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Repeated θ′ precipitation at dislocations in Al-4 wt % Cu

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Repeated precipitation of the θ' phase has been observed to occur on dislocations on {110} planes of an Al-4 wt % Cu alloy, particularly when the alloy was in the reverted state. It is shown that θ' is nucleated at prismatic dislocation loops, the climb of which determines the growth of the precipitates in the matrix.

1. Introduction

The heterogeneous nucleation of precipitates at dislocations is a phenomenon frequently observed, which occurs for instance during the decomposition of supersaturated alloys: precipitation of the γ' phase in Al-Ag [1], of the S phase in Al-Cu-Mg [2], of the θ' phase in Al-Cu [3, 4]. Preferential nucleating sites are often helical dislocations, namely for θ' in Al-Cu alloys [4, 5].

The plate-shaped θ' precipitates are partially coherent, lying in the {100} planes of aluminium, where full coherency is realized. The misfit vector **R***, generally accommodated by interface dislocations, is of interstitial type, and normal to the plane of the precipitate. The negative elastic interaction energy between a precipitate and a dislocation explains why only two of the three families of θ' precipitate are nucleated on a dislocation of a given Burgers vector $\boldsymbol{b}$. The family with **R** perpendicular to $\boldsymbol{b}$ is not observed [4], because the interaction energy is zero.

It has to be noted that nucleation on an edge dislocation is favoured with respect to nucleation on a screw one, because the principal part of this interaction strain energy is due to a size effect of the precipitate, which is at first order zero for a screw dislocation; similarly the Cottrell clouds are more dense at edge dislocations. This particular role of the edge character has been outlined in Al-8 % Mg alloy where rod-shaped particles seem to precipitate along pure edge sides of angular {111} prismatic loops [4]. To our knowledge such effect has not been reported in Al-Cu alloys.

We describe here some transmission electron microscopy observations of a new type of heterogeneous precipitation on dislocations in Al-4 wt % Cu. Evidence is found of a θ' precipitation process occurring at pure edge prismatic dislocations loops lying in {110} planes. Escape from the precipitates by climb in its habit plane makes the loop available for further θ' nucleation, finally giving rise to repeated precipitation. The phenomenon appears, therefore, as a form of planar discontinuous precipitation process [12].

2. Experimental results

This precipitation has been principally observed in Al-4 wt % Cu alloys having undergone the following treatment: sheets, 1 mm thick, of the alloy have been annealed at 525° C for 15 h in air, iced water quenched, aged 6 h at 100°C and reverted (5 min at 210° C). It is then a secondary phenomenon which occurs during the reversion. It has also been observed, but less clearly, in alloys simply aged 100 h at 160° C after quenching. Thin foils have been cut from these materials and specimens suitable for electron microscopy have been electropolished at ~25° C in a A-3 Codal electrolyte.

Fig. 1 shows the same area of a thin foil of a reverted alloy under two electron beam directions: (a) [001] and (b) [011]. Precipitation of the θ' phase (identified by selected-area diffraction patterns) occurs in two crossing {110}

*The misfit parameter is about 8 % [11].

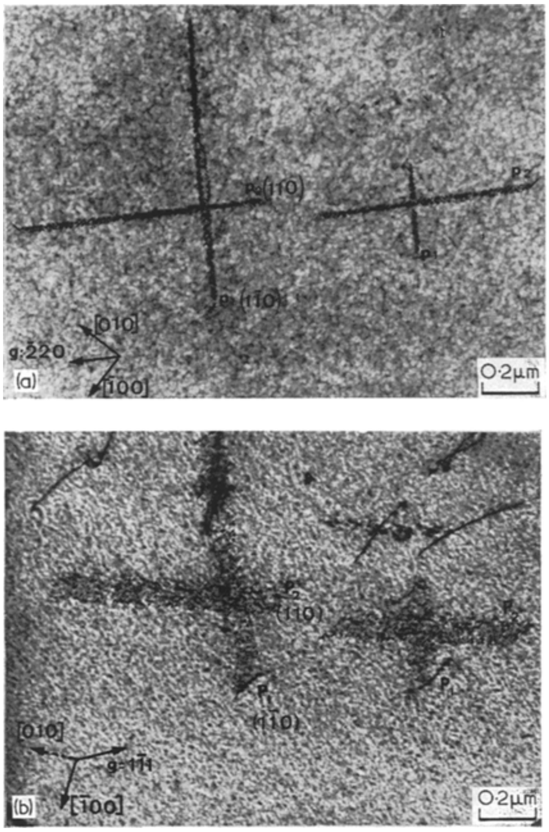

Figure 1 Al-4 wt % Cu alloy, reverted state [12]. (a) Zone axis: [001] – g = $\bar{2}20$ – θ' has precipitated in the seen edge-on planes P_1 = $(1\bar{1}0)$ and P_2 = (110). (b) Zone axis: [011] – g = $1\bar{1}1$ – dislocations $\boldsymbol{b}_1 = (a/2)$ $[1\bar{1}0]$, bounding P_1, are in contrast, whereas dislocations $\boldsymbol{b}_2 = (a/2)$ [110], bounding P_2, are not (see text).

planes. No confusion is possible with precipitation on straight dislocations, as could be deduced from Fig. 1a alone. The planes of precipitation of θ' have been truncated by the foil surfaces and are bounded in the longitudinal direction by two segments of dislocation lying in the plane of precipitation. The two precipitation planes are P_1 $(1\bar{1}0)$ and P_2 (110). P_1 is bounded by two arcs of dislocations of Burgers vector $\boldsymbol{b}_1 = (a/2)$ $[1\bar{1}0]$ and similarly P_2 by $\boldsymbol{b}_2 = (a/2)$ [110], i.e. normal to P_1 (and P_2): they are pure edge dislocations. The identification of the Burgers vectors has been made with the [011] zone axis: with $\mathbf{g} = 1\bar{1}1$ (Fig. 1b), dislocations $\boldsymbol{b}_1$ are in contrast whereas dislocations $\boldsymbol{b}_2$ are not ($\mathbf{g} \cdot \boldsymbol{b}_2 = 0$); with $\mathbf{g} = 11\bar{1}$, dislocations $\boldsymbol{b}_1$ are out of contrast ($\mathbf{g} \cdot \boldsymbol{b}_1 = 0$), dislocations $\boldsymbol{b}_2$ are in contrast. Furthermore two θ' families, with habit plane (100) and (010) belong to the planes P_1 and P_2 and, as expected, their corresponding misfit vectors are not perpendicular to $\boldsymbol{b}_1$ or $\boldsymbol{b}_2$.

Similar features are present in Figs. 2 and 3, where several sets of θ' have precipitated in {110} planes. As before, two θ' families precipitate in each set, bounded by two arcs of the same edge dislocation line with a Burgers vector normal to the precipitation plane but not perpendicular to the two misfit vectors of the precipitates. The disc-shaped θ' precipitates are small, about 15 to 20 Å thick and 100 to 150 Å diameter and lie on {100} planes of the matrix. The same phenomenon seems to occur in the alloy simply aged in the temperature range where the θ'' phase precipitates (160° C), as shown in Fig. 4 from [6].

3. Discussion

The previous Figures suggest that the development of the precipitation of θ' in a particular (110) plane is related to the climb of the bounding dislocation loop in this plane, the loop being prismatic and purely edge, with $\boldsymbol{b} = (a/2)$ [110]. During climb the dislocation drags copper atoms in the solid solution, which by rapid diffusion along the core nucleate θ' on the dislocation.

Owing to their interstitial nature, the θ' nuclei are formed on the expanded side of the dislocation, inside the loop, the loop having a vacancy origin (see later). Growth by climb of the loop then occurs by vacancy absorption; besides their thermal origin, excess vacancies can be

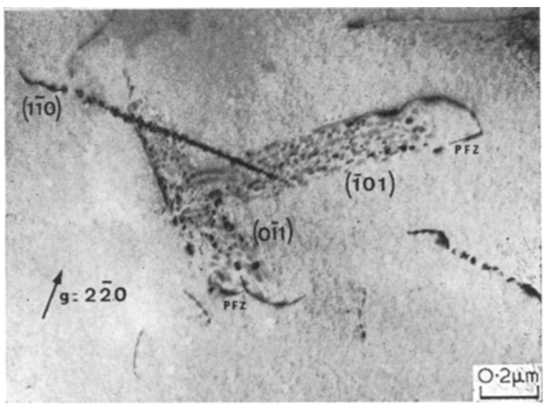

Figure 2 Al-4 wt% Cu alloy, reverted state [12]. Zone axis: [001] – g = $2\bar{2}0$; three {110} sets of θ' are observed.

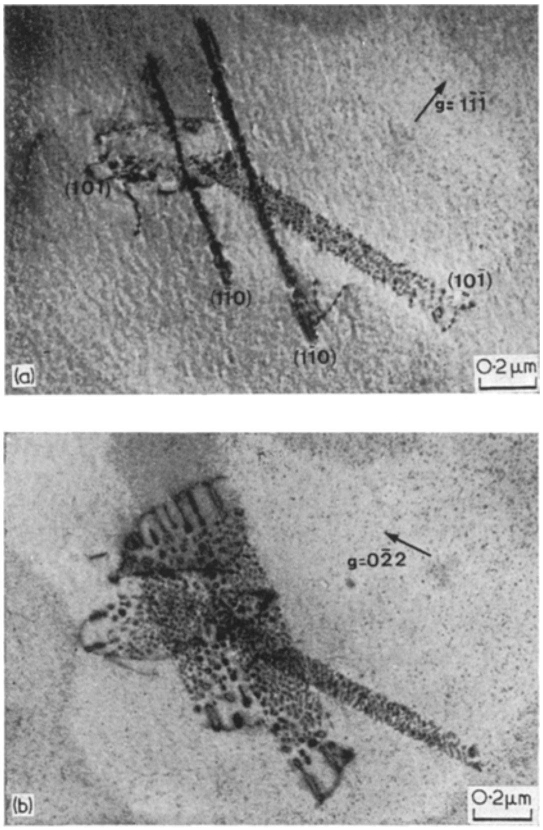

Figure 3 Al-4 wt % Cu alloy, reverted state [12]. (a) Zone axis: [110] – g = 1$\bar{1}\bar{1}$. (b) Zone axis: [211] – g = 0$\bar{2}$2. Kinematical image. Four {110} sets of θ' are distinguished.

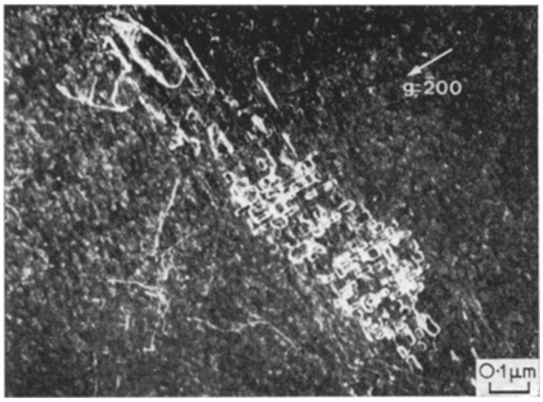

Figure 4 Al-4 wt % Cu alloy, aged 100 h at 160°C [6]. Zone axis [001] – g = $\bar{2}$00. Weak beam conditions, making interface dislocations in high contrast.

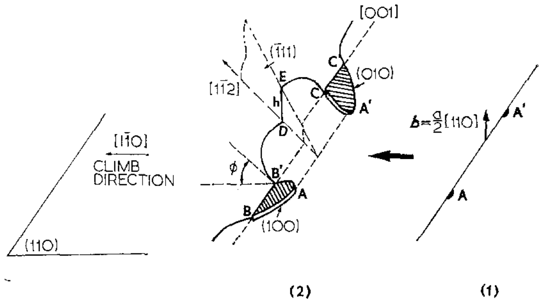

Figure 5 Diagram of precipitation of two (100) and (010) θ' precipitates on a $\boldsymbol{b} = (a/2)$ [110] dislocation. The segment of the loop initially parallel to [001] has only been drawn. In (1) two nuclei are formed at A and A′. The dislocation climb in two half (110) planes until position (2), forming a screw jog DE which slips in the ($\bar{1}$11) plane.

emitted by the growth of the θ' phase, the average atomic volume of which is lower than for Al (about 4%, using the tetragonal θ' structure given by Graf [3]). Therefore, the growth of the loop by climb and the nucleation and growth of θ' occur together. The process is schematically drawn in Fig. 5. In this case, the near neighbour nuclei have two different habit planes (100) and (010). The loop $(a/2)$ [110] climbs to the left on the figure. Originally the nuclei are formed at A and A′ along the dislocation. Growth of the two nuclei necessitates: (1) a combination of climb and slip of the two segments BB′ and CC′, in order to stay in the precipitate {100} planes; (2) the creation of a jog DE on the bowed-out segment B′C. This jog, of height, $h = 2\sqrt{2}\,R$, R being the radius of the nuclei, follows the dislocation motion by slipping in the ($\bar{1}$11) plane*.

Escape of the dislocation from the nuclei is necessary for making the loop available for a further precipitation event, in order to lead to repeated precipitation. A complete description of the escape requires a knowledge of the value of the interaction energy between the dislocation and the precipitate, but the escape condition can be estimated as follows: the energy to separate the dislocation from the precipitate is roughly $2Re\gamma$, where e is the thickness of the discs, and γ the interface energy along their edge in the presence of a dislocation segment such as BB′ in Fig. 5; this energy must be equal to the work done to move the segment BB′ over a distance of

*It can be noted than the jog will disappear if in the course of the next precipitation event, the two nuclei are reversed, i.e. (010) at A, (100) at A′.

say R, i.e. $2\tau R \cos\phi$, where τ is the line tension of the line and ϕ the angle shown in Fig. 5. Therefore, escape occurs for a critical value ϕ_c given by

$$\cos\phi_c = \frac{e\gamma}{\tau} \qquad (1)$$

From the Figures, as for instance Fig. 3b, it can be seen that $\phi_c > 75°$. Taking $e = 15$ Å and $\tau = \mu b^2/2 = 11 \times 10^{-5}$ dyn, this leads to $\gamma > 190$ erg cm^{-2}, which is reasonable for a partially coherent interface.

The following arguments are in favour of the present analysis:

(a) the binding energy of copper atoms with an edge dislocation is high (~0.35 eV, [7]), determining a strong driving force for bowing-out of the dislocation in order to drag the copper atoms. Obviously the other term of the driving force is the normal change in chemical free energy (solid solution – θ′).

(b) the copper atom diffusivity is probably higher along edge dislocation core than along screw one [8]. The role played by the edge dislocation is, therefore, threefold: strong relaxing role for θ′ nucleation, strong driving force for copper atom drag and high core diffusivity.

(c) numerous edge prismatic (110) loops are pre-existing after ageing at 100° C, constituting the precipitation sites. The loops can be formed either (i) by precipitation of vacancies, the Frank loop so produced being further transformed into a perfect loop by sweeping of a Shockley dislocation, a rotation towards a {110} plane decreasing the elastic energy of the loop [9], or

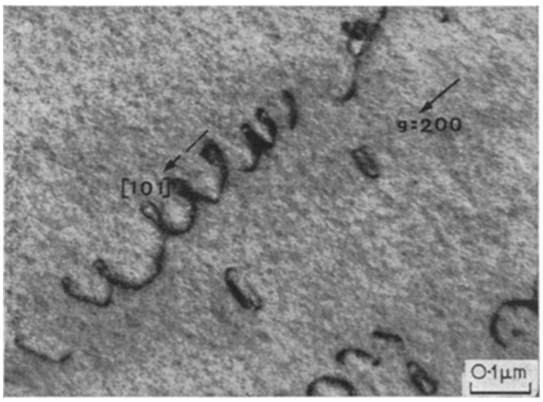

Figure 6 Al-4 wt % Cu alloy, aged 50 h at 100° C, showing helical dislocations and pure edge loops in (101) plane.

(ii) by decomposition of helical dislocations. Such loops are shown on Fig. 6.

Relatively large "precipitate-free zones", are sometimes observed behind the dislocation loop, as for instance on Fig. 2 (indicated PFZ). Such zones are probably due to a pure slip of the segments of the loop parallel to the intersection of its (110) habit plane with a (111) slip plane. Such slip breaks down the full edge character of the dislocation, making, for the reasons previously mentioned, the θ′ nucleation process less efficient. The phenomenon described here is quite similar to the precipitation of NbC on dislocations in austenitic steels [10].

The reverted state is favourable for the above θ′ precipitation process, because it provides a large driving force for the growing loop, due to the large change in free energy between θ′ inside the loop and the reverted solid solution outside the loop. But it is not indispensable since the precipitation occurs during simple ageing at 160° C, when θ″ is also present, Fig. 4; nevertheless it is less frequent in this case, the driving force being now due to the change in free energy between θ′ and θ″, which is smaller than previously.

Besides the thermodynamic considerations, the temperature itself plays an important role; it should be sufficiently high for a high dislocation core diffusivity and climb efficiency (heterogeneous θ′ nucleation is absent on ageing at 100° C where Guinier-Preston zones, loops and helical dislocations are formed) but not too high in order to avoid firstly the homogeneous θ′ precipitation and secondly the fast growing θ′ precipitates which would pin the dislocation on which they have been nucleated.

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