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DIRECT OBSERVATIONS OF HETEROGENEOUS PRECIPITATION

J. A. Hren and G. Thomas

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by

J.A. Hren and G. Thomas

Inorganic Materials Research Division
Lawrence Radiation Laboratory
University of California, Berkeley, U.S.A.

A high temperature stage has been used in the Siemens Elmiskop I and Hitachi H.U. 10 electron microscopes to follow directly the stages of decomposition of a supersaturated Al-20% Ag alloy, and the results recorded by cine photography. The experimental techniques have been described previously (Thomas and Whelan, 1961). The purpose of this note is to present direct evidence for the dislocation reactions involved in the nucleation, growth, and dissolution of γ' (Ag_2Al) precipitates.

The γ' phase is hexagonal (e.g., see Guinier, 1952; Ziegler, 1952; Glocker, et al, 1952), and precipitates on {111} planes in the FCC Al-Ag solid solution. Thus, the nucleation of γ' is expected to occur at stacking faults in the matrix. This process has been observed indirectly in foils made from bulk specimens (Nicholson and Nutting, 1961; Frank, et al, 1961), but no direct evidence for such heterogeneous precipitation has so far been reported.

There are two general possibilities for dislocations to promote precipitation of a HCP structure from a FCC lattice. First, a whole dislocation can split to produce a fault on only one of the {111} planes, e.g., by the reaction

$$1/2a[\bar{1}10] \longrightarrow 1/6a[\bar{1}2\bar{1}] + 1/6a[\bar{2}11]; \quad \text{fault on } (111) \qquad (1)$$

Second, a whole dislocation can dissociate to produce a Frank sessile dislocation and a Shockley dislocation to form a fault on one {111} plane; the Frank sessile can then break down to form a stair-rod and a Shockley dislocation which produces another fault on one of the intersecting (111) planes. The two faults are then connected by the stair-rod, e.g.,

$$1/2a[\bar{1}10] \longrightarrow 1/3a[\bar{1}11] + 1/6a[\bar{1}1\bar{2}] \text{ fault on } (\bar{1}11) \quad (2)$$

$$1/3a[\bar{1}11] \longrightarrow 1/6a[011] + 1/6a[\bar{2}11] \text{ fault on } (111) \quad (3)$$

Reactions (2) and (3) can thus produce two orientations of precipitate from a single dislocation. In order for these processes to occur in the Al-Ag solid solution, the stacking fault energy must first be lowered. Thus, silver must segregate to dislocations. Figures 1a, b, show a sequence from a cine film of whole dislocations present at 500°C(a), breaking down on quenching and aging (b), to give a single orientation of γ' by a reaction similar to (1) above. The precipitates form as plates. Figures 2a,b,c, show a similar sequence but in which single dislocations D give rise to two orientations of γ' in accord with equations 2,3. The line of intersection EF in Fig. 2c makes a trace on the foil surface parallel to the trace of $[0\bar{1}1]$ which is consistent with the mechanism proposed. The observations show that since γ' plates form only at dislocations, their density should be the same as that expected for the initial dislocation density of the solid solution. Observations at the solid solution temperature (>450°C) and during aging to form γ', confirm that this is true. The maximum observed density in both cases is $\sim 10^7$ cm^{-3}. The results also suggest that silver atoms are associated with dislocations even at the solid solution temperature.

Depending on the local concentration of silver atoms, the growth of γ' occurs lengthwise very readily by the propagation of the partial dislocations. Thus precipitates formed on isolated dislocations, e.g., G and H, Fig. 2, grow very rapidly. The growth in directions normal to the habit plane is not nearly as rapid since faults must be created on alternate (111) planes in order to preserve a perfect HCP structure. However, from a thermodynamic viewpoint, spontaneous nucleation of partial dislocations will be favored in order to allow continued growth and to preserve a stable interface between each precipitate and the matrix. New partials could also be nucleated as a result of the shear strain in each layer, thus successive partials tend to move in opposite directions to minimize this strain. This has been observed directly. Often successive loops of partial dislocation are created which then expand over the {111} planes. The contrast effects observed at growing or dissolving particles are similar to those for overlapping stacking faults, hence the growth in the direction normal to the habit plane occurs by the addition of successive layers. Part of a newly forming layer can be seen at L in Fig. 2c. There is absolutely no evidence for a pole mechanism. Upon dissolution, the process is completely reversible. By heating the specimen above 450°C, each layer is successively removed by the contraction or elimination of the partial dislocations. The resultant is either zero or the formation of a perfect < 110 > dislocation, e.g., by the reverse of reaction (1). Figures 2a,b,c, and d show such a dissolution sequence occurring at 475°C. Dislocations A', B', C, etc., have been emitted as successive layers are removed. Re-precipitation on

these dislocations can be effected simply by quenching the specimen in the microscope (i.e., by switching off the heating current). In fact, the sequences shown in Figs. 1 and 2 can be repeated by this operation.

Kinetic data have been obtained from measurements of the rate of growth and dissolution of γ' precipitates. The process is one of bulk diffusion and occurs with an activation energy of 37.5(±4)k. cal. mol^{-1}, which is the same as that reported for diffusion of silver in aluminum (see e.g., Smithells, 1955). This result confirms earlier suggestions (Nicholson and Nutting, 1961; Frank, et al, 1961) and proves that silver must initially diffuse preferentially to the dislocations. Thus, the sequence of events can be summarized as follows:

1. Growth: Silver diffuses to dislocations and lowers the stacking fault energy. The dislocations split to form the nucleus of the HCP precipitate and the growth rate depends on the rate of diffusion of silver to the faults. The precipitates thicken in layers by the spontaneous nucleation of stacking faults every alternate (111) plane.
2. Dissolution: Silver diffuses away from the precipitate increasing locally the stacking fault energy so that the partials are successively eliminated and the precipitates dissolve in layers. The velocity of the dislocations involved is thus determined by the rate of diffusion of silver atoms away from the ends of each layer.

The events described here are most conveniently demonstrated by ciné-photography; more complete details will be published.

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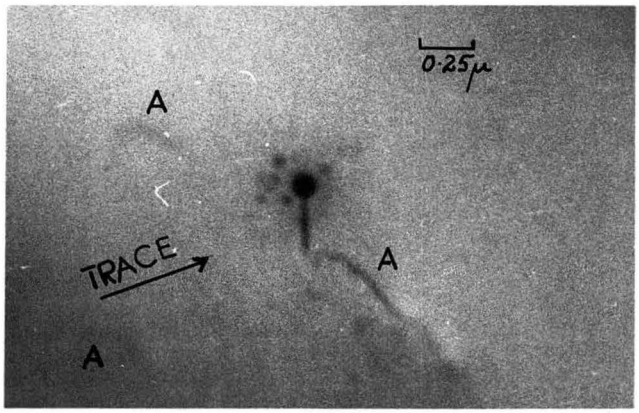
FIGURE CAPTIONS

Fig. 1 -- Thin foil of Al-20% Ag. (a) Dislocations A moving slowly at 500°C; (b) quenched in the microscope, 15 sec later showing splitting of dislocations A to form γ^1 precipitates. The dislocations extend preferentially at the surfaces, probably because of enhanced diffusion of silver.

Fig. 2 -- As Fig. 1, orientation [112]. (a) dislocations A,B,C,D at 475°C; (b) quenched, 10 secs later; the dislocations C forming precipitates edge-on along $(\bar{1}\bar{1}1)$, dislocations D nucleating precipitates on (111); (c) 15 secs later: two orientations of γ^1 have now formed at D and new long precipitates G and H have appeared from isolated dislocations (not in view in this sequence). The fringe contrast due to the appearance of γ^1 is similar to that for stacking faults.

Fig. 3 -- Showing a dissolution sequence at 450°C; (a) two partials AA about to combine; (b) combination to form a whole dislocation A'; (c) partials BB about to combine; (d) dislocations A' and B' C gliding on the cross-slip plane; a new dislocation D about to be emitted; A layer is removed each time this happens. Notice also decrease in length of the precipitate. Time interval ~ 0.2 sec.



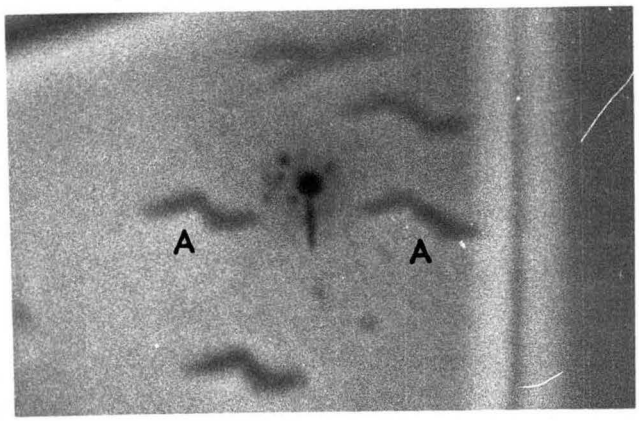
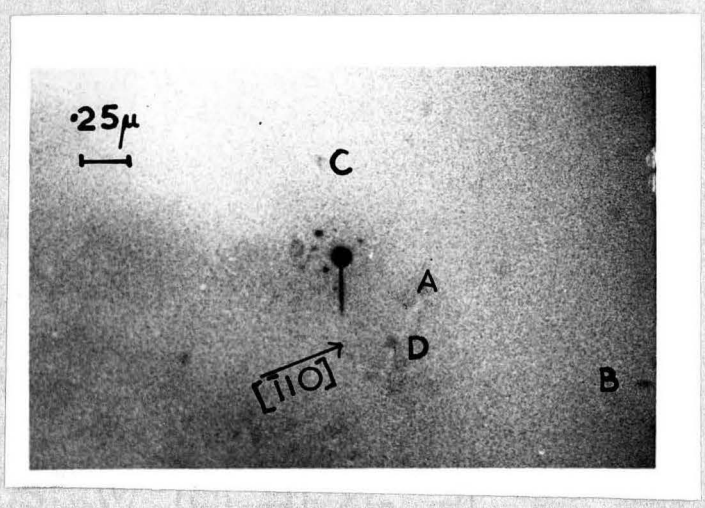
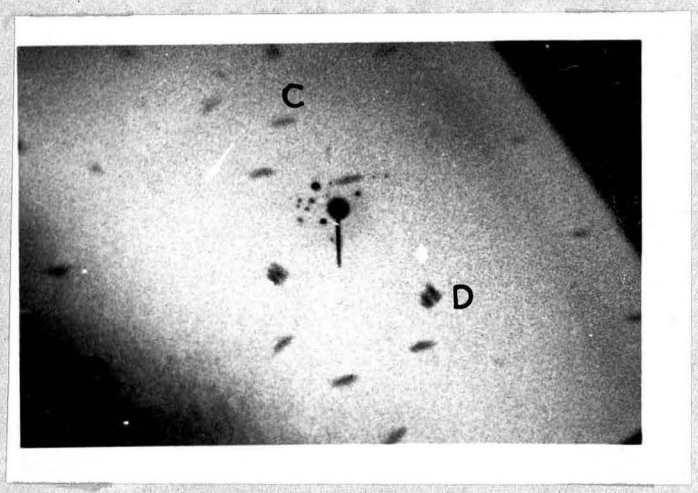


Fig. 1.





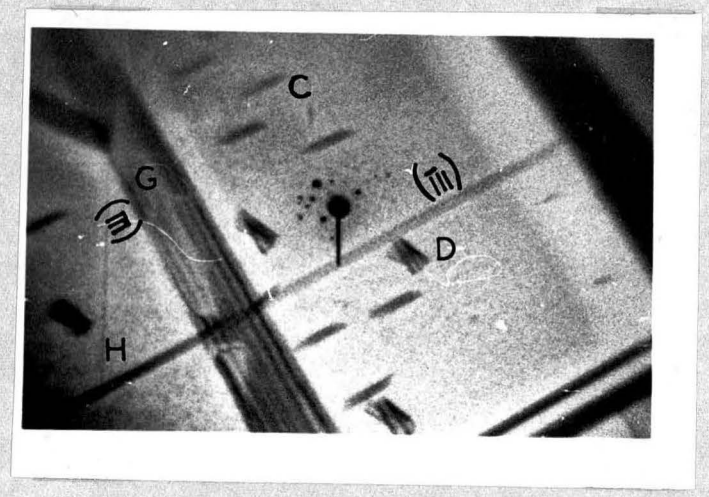


Fig. 2.

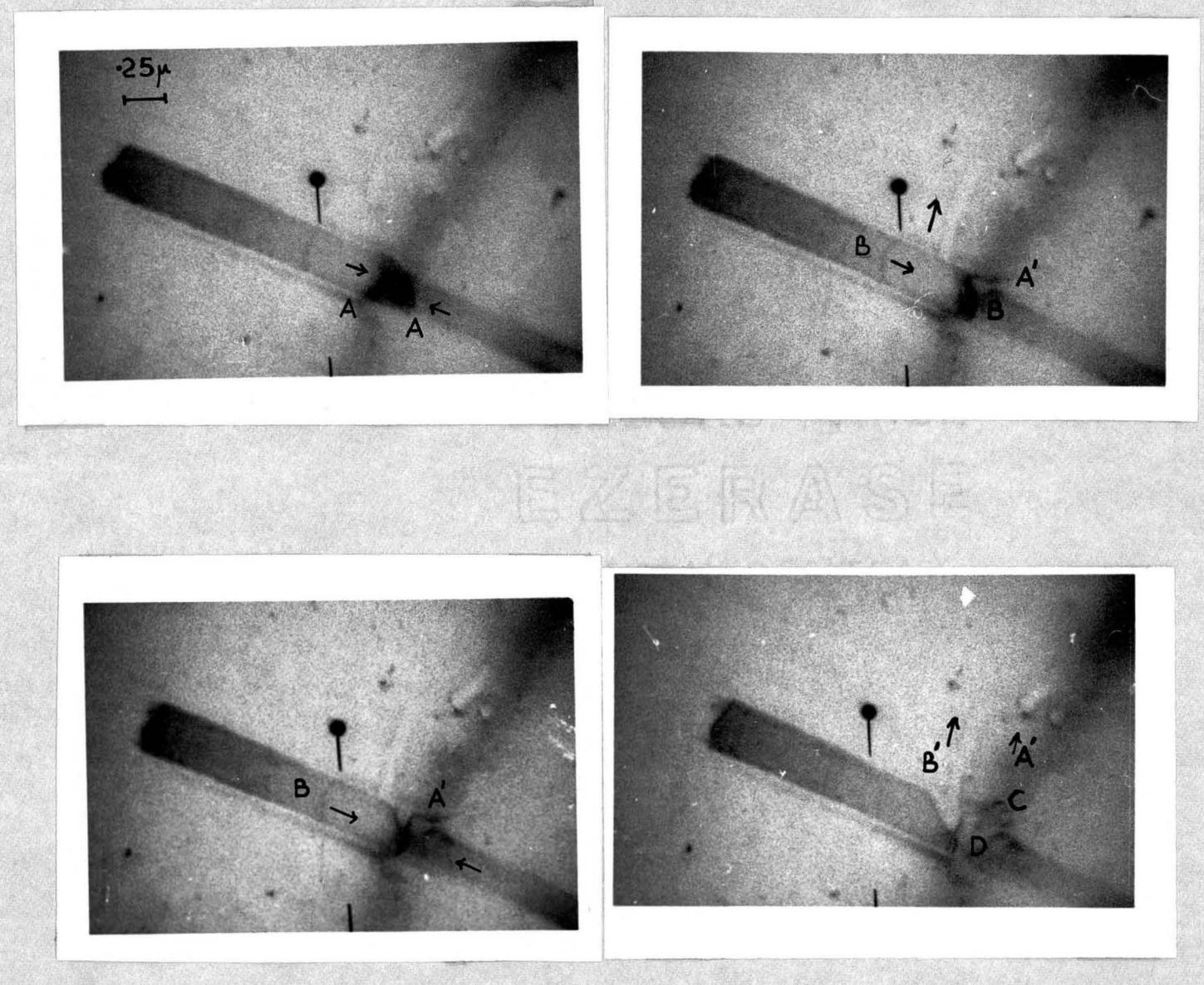


Fig. 3.