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On the micromechanisms of repeated precipitation on edge dislocations

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Refinements on the model for repeated precipitation on dislocations are advanced, taking account of the anisotropy of the matrix structure. In anisotropic materials the climbing dislocations tend to take up low-energy directions between the precipitates, and it is suggested that this forces the growing precipitates and the connecting dislocation segments to migrate with the same speed throughout each growth cycle. A periodically varying precipitate density along the advancing dislocation may facilitate this energetically favourable appearance of the growth front. The dendritic growth phenomenon encountered in some precipitation systems is suggested to be a result of high jog energies and a low nucleation frequency.

1. Introduction

Precipitation by repeated nucleation and growth on climbing dislocations has been reported in a variety of systems. A model for this precipitation mechanism was first given by Silcock and Tunstall [1] in connection with NbC-precipitation in austenitic stainless steel. In their model, the dislocation climbs ahead of the pinning particles to provide vacancies for the precipitate growth.

On the basis of experimental results on Cu–Si precipitates in silicon [2–4], one of the present authors (Nes [5]) has advanced a refined model which allows the precipitates to migrate with the climbing dislocation between successive nucleation events. This model is sketched in Fig. 1. In the initial stage the climb of the straight dislocation segments between the particles in Fig. 1a depends on the density of thermal jogs along the segments. This mobility is therefore quite low compared to that of the curved segments behind the particles, where geometric jogs facilitate the climb. As a consequence, the latter segments are assumed to advance faster, dragging the particles along (Fig. 1b). By exchanging point defects with the precipitates, the curved interface dislocation segments will climb increasingly further ahead of the connecting segments, the climb rate of the latter being smaller because of longer jog drift paths. But as the precipitates grow their mobility, and consequently their migration speed, decreases. Also, line tension forces acting against the dislocation/particle motion arise because of the curved shape adopted by the connecting segments. The latter segments, now climbing by drift of geometric jogs, will then gradually catch up with the precipitates and straighten as in Fig. 1c.

Nes assumes the unpinning of the dislocation from the particles to be a process dependent on the jog nucleation energy. In materials with low jog energies the dislocation is assumed to bow out between the precipitates (Fig. 1d), while in high jog energy materials the unpinning is suggested to occur where small particles nucleate between the large ones and take over the climb–dragging process (Fig. 1e).

In the above analysis little attention is given to the anisotropic conditions present in the crystal lattice. Neither is the influence of precipitate coarsening during growth considered. However, from detailed TEM investigations of the reaction

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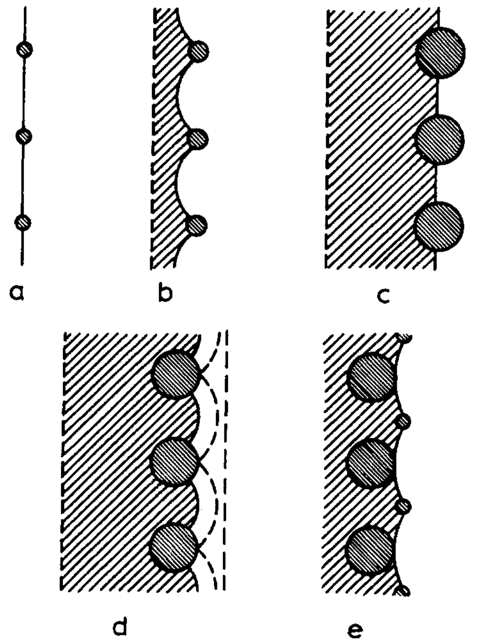

Figure 1 Stages in Nes's model for repeated precipitation on climbing dislocations. (d) and (e) illustrate alternative unpinning processes. (After Nes (1974)).

front in the Si–Cu system it seems that these effects are relevant for a more complete understanding of the growth mode. In the present paper these results are presented, and the qualitative effect of both crystal anisotropy as well as particle coarsening on the repeated precipitation reaction are considered.

2. Experimental

The silicon single crystals used in the experiments were of the Czochralski type. Copper precipitate colonies were introduced by evaporating high purity copper films on thin crystal wafers, followed by a 20 min anneal at 900° C in evacuated quartz capsules. The specimens were subsequently air cooled to room temperature. In one case the air cooling process was interrupted at 725° C by a rapid quench in silicon oil.

The precipitate colonies were studied in a Philips EM 300 electron microscope. Foils for the microscope were prepared either by using a standard chemical polishing technique [6], or by ion etching.

3. Results and discussion

3.1. Crystal anisotropy

In a real crystal the dislocations tend to align themselves in directions which minimize their self-energy. Fig. 2 shows typical configurations taken up by the climbing edge dislocations in Cu–Si precipitate colonies in silicon. The colony occupies a $\{1\,1\,0\}$ plane, and the main growth direction is along the given $\langle 1\,1\,0\rangle$ vector. (The colony in Fig. 2c is formed by the climb of several dislocations. Therefore, many precipitates are seen in front of the dislocation.) For these colonies the low-energy directions for the climbing dislocations are $\langle 1\,1\,0\rangle$ and $\langle 2\,1\,1\rangle$, the former being the most close-packed direction in silicon. Segments in the $\langle 2\,1\,1\rangle$ directions have $\{1\,1\,1\}$ glide planes, the low-energy stacking-fault planes in diamond structures. Such segments can therefore reduce their self-energy by dissociating into an extended dislocation consisting of two Shockley partials and an enclosed stacking fault [7]. The micrographs in Fig. 2 clearly reveal that the connecting dislocation segments tend to take up these low-energy directions, and that this forces the dislocation to bow out either behind or ahead of the particles. In all micrographs, dislocation segments aligned along $\langle 2\,1\,1\rangle$ and $\langle 1\,1\,0\rangle$ are respectively denoted by the numbers 1 and 2. The segments 3 are oriented along $\langle 1\,0\,0\rangle$. This is the third-closest-packed direction in the silicon lattice, and it seems to be one of the preferred low-energy directions. In Fig. 2a the relative length of the segments along $\langle 1\,0\,0\rangle$ and $\langle 2\,1\,1\rangle$ is seen to vary with the orientation of the straight line segments connecting the precipitates. By comparing the various configurations in Fig. 2, it is seen that the orientation of the growth front determines the directions taken up by the piecewise straight dislocation segments.

3.2. Precipitate coarsening

Figs. 3 and 4 show examples of precipitate coarsening. Along the surrounding dislocations there is a smaller particle size and a higher particle density than withing the colony. A coarsening process must therefore take place during growth. The precipitate size and density just on the inside of the dislocations are roughly the same as in the interior of the colony. It is therefore believed that the coarsening process only takes place while the precipitates are attached to the climbing dislocations. The colony in Fig. 3 was air cooled to room temperature, while the growth of the colony in Fig. 4 was interrupted at 725° C. Since both colonies expose the same features with respect to particle density/size distribution, it is concluded

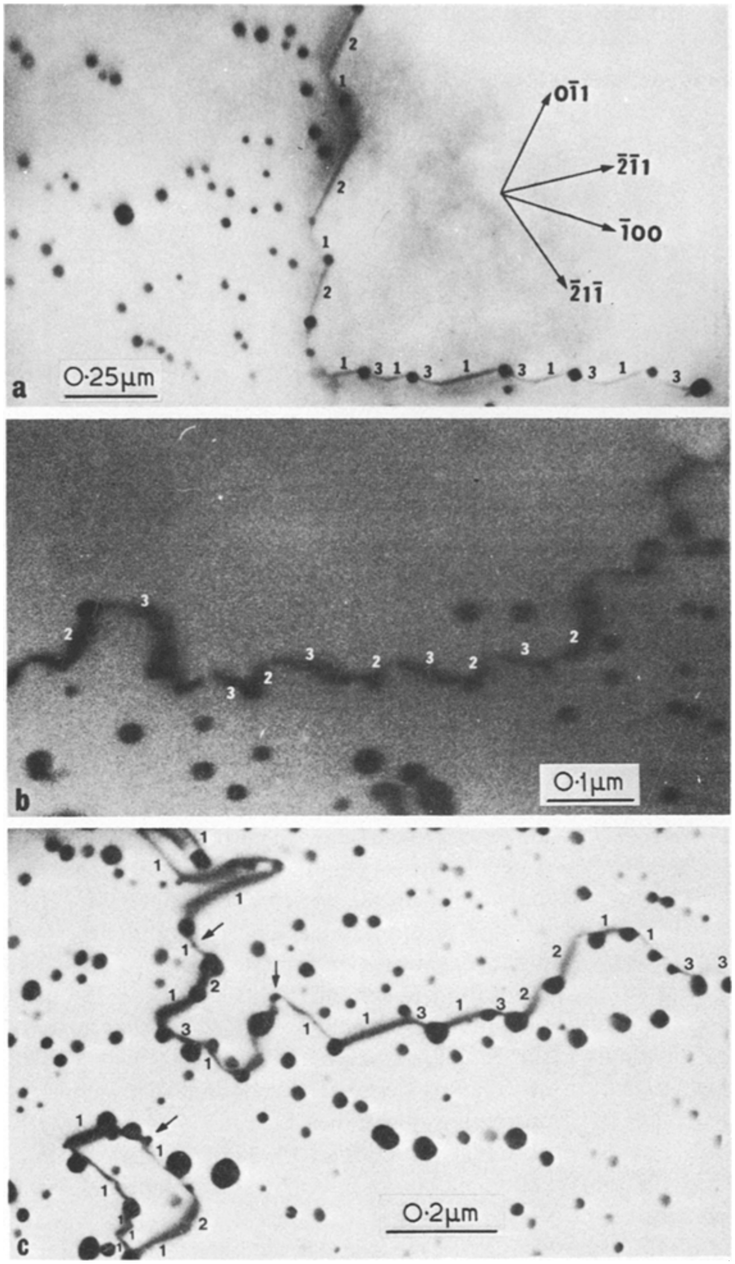

Figure 2 The effect of anisotropic conditions. The connecting dislocation segments align themselves in low-energy directions. Segments marked 1, 2 and 3 are parallel to ⟨2 1 1⟩, ⟨1 1 0⟩ and ⟨1 0 0⟩, respectively.

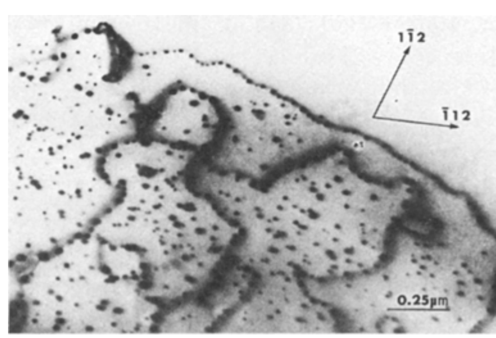

Figure 3 Dislocations densely populated with precipitates. Note that no dipoles are formed along these dislocations.

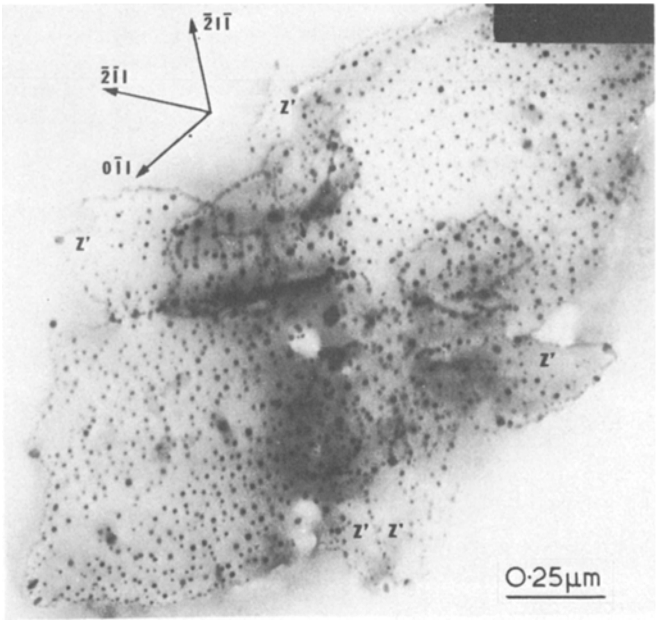

Figure 4 Dense population with small precipitates along the climbing dislocation. The colony growth was interrupted at 725° C. Note the depleted zones in the ⟨2 1 1⟩ directions.

that precipitate coarsening along the colony front progresses during the entire colony growth.

3.3. Colony growth

In the cases shown in Fig. 2 the climbing dislocations have invariably taken up low-energy configurations between the precipitates. Even though these micrographs show final colony morphologies, it is believed that the configurational energy may be of major importance during the entire colony growth in silicon. In materials with diverging properties in different directions, the growth mode may therefore not be as simple as depicted in Fig. 1b. In order to retain low-energy configurations the dislocation will probably tend to migrate with the same speed as the precipitate particles (after the unpinning has occurred). The connecting segments can either be ahead of or trail behind the precipitates, since the dislocation energy will be practically the same for these two configurations. The climb of these segments is probably a result of the nucleation and lateral drift of geometric jogs which nucleate near the particles as these move forwards, dragged or pushed by the climbing curved dislocation sections in contact with them. In silicon the jogs associated with the segments along ⟨2 1 1⟩ will probably be aligned in the other ⟨2 1 1⟩ direction in the colony plane and thus be extended, i.e. split into Shockley partials.

The relative velocities of the particles and the connecting dislocation segments depend on the particle radii and the segment lengths. During the first stage of each growth cycle, when the particles are very small, the connecting segments may generally drop behind. In the case of copper precipitates in silicon, however, the TEM micrographs of Figs. 3 and 4 reveal that during this stage the distance between precipitates along the climbing dislocation is extremely small. Therefore even in the initial stage of the growth cycle the velocity of the connecting segments may be as high as that of the particles. The continued growth and coarsening might then be controlled by the proportional reduction of the particle— and the dislocation mobility. In this way the morphology of the growth front will be more stable than depicted in Fig. 1, the particles and the dislocation will migrate with the same speed throughout the growth cycle. Figs. 3 and 4 reflect this aspect of the growth; the connecting segments nowhere trail far behind the precipitates. On the contrary, in some cases the dislocation seems to climb ahead of the particles.

3.4. Dendritic growth phenomena

The dendritic growth observed in copper–silicon colonies, characterized by the formation of long dislocation dipoles in the ⟨2 1 1⟩ directions, also seems to be a consequence of lattice anisotropy.

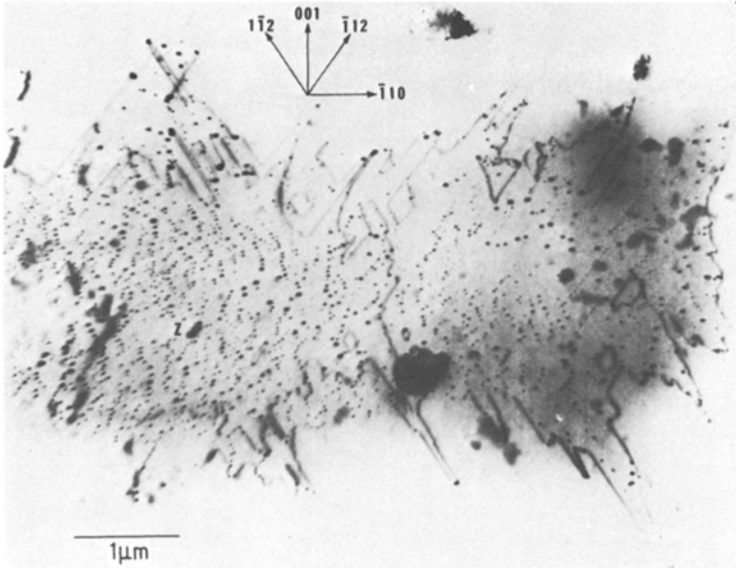

Figure 5 Precipitate colony revealing several effects of the crystal anisotropy.

The phenomenon appears to be associated with the expansion of the colony normal to the main growth direction ⟨1 1 0⟩. From the shapes of the colonies in Figs. 4 and 5, the growth mobility seems to be very low in this direction, presumably due to the high jog formation energy along dislocation segments in the ⟨1 1 0⟩ direction (the glide planes being parallel to {0 0 1}). A protrusive growth associated with dipole formation in the low energy ⟨2 1 1⟩ directions may therefore be an efficient way of expanding the colony normal to ⟨1 1 0⟩. The relaxation into partials causes the dipoles to be very stable configurations.

The precipitate density along the dislocation seems to be another factor controlling the dendritic growth. The local precipitate density in regions of dipole formation is rather low (Fig. 5) and indicates a large particle spacing along the climbing dislocation. For that reason the dislocation segments joining the particles may have been particularly immobile – long jog drift distances – and this may have favoured dendritic growth. This hypothesis is supported by the observation that no dipoles form along dislocations which are densely populated with precipitates, Figs. 3 and 4. The local Cu super-concentration may be the factor determining the nucleation frequency of precipitate particles, and thus the degree of dendritic appearance of the colonies.

A characteristic feature of the dendritic growth phenomenon is that a freshly formed dipole, during continued colony growth, may be annihilated by particles which nucleate and migrate as superjogs along the straight dipole segments. Several examples of this effect are seen in Fig. 5, from which enlarged sections are shown in Fig. 6. Through alternating formation and annihilation of dislocation dipoles the colonies can expand considerably normal to the main growth direction, e.g. as in the upper left part of Fig. 5.

The presence of long precipitate-free zones, Z in Fig. 5, is typical of {1 1 0} copper–silicon colonies. Nes and Washburn [8, 9] report depleted zones in the ⟨1 1 0⟩ directions only. However, the micrograph in Fig. 4 provides evidence for zones also along ⟨2 1 1⟩, marked Z′. The latter zones are probably formed via dipoles in the ⟨2 1 1⟩ directions. The mechanism may be as outlined in Fig. 7. A dipole is created in Fig. 7a. In Fig. 7b precipitates have nucleated along the straight dipole segments, and the growth of these leads to continued dislocation climb, broadening the dipole (Fig. 7c). Simultaneously, the dislocation on each side of the dipole may climb ahead, as indicated by the arrows in Fig. 7c. Finally the dipole segments unpin from the precipitates through the nucleation and growth of new precipitates (Fig. 7d). During the stages in Figs. 7b to d the original precipitate located at the tip of the dipole continues to grow. The precipitates observed at the end of the zones are so large that it is very unlikely they are dragged by the dislocation during the final stage of their growth. The depleted zones in the ⟨1 1 0⟩ directions may have

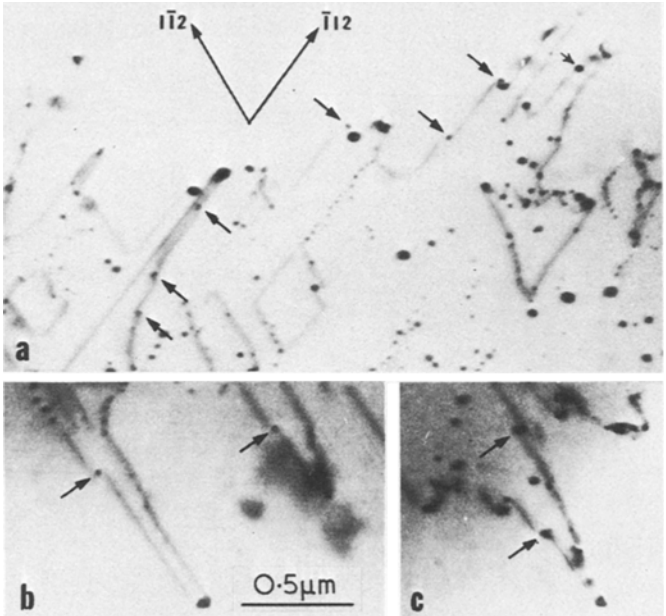

Figure 6 Annihilation of dislocation dipoles by the migration of precipitates (arrowed) along the straight dipole segments. (Enlarged sections of Fig. 5).

been formed by the same mechanism. However, dipoles in ⟨1 1 0⟩ directions have never been observed. One can therefore not exclude a mechanism involving a particularly long "normal" precipitate-dragging for these zones.

The dislocation dipoles often appear to be aligned in slightly different directions, e.g. in Fig. 8 (A, B, C and D). This is probably due to dislocation glide out of the {1 1 0} colony plane. The (1 1 0) colony in Fig. 9a was tilted so that it could be imaged edge on, Fig. 9b. The slip planes in silicon are {1 1 1} [10]. In Fig. 9 the crystallographic (1 1 1) planes contain the Burgers vector of the dislocation and intersect the colony plane along [$\bar{1}\,\bar{1}\,2$]. A dislocation segment in this direction can therefore glide and, as is revealed in Fig. 9b, a glide component is associated with the dipoles 1 and 4 and with the lower segment of 3, while dipole 2 has practically grown in the colony plane. The glide component of dipole 4 is larger than that of number 1. Furthermore, it appears that one of the dipole segments may glide more than the other so as to twist the plane containing the dipole. The colony in Fig. 9c is also imaged edge on, and the glide component of dipole 6 is seen to be smaller than that of 5 and 7.

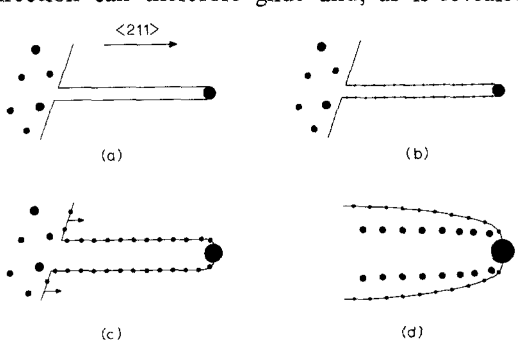

Figure 7 A possible mechanism for the formation of depleted zones.

These observations show that dipole branches are not always aligned in the ⟨2 1 1⟩ directions, but may grow in non-crystallographic directions in the {1 1 1} slip planes intersecting the colony plane along ⟨2 1 1⟩. The glide component of the dislocation motion is possibly due to anisotropic strain fields arising from the precipitation.

The work by Nes and Washburn [8, 9] demonstrates that precipitate colonies can also grow on {1 0 0} planes in silicon. These colonies had a low particle density (large precipitates) and invariably a dendritic appearence. Hence, the dipole formation seems to be associated with a low nucleation rate in this case too. The dipoles were aligned in the low-energy ⟨1 1 0⟩ directions. This fact accounts for the high stability of the dipoles and, consequently for the straight-line appearance of the colonies.

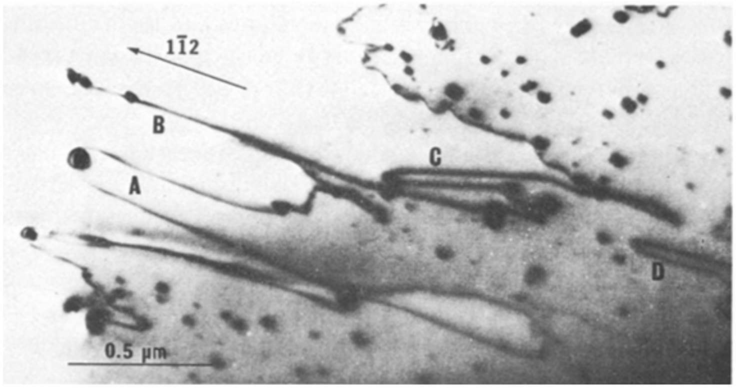

Figure 8 Non-parallel dislocation dipoles growing in the same set of glide planes.

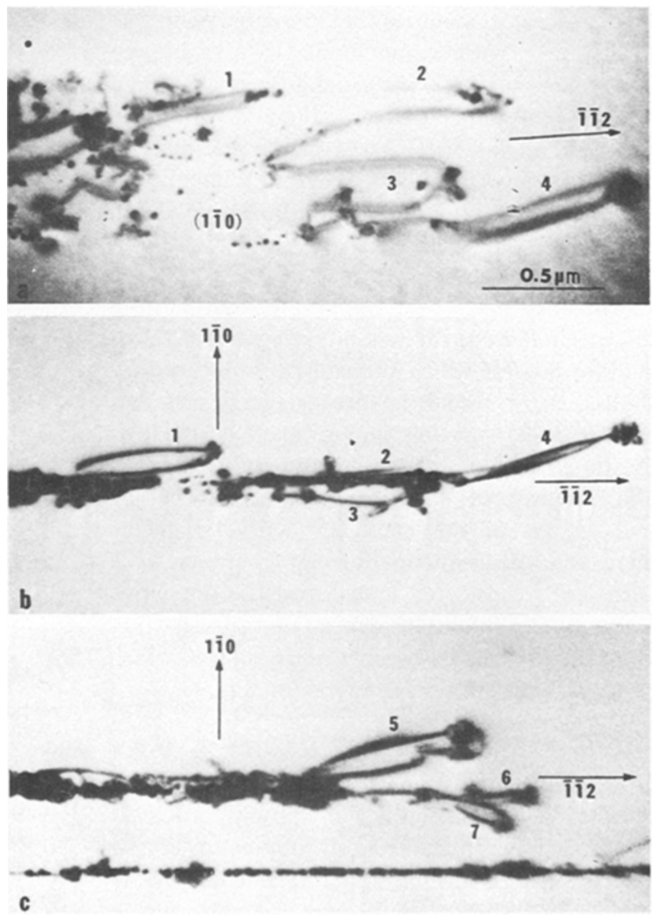

Figure 9 Dislocation dipole branches in (1 $\bar{1}$ 0) colony arms in a (1 1 2) surface foil, ion etched. The incident beam is along {1 0 1} in (a) and along {1 1 1} in (b) and (c) where the colonies are seen edge on. (a) and (b) are from the same colony. The double image of the dislocation in (a) is due to the simultaneous operation of two reflections [11]. (The colonies were annealed for 1 h at 650°C, and this is responsible for the dislocation tangles around some of the precipitates [2, 4]).

3.5. Planar precipitate colonies in other alloys

Repeated precipitation on climbing dislocations is reported in a series of materials, including various steels, copper and aluminium. The same growth model may apply to all these alloys, but differences associated with dislocation energies may result in varying growth models, High jog energy values seem, for instance, to be decisive for the formation of stable dislocation dipoles which is typical for copper precipitate colonies in silicon. Bcc iron provides another example of this dendritic growth phenomenon. Micrographs published by Heikkinen and Hakkarainen [12] reveal that dipole growth can occur during the precipitation of vanadium carbide in an α-Fe–2.8

wt % V alloy containing a small amount of carbon. α-iron is b c c and the precipitate colonies form on ⟨1 0 0⟩ planes with climbing a ⟨1 0 0⟩ Burgers vector dislocations as vacancy sources. The dipoles, about 350 Å long, lie approximately in the ⟨1 0 0⟩ and ⟨1 1 0⟩ directions, so their glide planes are of {1 0 0} and {1 1 0} types. The corresponding jog energies are respectively 0.7 and 1.0 eV, and these relatively large values may explain the generation of dipoles.

F c c metals like austenitic iron, copper and aluminium, on the other hand, provide jog energies of magnitudes 0.2 to 0.3 eV, and colonies in these metals do not seem to be associated with the formation of dislocation dipoles. Works by van Aswegen *et al.* [13], Silcock and Tunstall [1] and Silcock [14] on NbC-precipitation in γ-iron, by Raty and Miekk-Oja [15, 16] on the precipitation of Ag in copper, and by Guyot and Wintenberger [17] on the precipitation of Cu in aluminium all reveal a very fine dispersion of particles without any indication of dipole formation.

The unpinning of the climbing dislocation from the precipitates at the end of each growth cycle is another process which probably is influenced by the jog energy value. In low jog-energy materials (f c c metals) the unpinning may proceed as illustrated in Fig. 1d, i.e. as proposed by Silcock and Tunstall [1]. In silicon, however, the jog energies are in the range 2.5 to 3 eV, and an increasing dislocation bow-out between the particles is considered unrealistic. The unpinning is therefore supposed to depend on the nucleation of small particles between the large ones, which take over the climb/dragging process, Fig. 1e.

4. Conclusions

Some comments have been made on the model for repeated nucleation on a climbing dislocation. It has been shown that the anisotropy of the crystal lattice may influence the structure taken up by the climbing dislocation. It is assumed that, in highly anisotropic materials, the anisotropic behaviour of the dislocation has a strong influence during the whole colony growth, and that it tends to force the growing precipitates and the connecting dislocation segments to advance at the same speed throughout each growth cycle. It has also been discussed how a periodic varying precipitate density along the climbing dislocation may make it easier for the connecting dislocation segments to take up low-energy directions throughout each cycle.

The formation of stable dislocation dipoles is suggested to be a result of particle migration, a low nucleation frequency, as well as high jog energies. Furthermore, the creation of long depleted zones in the case of copper precipitation in silicon is proposed to be associated with the dendritic growth phenomenon.

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