15]. In addition, 500°C seems to be a too high temperature to allow us to neglect volume diffusion. As a matter of fact, in their study of grain boundary diffusion of bismuth into copper, Divinski et al. [16] limit the C regime to the temperature interval 263-386°C with the B regime beginning at 570°C. Volume diffusion is therefore to be taken into account. Nevertheless, a "classical" description of the interaction between grain boundary diffusion and volume diffusion would undoubtedly lead to non-parabolic time dependence of the iso-concentration surfaces. The time exponent falls in fact from $\frac{1}{2}$ to $\frac{1}{4}$ when going from a C regime to a B regime [15].

Figure 4 shows calculated bismuth intergranular concentration profiles evolution using both grain boundary diffusion formalism with B regime assumptions and Mac-Lan segregation isotherm (after [17] with numerical values [16] listed in table 1). These profiles look very similar to our experimental results, introducing notably the same typical Br₁ zone. However, the iso-concentration surfaces grow with $t^{1/4}$ (as opposed to $t^{1/2}$ in our results). Consequently, the penetration lengths calculated with this approach (for both the Br₁ and the brittle zones) are inferior to experimental ones (if attention is paid on the abscises scales). This apparent incompatibility (parabolic kinetic

only possible in the C regime and the need for taking volume leakage into account avoiding the possibility of C regime) has now to be answered with the help of an original model.

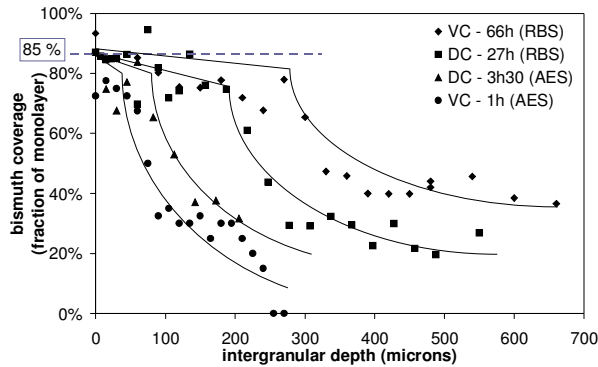


Figure 3: Experimental bismuth intergranular concentration profiles obtained either by AES or RBS for several durations

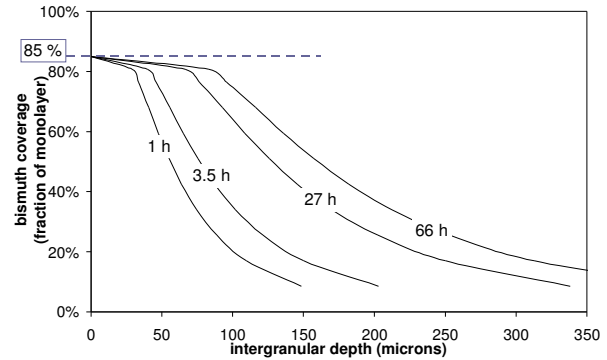


Figure 4: Calculated bismuth intergranular concentration profiles evolution obtained in B regime with McLean segregation isotherm after [17]

$D_{gb} [m^2 \cdot s^{-1}]$	$D_v [m^2 \cdot s^{-1}]$	s	$\delta [m]$
$6.7 \cdot 10^{-12}$	$7.6 \cdot 10^{-17}$	220	$5 \cdot 10^{-10}$

Table 1: Numerical values used in the calculations for figure 4 (after [16])

Model proposed to describe the concentration profiles

As bismuth is a strong segregant into copper grain boundaries [2, 4], non-linear segregation is expected to happen [16, 17]. Moreover, bismuth atoms can interact with each other when they are in copper grain boundaries (an attractive interaction energy $\alpha = -13$ to -43 kJ.mol⁻¹ was deduced for the segregated bismuth atoms in copper grain boundaries in [6]). Fowler-Guggenheim isotherm can therefore be used to describe the Cu/Bi system segregation behavior [2, 4]. Figure 5 shows several segregation isotherms with different values for the attractive interaction energy α . It shows that, when α decreases to very negative values, a domain appears where very slight c_v evolutions can lead to large c_{gb} evolutions (see cases ① and ② in figure 5). This is thought to explain the previously mentioned apparent contradiction. Two points should be now discussed.

Figure 5: Evolutions of $\frac{c_{gb}}{c_{gb}^0}$ as a function of c_v according to Fowler-Guggenheim segregation isotherm obtained at 500°C with equation (1),

$$\exp\left(\frac{-\Delta G_s}{RT}\right) = 220 \text{ and}$$

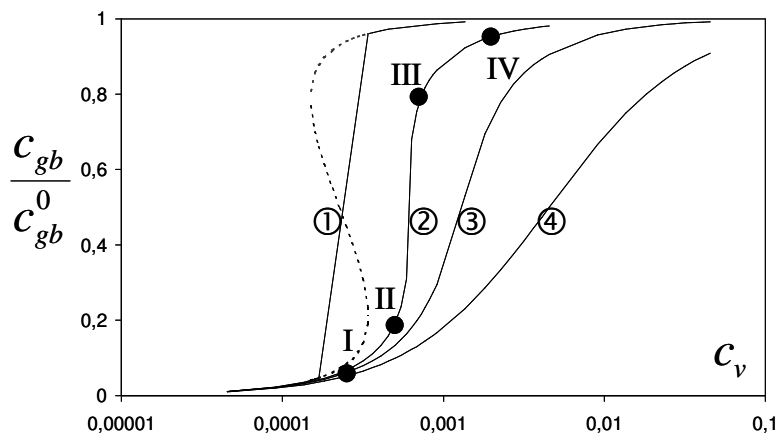
$$\textcircled{1} \alpha = -39 \text{ kJ.mol}^{-1}$$

$$\textcircled{2} \alpha = -26 \text{ kJ.mol}^{-1}$$

$$\textcircled{3} \alpha = -16 \text{ kJ.mol}^{-1}$$

$$\textcircled{4} \alpha = 0 \text{ kJ.mol}^{-1}$$

(the last case ④ leads to McLean description)



First, at 500°C, volume diffusion is effectively to be taken into account [16]. Then, if local equilibrium is assumed close to the grain boundary, at each grain boundary position, the actual grain boundary coverage is determined by Fowler-Guggenheim segregation isotherm and follows

the path I-II-III-IV in figure 5. It means that grain boundary bismuth content abruptly attains almost c_{gb}^0 (jump from $0.2 c_{gb}^0$ in II to $0.8 c_{gb}^0$ in III along the case ②) and that explains the observed profiles (cf. figure 3). Second, as only very small c_v values are involved (and also accessible because bismuth solubility in copper is very low), the kinetics keeps close to the parabolic one as in the C regime. Note that the exact evolution (from $n=1/2$ in C regime to $n=1/4$ in B regime) of the temporal exponent n as a function of the D_v/D_{gb} ratio is still unknown and should be studied. This might be along the following lines presenting the equations system that has to be numerically resolved.

$$\frac{c_{gb}}{c_{gb}^0 - c_{gb}} = \frac{c_v}{1 - c_v} \cdot \exp \left[- \frac{\Delta G_s + \alpha \cdot \frac{c_{gb}}{c_{gb}^0}}{RT} \right] \quad (1)$$

$$\frac{\partial c_v}{\partial t} = D_v \cdot \left(\frac{\partial^2 c_v}{\partial x^2} + \frac{\partial^2 c_v}{\partial y^2} \right), \text{ for } |x| > \delta/2 \text{ and} \quad (2)$$

$$\frac{\partial c_{gb}}{\partial t} = D_{gb} \cdot \frac{\partial^2 c_{gb}}{\partial y^2} + \frac{2 \cdot D_v}{\delta} \cdot \left(\frac{\partial c_v}{\partial x} \right)_{x=\delta/2} \quad (3)$$

$$c_v(x, y, 0) = 0 \text{ (for } y > 0) \text{ and } c_v(x, y = 0, t) = c_v^0 \quad (4)$$

$$c_{gb}(y, 0) = 0 \text{ (for } y > 0) \text{ and } c_{gb}(y = 0, t) = c_{gb}^0 \quad (5)$$

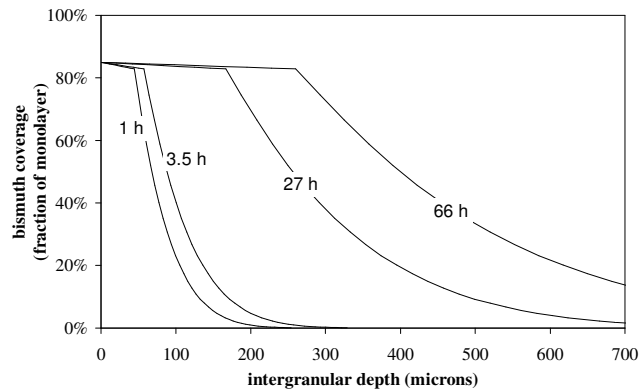
where δ is the grain boundary width and D_v is the volume diffusion coefficient. Except for equation (1), this description coincides with the grain boundary diffusion model proposed by Fisher with a constant source [18]. Numerical calculations are presently in progress.

Figure 6: Calculated bismuth intergranular concentration profiles obtained in C regime with a concentration dependence of D_{gb} :

- for $c_{gb} \leq 0.7$ monolayer,
 $D_{gb} = 3.10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$
- for $c_{gb} > 0.7$ monolayer,
 $D_{gb} = 1.10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$

The differential equation is the following:

$$\frac{\partial c_{gb}(y, t)}{\partial t} = \frac{\partial}{\partial y} \left[D_{gb}(c_{gb}(y, t)) \frac{\partial c_{gb}(y, t)}{\partial y} \right]$$



Looking now for alternative explanations, the diffusion-drift model proposed by Bokstein et al. [19] could represent a good candidate, as it leads to similar concentration profiles and moves the grain boundary penetration process in direction of C regime. However, it uses Henry's segregation isotherm, which doesn't seem relevant in this case, as it is only true for dilute solutions whereas bismuth is a strong segregant into copper grain boundaries [2, 4]. Another alternative description could lie on the use of a concentration dependence of the grain boundary diffusion coefficient in a pure C regime. As a matter of fact, if it is assumed that D_{gb} is constant for small c_{gb} values and then jumps to a higher value for higher c_{gb} values (because of a grain boundary phase transformation or grain boundary diffusion with traps, for example), calculated bismuth intergranular concentration profiles appear rather similar to those obtained experimentally (figure 6) and the kinetics are also parabolic as desired. However, as it has been already noticed before, it seems irrelevant to neglect

volume diffusion at this temperature. Nevertheless, it is not possible to exclude definitively this description based on the concentration dependence of the grain boundary diffusion as it leads to a remarkable agreement with the experimental results, but the physical justification of such a jump for D_{GB} would still have to be found. On the other side, we feel confident in the fact that the use of the Fowler-Guggenheim isotherm can both give a good description of the different zones composing the experimental concentration profiles (Br_1 zone - decrease - ductile core) and move grain boundary diffusion process in direction of C regime.

Conclusions

Bismuth intergranular concentration is investigated in a copper bicrystal previously maintained in contact with liquid bismuth at 500°C, in the absence of any applied stress. The maximal measured concentration is about 1.7 monolayers, showing the absence of any grain boundary wetting. Grain boundary diffusion is therefore thought to be the controlling mechanism of bismuth intergranular penetration into copper at 500°C (and, a fortiori, below 500°C).

Bismuth concentration profiles show 3 zones when moving from the external surface to the specimen core: (i) a first zone where bismuth intergranular concentration c_{gb} is maximal and almost constant, (ii) a decrease of c_{gb} until the end of the brittle zone and (iii) a ductile core where intergranular bismuth was undetectable.

Both the first zone and the brittle zone lengths follow a square root of time dependence. A model is proposed, based on the introduction of the Fowler-Guggenheim isotherm in grain boundary formalism, which aims to describe these experimental results.

References

- [1] L.S. Chang, E. Rabkin, B.B. Straumal, P. Lejcek, S. Hofmann and W. Gust: *Scripta Materialia* Vol. 37 (1997), p.729
- [2] L.S. Chang, E. Rabkin, B.B. Straumal, B. Baretzky and W. Gust: *Acta Materialia* Vol. 47 (1999), p.4041
- [3] L.S. Chang, E. Rabkin, S. Hofmann and W. Gust: *Acta Materialia* Vol. 47 (1999), p.2951
- [4] M. Menyhard, B. Blum and C.J. McMahon Jr: *Acta Metallurgica* Vol. 37 (1989), p.549
- [5] B.S. Bokstein, V.E. Fradkov and D.L. Beke: *Philosophical Magazine A* Vol. 65 (1992), p.277
- [6] U. Alber, H. Müllejans and M. Rühle: *Acta Materialia* Vol. 47 (1999), p.4047
- [7] D. McLean: *Grain boundaries in metals* (Clarendon Press, Oxford 1957)
- [8] H.J. Vogel and L. Ratke: *Acta Metallurgica Materialia* Vol. 39 (1991), p.641
- [9] B. Joseph, F. Barbier, G. Dagoury and M. Aucouturier: *Scripta Materialia* Vol. 39 (1998), p.775
- [10] B. Joseph, F. Barbier and M. Aucouturier: *Materials Science Forum* Vol. 294-296 (1999), p.735
- [11] B. Joseph, F. Barbier and M. Aucouturier: *Scripta Materialia* Vol. 42 (2000), p.1151
- [12] K. Wolski, N. Marie, V. Laporte and M. Biscondi: *Defect and Diffusion Forum* Vol. (2004),
- [13] V. Laporte and K. Wolski: to be submitted to *Scripta Materialia*,
- [14] V. Laporte, P. Berger and K. Wolski: to be submitted to *Surface and Interface Analysis*,
- [15] I. Kaur, Y. Mishin and W. Gust: *Fundamentals of Grain and Interphase Boundary Diffusion* (Wiley, United Kingdom 1995)
- [16] S. Divinski, M. Lohmann and C. Herzig: *Acta Materialia* Vol. 52 (2004), p.3973
- [17] Y. Mishin, C. Herzig, J. Bernardini and W. Gust: *International Materials Reviews* Vol. 42 (1997), p.155
- [18] J.C. Fisher: *Journal of Applied Physics* Vol. 22 (1951), p.74
- [19] B. Bokstein, T. Karanadze, A. Ostrovski, A. Petelin, B. Razumeiko, A. Rodin and V. Viktorov: *Defect and Diffusion Forum* Vol. 216-217 (2003), p.217