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Heterogeneous precipitation on a low-angle grain boundary in Al-4 wt % Cu

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When a (1 1 0) tilt boundary plane deviates from its symmetrical position in an Al–4 wt % Cu alloy, a single θ' family precipitates in only one grain. An elastic calculation of the stresses applied by the dislocation wall on the $\{1\,0\,0\}$ habit planes of the plate-shaped θ' precipitates determines the family with the easiest nucleation; it is found to be that making the smallest angle with the boundary plane. Furthermore it is shown that the precipitate growth is favoured in one grain, thus explaining the electron microscopic observations.

1. Introduction

After ageing an Al–4 wt % Cu alloy between 100 and 400° C, the θ' phase precipitates in subgrain boundaries in which misorientation does not exceed 10° [1, 2]. The plate-shaped θ' precipitates are partially coherent, lying in the $\{1\,0\,0\}$ planes of the aluminium matrix. The coherency misfit, of about 8% [3], of interstitial type, is localized on the edge of the plates and can be described by a misfit vector **R** normal to the precipitate plane.

The heterogeneous nucleation of θ' on isolated dislocations is well known: only two of the three θ' families, with a negative elastic interaction energy with the dislocation, precipitate [4, 5]. For tilt subboundaries, the precipitation of a single family is generally observed [1]. A qualitative explanation, similar to that given for the dislocations, has been advanced [6]: at a distance from the boundary greater than the separation between the dislocations, the stress field is practically perpendicular to the wall, therefore the $\{1\,0\,0\}$ family, making the smallest angle with the boundary plane, precipitates. But this model does not explain why growth takes place in one grain and not in the other.

The purpose of the present work is to show how this precipitation is conveniently explained by the detailed consideration of the elastic strain field of the subgrain boundary.

2. Experimental results

A small grain structure (100 μm) has been introduced in an Al–4 wt % Cu alloy by cold working and slow annealing at a heating rate of 30° C h^{-1} up to 540° C. After quenching and annealing for 4 h at 235° C, foils were cut from this material, electropolished by the jet method in 33% HNO_3 + 67% CH_3OH at − 50° C, and observed by 100 kV electron microscopy.

Fig. 1 shows a low-angle tilt grain boundary misoriented 9° around [001]. Its asymmetry is characterized by the angle ϕ between the grain-boundary plane J and the plane P bisecting the planes $(1\,1\,0)_A$ and $(1\,1\,0)_B$. In the present case, $\phi = -5°$. Only the $(0\,1\,0)_B$ θ' family precipitates: this (0 1 0) family makes, in fact, the smallest angle with plane J. According to the observations of Vaughan [1] in a low-angle tilt boundary misoriented by 3°, the families (1 0 0) and (0 1 0) precipitate in the symmetrical position ($\phi = 0$) instead of at $\phi \neq 0$: $(1\,0\,0)_A$ for $\phi > 0$ (Fig. 4a of [1]) or $(0\,1\,0)_B$ for $\phi < 0$ (Fig. 4c of [1]). Our observation is in agreement with this. Therefore, we can assume that the grain-boundary asymmetry

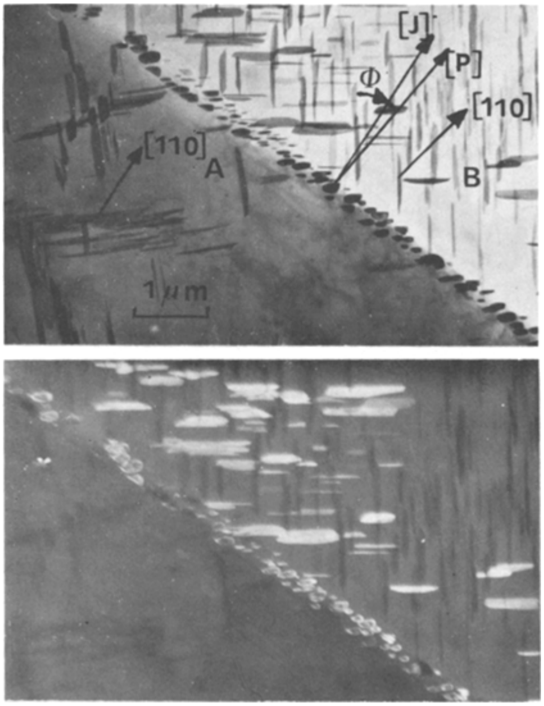

Figure 1 Heterogeneous precipitation of the $\theta'_{(1\,0\,0)\mathrm{B}}$ family on a tilt boundary of 9° round [0 0 1] in an asymmetrical case. (a) bright-field $\mathbf{g} = (0\,2\,0)_{\mathrm{B}}$; (b) dark-field $\mathbf{g} = (0\,1\,0)_{\theta'\mathrm{B}}$, showing that the precipitates in the boundary belong to grain B.

is responsible for the discrimination between the different θ' families.

3. Interpretation

A preferential precipitation in one grain can be explained either by rapid diffusion in that grain, or by easier nucleation and growth near the grain boundary. These two points will be considered on the basis of the elastic strain field of subgrain boundaries evaluated by Li [7].

The diffusion of solute atoms towards the subgrain boundary can be accelerated if the solute atoms have a long range elastic interaction with it. Although such an interaction by size effect does exist for an asymmetrical wall, the resulting driving term is negligible: it is nearly proportional to $\exp(-4x/h)$ as soon as the distance x between the solute atom and the boundary is higher than $2h$, h being the separation between dislocations in the boundary. Near the boundary, the effect is similar to that occurring near an isolated dislocation, giving rise to a higher concentration of copper in the compressed zones. This local enrichment cannot, however, be attributed to one particular grain.

The nucleation energy of a θ' precipitate near the boundary is:

$$\Delta G_{\mathrm{c}} = \Delta G_{\mathrm{v}} + E_{\mathrm{s}} + W_{\mathrm{e}} + W_{\mathrm{e}}^{\mathrm{i}} \qquad (1)$$

where ΔG_{v} is the chemical energy variation of the nucleus, E_{s} its surface energy, W_{e} its elastic energy and $W_{\mathrm{e}}^{\mathrm{i}}$ its elastic interaction energy with the dislocation wall, principally due to the size effect of θ'. Only $W_{\mathrm{e}}^{\mathrm{i}}$ may differ in the three θ' families.

$$W_{\mathrm{e}}^{\mathrm{i}} = \iiint_V \sigma_{\mathrm{x_i x_j}} \epsilon_{\mathrm{ij}} \,\mathrm{d}V$$

integrated over the volume V of the precipitate. Whence

$$W_{\mathrm{e}}^{\mathrm{i}} \simeq \iint_S \sigma_{\mathrm{x_i x_i}} R_{\mathrm{i}} \,\mathrm{d}S$$

where $\sigma_{\mathrm{x_i x_i}}$ is the stress normal to the coherent place faces of surface S.

The present tilt boundary can be considered as a wall of parallel edge dislocations of $\boldsymbol{b} = \frac{1}{2}a$ [1 1 0] distant of h. Assuming that nucleation occurs in the boundary plane ($x = 0$, Fig. 2d), the stresses $\sigma_{\mathrm{x_i x_i}}$ (in units $\mu b/[2h(1-\nu)]$, are given by:

$$\sigma_{1\,0\,0,\,1\,0\,0} = \cot\frac{\pi y}{h}\left(\tfrac{1}{2}\sin 3\phi - \tfrac{1}{2}\sin\phi + \cos\phi\right)$$

$$\sigma_{0\,1\,0,\,0\,1\,0} = \cot\frac{\pi y}{h}\left(\tfrac{1}{2}\sin\phi - \tfrac{1}{2}\sin 3\phi + \cos\phi\right)$$

$$\sigma_{0\,0\,1,\,0\,0\,1} = \cot\frac{\pi y}{h}\left(2\nu\cos\phi\right).$$

Therefore, the following inequalities:

$$\phi = 0 : |\sigma_{1\,0\,0}| = |\sigma_{0\,1\,0}| > |\sigma_{0\,0\,1}|$$

$$\phi > 0 : |\sigma_{1\,0\,0}| > |\sigma_{0\,1\,0}| > |\sigma_{0\,0\,1}|$$

$$\phi < 0 : |\sigma_{0\,1\,0}| > |\sigma_{0\,1\,0}| > |\sigma_{0\,0\,1}|$$

determine the family(ies) with the highest $|W_{\mathrm{e}}^{\mathrm{i}}|$: (1 0 0) for $\phi > 0$, (0 1 0) for $\phi < 0$ and both (1 0 0) and (0 1 0) in the symmetrical case $\phi = 0$.

The map of these stresses in the $(x\,0\,y)$ plane, normal to the wall, leads to the same results (Fig. 2a to c) for $\phi = +10°$: the surface where the stress is higher than a given value, is larger for $\sigma_{1\,0\,0}$ than for $\sigma_{0\,1\,0}$ or $\sigma_{0\,0\,1}$, favouring the nucleation of $\theta'_{(1\,0\,0)}$. As an order of magnitude, for a 5° misoriented sub-boundary which asymmetry is $\phi = +10°$, the tensile stress contour $\sigma_{0\,0\,1} = +3$ contains a plate-shaped nucleus of a dozen of atoms. We can also observe that this $\theta'_{(1\,0\,0)}$ precipi-

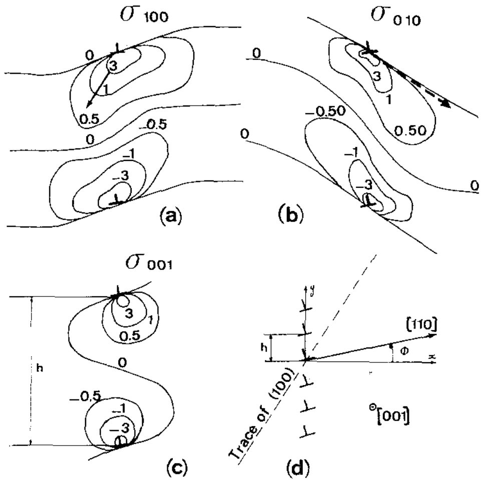

Figure 2 Isostress lines (in units $\mu b/[2h\,(1-\nu)]$) normal to the planes (a) (1 0 0), (b) (0 1 0), (c) (0 0 1) for a tilt boundary misoriented of b/h with an asymmetrical angle $\phi > 0$ (d). The arrow indicates the growth direction of the $\theta'_{(1\,0\,0)}$ plate (a). The dashed arrow indicates the growth direction of the θ' (0 1 0) plate (b).

tate grows towards the dilatation zones, i.e. in the direction of the arrow in Fig. 2a, parallel to the intersection of $(x\,0\,y)$ with (1 0 0) (Fig. 2d), i.e. in the grain A. On the contrary, if a (0 1 0) nucleus, for which the normal stresses $\sigma_{0\,1\,0}$ and their gradients are not much smaller than the $\sigma_{1\,0\,0}$ stresses, is formed, it would grow in the direction of the dashed arrow in Fig. 2b, at the intersection of (0 1 0) with $(x\,0\,y)$: this growth direction is near a zero stress contour and would not be favoured, resulting in a slow growth rate with respect to (1 0 0). The coarsening occurring during ageing at 235° C is, therefore likely to dissolve the small (0 1 0) θ' precipitates rather than the (1 0 0) precipitates in the other grain.

4. Discussion

When dealing with the modification of the heterogeneous θ' precipitation when the tilt boundary plane deviates from its symmetrical position (1 1 0), we have assumed that there was no structural change in the core of the boundary. In an asymmetrical position, the boundary develops long range stresses and consequently is unstable. It can, nevertheless, be stabilized by a segregation of copper atoms. For instance, a simple calculation shows that a concentration of copper atoms along the dislocation of about 0.2 is sufficient to pin a tilt boundary ($\theta = 10°$, $\phi = 10°$) in its misequilibrium position. This concentration is smaller than the saturation which can be predicted at these temperatures [8]. The slow heating rate of our samples could explain the occurrence of such a segregation.

Modification of the stress field by this segregation is difficult to evaluate, due to the fact that the copper atoms are located in the dislocation cores. Bullough and Newman [9] have considered the perturbation of the kinetics of precipitation which should result from saturating dislocation cores. Nevertheless, the long range stress of the dislocation still falls of as r^{-1}. Therefore, the stress field of the wall calculated at present varies little, presumably in the same way for all three components.

We have noticed that the 9° sub-boundary observed here, with $h = 6b$, is a limiting case for the use of linear elasticity. The similarity of our results with those of Vaughan, as well as the observation of the θ' precipitation instead of θ, the phase which generally precipitates in high-angle boundaries, seems to show that the elastic interaction between the dislocations of the wall and the nucleus is, nevertheless, correctly described.

A (1 1 0) asymmetrical sub-boundary can also be stabilized by the introduction of a second family of parallel dislocations of $b = a/2\ \langle 1\,\bar{1}\,0\rangle$, which cancels the long range stresses of the first family; their edge component being nearly equal to the Burgers vector of the first family, their spacing $H = h \cot\phi \simeq h\phi^{-1}$ (Fig. 3a) is large and increases as the asymmetry decreases. If the second family plays a direct role in the θ' nucleation, the θ' density should increase with the asymmetry of the boundary, which has not been observed within the limits of our experiments.

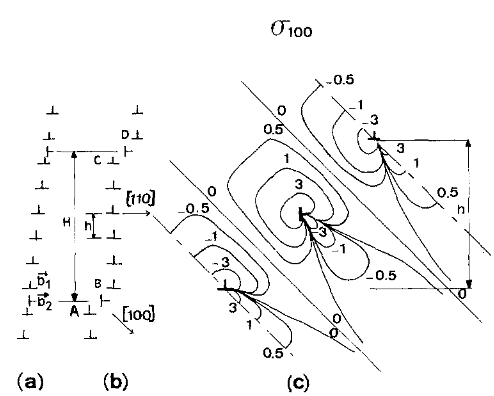

Figure 3 (a) and (b) Possible shapes of a 10° asymmetrical (1 1 0) low-angle boundary. The dislocations family $b_1 = (a/2)\ [1\,1\,0]$ is stabilized by an adjoined family $b_2 = (a/2)\ [1\,1\,0]$. (c) Isostress lines (in units $\mu b/[2h\,(1-\nu)]$) normal to the plane (1 0 0) in the AB region of (b).

Although the calculation of the equilibrium shape of this wall as well as the resulting stress distribution, have not been performed, two limiting cases can be considered.

(1) The wall remains nearly plane (Fig. 3a): the stresses on the major part of the surface of the wall are the same as in the one family case.

(2) The wall takes on a "staircase" shape (Fig. 3b). Two regions must be distinguished: (a) in the symmetrical (BC) steps, representing the greater part of the wall, the nucleation of the (1 0 0) and (0 1 0) families should evidently be equally favoured; (b) in the (AB) sites, it is easy to show that a single nucleation should take place: assuming that the stresses are nearly equivalent to those of an infinite (1 0 0) wall, as described by Li [7], σ_{100} is also larger than σ_{010} and σ_{001}; furthermore the magnitude of σ_{100} (Fig. 3c) is nearly the same and on the same volume as for σ_{100} in the first wall.

Therefore, the (AB) sites being fewer, a predominantly double precipitation should be observed rather than a single one. However, the relative importance of the single precipitation should increase with the boundary asymmetry.

As these two points were not observed in the experiments, we conclude that the "staircase" shape can be dismissed, at least for the boundaries observed in the present study, for which the local asymmetry, as described in Section 3, explains more conveniently the characteristics of the θ' heterogeneous precipitation.

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