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INTERGRANULAR SEGREGATION OF BISMUTH IN COPPER BICRYSTALS

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Résumé. - On a analysé, par spectrométrie Auger, des joints fracturés "in situ" dans des bicristaux de cuivre, de flexion autour de $\langle 100 \rangle$, dopés en bismuth. Pour une désorientation donnée, on précise d'abord certains aspects thermodynamiques et cinétiques de la ségrégation intergranulaire du bismuth. Puis, pour des conditions fixées, on a déterminé comment varie cette ségrégation avec l'angle de désorientation.

Abstract. - In Cu-Bi $\langle 100 \rangle$ tilt bicrystals, "in situ" fractured grain boundaries have been analysed by Auger spectrometry. For a given misorientation, certain thermodynamic and kinetic features of segregation have been evaluated. Then, under a given set of conditions, the influence of misorientation angle on grain boundary segregation of Bi has been determined.

INTRODUCTION

Even though the phenomenon of grain boundary segregation has been the subject of many papers, the dependence of intergranular segregation on the grain boundary structure is not well known. Nevertheless, several studies, both direct and indirect, suggest the degree of segregation varies among grain boundaries. The indirect studies were recently reviewed by Balluffi (1). Direct studies of grain boundary segregation by Auger spectroscopy have shown considerable anisotropy of segregation in polycrystals of Cu-Bi (2), as well as in randomly oriented Fe-Si bicrystals (3). The reported anisotropy has been attributed to the dependence of segregation on grain boundary structure. To examine this effect in detail, segregation studies on oriented bicrystals, in which only one crystallographic parameter varies, are necessary.

In our laboratory, an investigation of oxygen segregation in molybdenum bicrystals was carried out (4). A strong influence of misorientation angle on the segregation level for both $\langle 100 \rangle$ and $\langle 110 \rangle$ tilt grain boundaries was found. Nevertheless, at present no systematic study of misorientation dependence of grain boundary segregation has been reported. Such a study was the object of the present investigation. There were two principal reasons for the choice of the Cu-Bi system. First, bismuth is known to induce a considerable degree of embrittlement in copper, thereby making it possible to use Auger electron spectroscopy. Secondly, the copper bicrystals with the required characteristics are relatively easy to obtain.

The present paper contains two principal parts. In the first one, we have examined the thermodynamic and kinetic aspects of bismuth segregation in copper. The second part deals with the effect of grain-boundary misorientation on the intergranular segregation of bismuth in $\langle 100 \rangle$ tilt bicrystals of copper.

1 - EXPERIMENTAL PROCEDURE

The copper bicrystals were prepared by the Chalmers method (5) from 99,99% Cu.

Bismuth was introduced in the samples by transport in the vapour phase. To achieve this, each bicrystalline sample along with defined quantity of master alloy (containing 0.1 Wt.% Bi) were annealed in sealed evacuated quartz ampoules at 950°C for a time calculated from the relation (6) : $t = L^2/4D$, where L is the thickness of the sample and $D = 2.10^{-8} \text{ cm}^2\text{s}^{-1}$ (7). Subsequently, the samples were quenched in water and the bismuth content was determined by a colorimetric method (8). The heat treatment for segregation was carried out in the temperature range of 400-650°C. The samples were fractured and analysed in the chamber of an Auger electron spectrometer ; the incident beam diameter was about 2 μm , with an energy of 3 KeV, and the sample current was low, about $5.10^{-3} \mu\text{A}$. Over twenty spots were analysed on each rupture surface. The calculation of surface coverage is questionable. The Palmberg method (9) defines the surface coverage by bismuth as :

$$C_j (\%) = \frac{\frac{J_{\text{Bi}}}{n_{\text{Bi}}}}{\frac{J_{\text{Bi}}}{n_{\text{Bi}}} + \frac{J_{\text{Cu}}}{n_{\text{Cu}}}} \cdot 100$$

were J_{Bi} (J_{Cu}) is the intensity of Auger peak of Bi (Cu). The coefficients n_{Bi} and n_{Cu} , which depend on the characteristics of pure metals Auger spectra, were calculated from data (9). This calculation yields very different values from those obtained by an experimental calibration (10) consisting of the deposition of bismuth onto a previously deposited layer of copper (2). For our experiments, Fig. 1 compares the results given by these methods.

Fig. 1 - Relationship between surface coverage calculated by the Palmberg method c_j (9) and by the calibration method of Molinari c_j^* (10).

In addition, the fractured surfaces were observed in the scanning electron microscope to insure that the fractures were intergranular, as well as to detect the presence of precipitates.

The bismuth concentration measured on one fractured surface presents only a half of its amount at the grain boundary, as the segregant atoms, upon intergranular fracture, are shared among the separating surfaces in average equally (11). Therefore, on the curves presented in this paper, we have twiced the measured bismuth concentrations. Mean C_j values (calculated with Palmberg method) and the corresponding 80 % confidence intervals are reported. A strong dispersion of the results for certain grain boundaries is observed. No faceting was observed in the scanning electron microscope but the grain boundary surfaces were not always flat. Therefore a geometrical effect on the Auger spectrometry measurement cannot be excluded, as well as an effect of the grain boundary asymmetry on the segregation level.

2 - THERMODYNAMIC AND KINETIC ASPECTS OF INTERGRANULAR SEGREGATION IN A GIVEN HIGH-ANGLE TILT BOUNDARY (30° AROUND <100>)

2.1 - Effect of the bulk concentration of bismuth on its intergranular concentration

In the case of solid solutions at equilibrium at a given temperature, the C_j value, as a function of the bulk concentration, increases up to a maximum (saturation) value which is attained for the bulk concentration corresponding to the solubility limit. In our case, the isotherm of segregation at 550°C, corresponding to a holding of 24h, shows another relationship (Fig. 2). The intergranular concentration increases, reaches a maximum, and then decreases, approaching a value which is about the same as that for a 50 $\mu\text{g/g}$ bulk concentration.

Fig. 2 - Intergranular concentration of Bi, as a function of the bulk concentration. Heat treatment at 550°C for 24h.

Moreover, in the samples with Bi bulk concentrations above 300 $\mu\text{g/g}$, second phase particules were observed on the fracture surface (Fig. 3a). Microprobe analysis revealed the presence of Cu and a large amount of Bi in these precipitates, but it was difficult to obtain more information about their composition and structure because of their small size ($\approx 1\mu\text{m}$).

An interpretation of our experimental curve first requires an estimation of the solubility limit at 550°C. The data are unclear (12) ; some authors (13,14) find a value of about 150 $\mu\text{g/g}$. Our observations suggest a value of about 50 $\mu\text{g/g}$ at this temperature instead, as is proposed by other authors (15). The curve of Fig. 2 could thus be explained by a kinetic effect. When the bulk concentration C_v lies below 50 $\mu\text{g/g}$, the solid solution Cu-Bi is at equilibrium and the intergranular concentration increases with C_v . At about 50 $\mu\text{g/g}$, the limit of solubility is exceeded, but in the range of 50-200 $\mu\text{g/g}$, the alloy remains a supersaturated solid solution and C_j continues to increase with C_v . Beyond about 200 $\mu\text{g/g}$, the supersaturation is sufficient for the precipitation of a Bi-rich phase. When C_v increases from 200 to 400 $\mu\text{g/g}$, the precipitation reaction progresses and the amount of Bi decreases both in the solid solution and at the grain boundaries. For the C_v values greater than 400 $\mu\text{g/g}$, the supersaturation is sufficient for approximative equilibrium to be reached after 24h at 550°C. The amount of dissolved Bi in the matrix, as well as the amount of segregated Bi, corresponds to the limit of solubility of this element.

Fig. 3 - Intergranular surfaces of samples with Bi bulk concentrations of :
a) 440 µg/g, b) 60 µg/g.

To the purpose to simplify our study, it would be preferable to investigate equilibrium segregations, and therefore the bulk concentration of Bi should be limited to 50µg/g. However, for such low Bi contents, it is impossible to obtain intergranular rupture of the bicrystals in the spectrometer for a sufficiently wide spectrum of misorientations. To avoid this difficulty, we have chosen to examine specimens in a state of supersaturated solution. A study of the kinetics of the segregation process was necessary to select heat treatment conditions, which give a maximum segregation level without the formation of precipitates.

2.2 - Effect of temperature on intergranular segregation of Bi (Fig. 4).

No second phase particles were observed on the fractured surfaces in the scanning electron microscope for the studied cases. The heat treatment time was apparently too short to achieve the maximum segregation for temperatures below 500°C. In the range 500-650°C, holding of 24h seems to be enough to allow for segregation at a level close to the maximum, and too short for the precipitation to start. In this range of temperatures, after 24h, the grain boundary segregation can be considered to be in temporary equilibrium with the supersaturated solution. As a first approximation, it can be described by the Mc Lean model (15) :

$$\frac{C_j}{1-C_j} = \frac{C_v}{1-C_v} \cdot \exp \left(\frac{E_s}{kT} \right), \quad [1]$$

where E_s is the characteristic free energy of segregation at the grain boundary. According to our results, the values of the interaction energy for an atom of Bi at a tilt-boundary misoriented of 30° around <100> in copper is between 0.68 and 0.73 eV. For a comparison with the experiment, the curve corresponding to equation [1] with $E_s = 0.7$ eV/atom is plotted in Fig.4 as a broken line.

2.3 - Effect of the time of heat treatment at 500°C on the Bi intergranular segregation

The results reported in Fig. 5 are consistent with the previous interpretation. In the case under investigation, the segregation process is observed during the first hours. The segregation level reaches a maximum value after about 24 h, an order of magnitude longer than the time observed by other authors (16). The decrease of the intergranular concentration of Bi with times greater than 24 h is caused by precipitation. Only in the 10 day annealed samples were intergranular particles of a second phase observed in the scanning electron microscope.

Fig. 4 - Intergranular Bi concentration as a function of temperature after 24h holding, for $C_v \approx 160 \mu\text{g/g}$.

Fig. 5 - Intergranular Bi concentration, as a function of the annealing time at 500°C , for $C_v \approx 160 \mu\text{g/g}$.

3 - EFFECT OF THE MISORIENTATION ON THE INTERGRANULAR SEGREGATION OF BISMUTH IN COPPER $\langle 100 \rangle$ TILT BOUNDARIES

Measurements have been performed on samples with a $120 \mu\text{g/g}$ Bi content, annealed at 500°C for 24h. For all misorientations, no intergranular precipitates were observed in the scanning electron microscope. Furthermore, as the segregation kinetics are governed by bulk diffusion, one may consider that intergranular segregation attains its maximal level in all cases after 24h. Therefore, comparison between different grain boundaries is justified.

In spite of scatter in the experimental results, some conclusions may be drawn (Fig. 6). No intergranular fracture was obtained for the low-angle (10° and 80°) boundaries; the intergranular concentration of bismuth can be estimated in these cases to be considerably lower than 15 at.%, i.e., much lower than the intergranular concentration in high-angle boundaries. For the latter, one observes appreciable dependence of segregation on the misorientation angle. Two maxima, the larger (≈ 55 at.%) at about 30° and the other (≈ 45 at.%) at about 60° , as well as a relative minimum (≈ 30 at.%) between 37° and 50° are found. Abrupt variations in the vicinity of misorientations corresponding to high-coincidence (or low periodi-

city) boundaries (for example about 37° , 53° , 67°) are not observed, in contrast to the case of sliding in copper $\langle 100 \rangle$ tilt bicrystals (17).

Fig. 6 - Intergranular concentration of bismuth as a function of the misorientation angle for copper $\langle 100 \rangle$ tilt bicrystals. Heat treatment at 500°C for 24h, $C_V \approx 120 \mu\text{g/g}$.
DF : ductile fracture.

For high-angle boundaries, the maximum enrichment factors for Bi that we have measured lay between $4 \cdot 10^3$ and $1.5 \cdot 10^4$, corresponding to mean segregation energies (deduced from equation [1]) between about 0.55 and 0.7 eV. These enrichment factors are not as high as those observed in previous works (2 to $5 \cdot 10^4$), where a monolayer of Bi has been found at grain boundaries in copper polycrystals (2, 13, 18). Therefore, it seems that a tilt grain boundary defined by a misorientation around a dense axis, along which the periodicity of the grain boundary structure is low, allows for a lower segregation than an entirely random grain boundary.

We can easily understand the reason why the segregation is at a low level for the low-angle boundaries and grows with the misorientation. The adsorption sites are very likely situated along the dislocations which form on such grain boundaries. However, we are not able to give a reliable interpretation of the segregation variation for high-angle boundaries. No correlation with the grain boundary energy exists ; for the type of grain boundary in f.c.c. structures being considered, the energy is almost constant for high-angle misorientations (19). Taking in consideration the large size of bismuth atom, compared to copper atom, we can expect that the intergranular adsorption sites are in tension in the pure metal. Thus, the intergranular formation volume might represent the segregation propensity of the grain boundary. We note there is a likeness between the present results and the variation of the formation volume with misorientation : simulation calculations of structures of the same kind of boundaries in Al (19), show two maxima, at about 20° and 60° , with a minimum range between 37° and 53° . Nonetheless, it seems to us that the best way for validly interpreting the connection between segregation and structure is to simulate grain boundary structures in the presence of foreign atoms, in order to obtain the possible adsorption sites and their interaction energies, and the maximum level of segregation. Such studies have begun (20, 21) and we intend to undertake such computer simulations.

CONCLUSION

The knowledge of the connection between the grain boundary structure and segregation is not very extensive. With the use of copper bicrystals, we were able to

determine the influence of the misorientation on the Bi segregation in Cu <100> tilt boundaries by Auger electron spectrometry.

Because of the plasticity of copper bicrystals, it is possible to provoke "in situ" intergranular fracture only if the Bi intergranular content is more than 10-15 at. %. To obtain intergranular ruptures in most cases (except for low-angle boundaries), we have studied supersaturated bicrystals with a Bi content of about 120-150 µg/g, even though the limit of solubility has been estimated to be 50 µg/g at about 500°C. We have shown that the maximum segregation level is attained after an annealing time of 24h at 500°C.

Under these conditions, the enrichment factor of the intergranular bismuth in copper bicrystals is less than 10^3 for small-angle boundaries and between 0.4 and $1.5 \cdot 10^4$ for misorientations lying in the range 20-70°. For high-angle boundaries we have actually observed significant variations of this factor with the misorientation angle, i.e., with the grain boundary structure. Computer simulations seem to be a promising way to understand the connections between the intergranular structure and segregation. To compare models with experimental results, it is still necessary to obtain more, reliable experimental data, if possible from oriented bicrystals.

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