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On the growth process of precipitate colonies

The appearance of precipitate colonies has been reported for a variety of alloy systems e.g. iron [1–6], copper [7, 8] and semiconductor materials [7–14]. Interpretations of the experimental observations have been proposed in terms of a repeated precipitation caused by the autocatalytic nucleation on the dislocations generated during precipitation [1] and in terms of the repeated precipitation on a climbing (partial or perfect) dislocation [2, 6–8].

It is the purpose of this note to derive a model for colony growth on the basis of observations by means of transmission electron microscopy on the growth of precipitate colonies of silver from supersaturated copper–silver solid solutions.

Single crystals (Cu–5 wt% Ag) were homogenized for 90 h at 700° C and subsequently quenched in water. Growth of precipitate colonies was induced by annealing the crystals at 500° C for various times between 3 and 60 min. Specimens suitable for transmission electron microscopy were prepared by slicing the crystals with a spark cutter and electropolishing (jet method) in a solution of 67% methanol and 33% nitric acid at −23° C and 20 V. The residual contamination at the surface of the electropolished specimens was removed by a subsequent bombardment with 6 kV argon ions (10 min, 30–40 μA). The transmission electron microscopy studies were carried out using a 200 kV electron microscope (Jeol 200A).

From the investigation of about 65 colonies the following facts emerged as the "typical features" of the colonies. The precipitate colonies observed had the shape of circular discs with rod-shaped silver precipitates arranged radially in a spoke-like fashion (Figs 1 and 2). The diameter of the rods was about 46 nm. The lengths varied between 25 and 300 nm. The spacing, s, (Figs 1 and 3) between neighbouring silver precipitates was approximately constant. If two neighbouring precipitates were divergently oriented, a new silver precipitate was observed to be formed in between if the spacing between the two precipitates became larger than about $2s$ (Figs 1 and 3). Each colony was surrounded by a chain of small precipitates (8 to 20 nm diameter) arranged along a dislocation loop. Occasionally the loop was observed to be removed from the chain of small precipitates (Fig. 1). From contrast experiments (Fig. 4) (**g.b**–

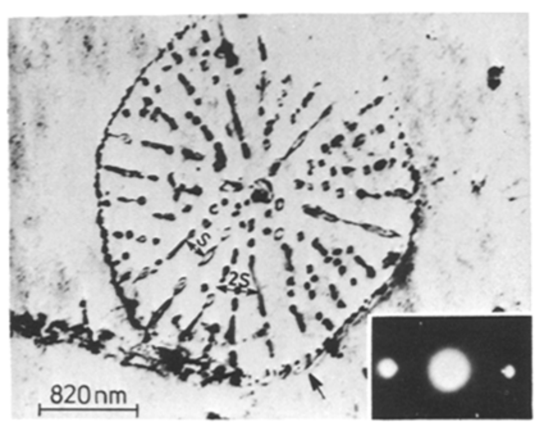

Figure 1 Bright-field electron micrograph of a precipitate colony in a Cu–5 wt% Ag alloy. In the region marked by an arrow the dislocation loop is separated from the chain of small precipitates surrounding the colony. The inserted diffraction pattern shows the parallel crystallographic orientation of the silver precipitates (weak diffraction spots) and the surrounding copper matrix (strong diffraction spots).

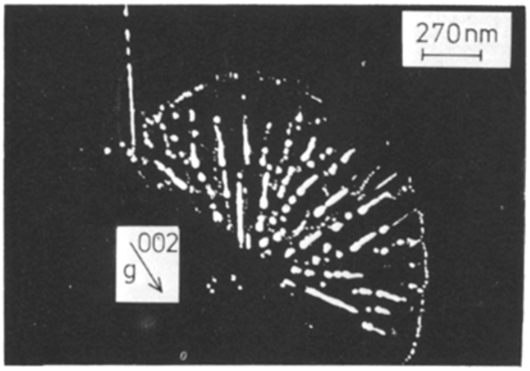

Figure 2 Dark-field micrograph of a precipitate colony in a Cu–5 wt% Ag alloy ($\bar{g} = 002$).

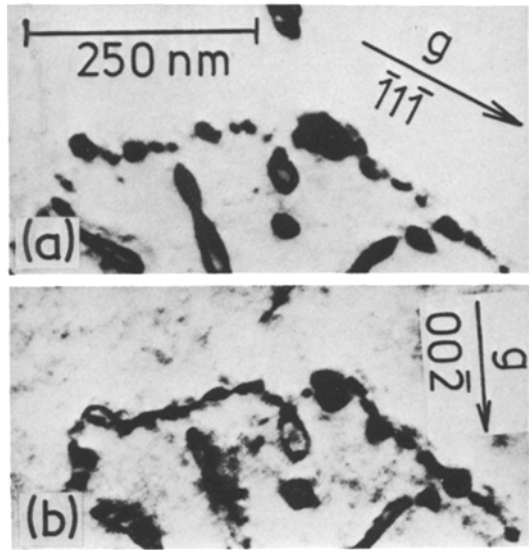

Figure 4 Contrast behaviour of the dislocation loop surrounding the precipitate colony (a) $\bar{g} = \bar{1}1\bar{1}$, (b) $\bar{g} = 00\bar{2}$. In (a) the dislocation is out of contrast.

criterion) the Burgers vector of the dislocation loop was found to be normal to the plane of the colony and was of the type $\frac{1}{2}\langle 110 \rangle$. The small silver particles along the dislocation loop, as well as the rod-shaped precipitates, had the same crystallographic orientation as the surrounding copper matrix (Fig. 1). No interfacial dislocations were detected between the silver precipitates and the copper matrix in weak beam images. The thickness of the colonies (normal to the plane of the disc) was measured by tilting experiments to be about 35 nm.

The observations reported suggest that the dislocation loop surrounding a colony expands radially during growth, generating the observed spoke-like arrangement of the silver precipitates.* According to the results of the contrast experiments (Fig. 4) and in agreement with the observations of Räty and Miekk-Oja [7, 8], the Burgers vector of the dislocation loop is normal to the plane of the colony and is of the type $\frac{1}{2}\langle 110 \rangle$. In other words, the colony is surrounded by a prismatic perfect dislocation loop. The reason for this type of loop seems to be the change of the lattice constants during precipitation. The lattice of the supersaturated copper–silver solution (outside the loop) is about 0.3% larger than the lattice of the copper-rich, copper–silver solid solution in the precipitate colony (i.e. inside the loop). In order to reduce the elastic stresses between the two coherent lattice regions of different interatomic spacings, misfit dislocations of the type

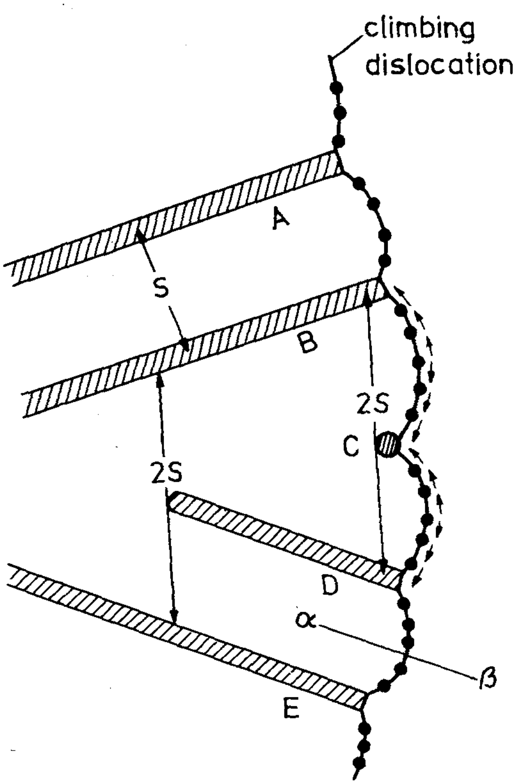

Figure 3 Schematic view of the observed arrangement of the precipitates in a colony (cf. Fig. 1).

*The nucleation process of a precipitate colony is not considered in this paper.

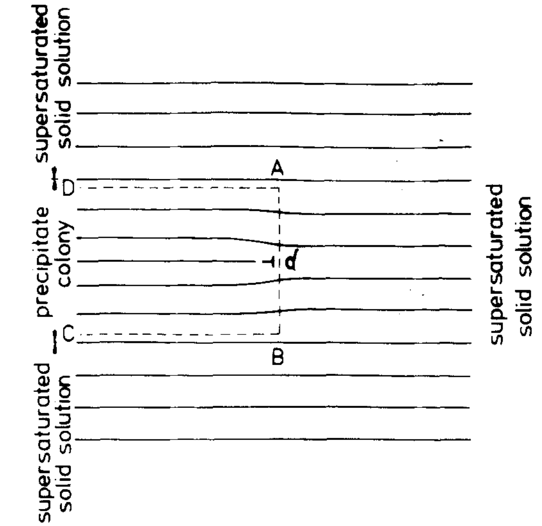

Figure 5 Schematic side-view of one set of lattice planes in the cross-section α/β in Fig. 3. The lattice planes are parallel to the plane of Fig. 3. The area ABCD represents the cross-section through the (copper-rich phase of the) precipitate colony left surrounded by the supersaturated Cu–Ag solid solution above, below and to the right of the colony. The strain due to the smaller lattice constant of the copper-rich phase of the colony requires a misfit dislocation, d, of the type shown at the interface between the two phases. If this dislocation climbs to the right during colony growth, vacancies are emitted into the lattice surrounding d. For simplicity only five lattice planes of the colony are shown. The actual thickness is about 300 lattice planes.

shown in Fig. 5 are known [15] to be incorporated in the interface between the two regions. The observed loop around the precipitate colonies may be a dislocation of this type and is therefore interpreted in terms of a stress reducing misfit dislocation. This interpretation is consistent with the observed colony thickness and the change of the lattice constant of 0.3% between the two copper-rich phases. A strain of 0.3% requires a misfit dislocation spacing of about 30 nm. Hence, a single dislocation loop approximately relaxes the strain generated by a precipitate colony that is about 30 nm thick which is approximately the observed thickness of the precipitate colonies being surrounded by a single dislocation loop. In order to understand the growth process and the morphology of the precipitate colonies, the answer to the following questions seem to be important.

(1) What is the reason for the spoke-like arrangement of the precipitates with an approximately constant interparticle space, s?

(2) What role does the surrounding dislocation loop and the fine precipitates decorating the loop play in the growth process of the colonies?

The observed spoke-like arrangement of the silver precipitates with a nearly constant spacing s (Fig. 1) may be understood by considering the energy driving the growth process and the kinetic factors involved. The process of colony growth is driven by the difference in free energy of the supersaturated solid solution and the precipitate colonies. The free energy of the precipitate colonies depends on the energy stored in interfaces between the silver precipitates and the copper matrix. As the interfacial energy decreases with increasing precipitate size and spacing (s) of the precipitates, the net driving force for the reaction increases as the precipitate size and spacing grows. However, the formation of large, widely spaced precipitates is kinetically unfavourable as it requires a slowly growing colony in order to provide the time for the long-range diffusion processes required. On the other hand, finely spaced precipitates would be kinetically more favourable as they require less diffusion time but the higher interfacial energy involved slows the reaction down as it decreases the net driving force. Basically similar factors are believed to control the spacing of the lamellae in a discontinuous precipitation reaction [16]. It is known that under steady-state conditions a discontinuous system approaches a constant characteristic lamellae spacing, the magnitude of which depends on the thermodynamic variables of the system (undercooling, interfacial energies, diffusion coefficients etc.). By analogy to the experimentally observed constant spacing of the lamellae of a discontinuous reaction, it is proposed that the growth of the precipitate colonies results under steady-state conditions in a constant characteristic spacing (s) of the silver precipitates which is controlled by the interfacial energy of the precipitates and the driving energy of the reaction. This idea is consistent with the observed nucleation of new precipitates between two divergent precipitates (Figs 1 and 3). If no new precipitates are formed during colony growth, the spacing between two divergent precipitates (e.g. B and D in Fig. 3) would increase continuously as colony growth proceeds. Due to the increasing diffusion path, the growth rate would be slowed down and finally colony growth would cease. However, the nucleation of a new precipitate between B and D permits further colony growth. In order to keep the growth rate constant, nucleation has to occur if the distance between B and D is $2s$. If nucleation occurred earlier (spacing BD $< 2s$) or later (spacing BD $> 2s$) the additional interfacial energy required (or the longer diffusion path) would become rate limiting [15]. This result is supported by the experimental observations (Figs 1 and 2).

The role played by the dislocation loop may be understood by considering the climb process of this loop (Fig. 5). The growth of the precipitate colony requires the expansion of the dislocation loop surrounding the colony. This expansion occurs by dislocation climb e.g. the dislocation (d) in Fig. 5 climbs from left to right. This climb involves the emission of vacancies from the climbing dislocation (d) into the surrounding lattice. Therefore the diffusivity in the vicinity of the growing edge of the precipitate colony is enhanced. In fact, at an undercooling of about 100° C, the vacancy supersaturation (and hence the diffusion enhancement) is estimated to be 10^3 to 10^5 [15]. This diffusion enhancement seems to be crucial for the growth process, as dislocation loops which expand by glide are not observed to generate precipitate colonies. The significance of the proposed diffusion enhancement is also consistent with the fact [7] that the precipitation of copper from a supersaturated silver-rich silver–copper solid solution does not result in precipitate colonies. In the silver–copper system the lattice of the solid solution expands during precipitation of copper. Therefore the misfit dislocation between the two phases is of opposite sign from the one in the copper–silver system (Fig. 5). The climb of such a misfit dislocation loop would require absorption of vacancies and thus would reduce the diffusivity at the growing edge of the colony. The observation of numerous small silver particles of different sizes 8 to 20 nm) along the dislocation loop surrounding the precipitate colony suggests that the growth of the precipitates in the colony involves the following two processes (Fig. 3). The precipitation of silver atoms at the dislocation loop surrounding the colony, in the form of small particles, and the accumulation of the silver atoms, in the form of the spoke-like arranged precipitates. These two processes may be understood in terms of the high diffusivity in the region surrounding the climbing dislocation loop. The silver atoms of the supersaturated solid solution in the region of high diffusivity in the vicinity of the growing edge of the colony can precipitate at two sites: at the climbing dislocation loop and at the spoke-like precipitates terminating at the loop. Those silver atoms which precipitate at the climbing loop, form a chain of small silver particles. However, due to the large interfacial energy, this arrangement of particles is thermodynamically unstable. The silver atoms of the particles may diffuse rapidly (by pipe diffusion along the dislocation core and the enhanced diffusion coefficient in the vicinity of the climbing dislocation loop) to the coarse precipitates of the colony (e.g. A, B, C. etc. in Fig. 3). This process results in the Ostwald ripening of the small precipitates and in the growth of the large precipitates A, B, C, etc. If no new silver atoms arrive at the climbing dislocation loop, finally, all small particle silver atoms would accumulate at the precipitates A, B, C, etc. In the steady-state growth of the colony there is, however, a constant flux of new silver atoms from the supersaturated matrix to the dislocation loop so that nucleation of new silver particles, coarsening of older particles and the growth of the coarse precipitates occurs simultaneously. These processes result in a climbing dislocation loop (decorated at all times by silver particles of various sizes) leaving behind rod-like precipitates (A, B, C, etc.) arranged in the radial direction with an approximately constant spacing (s). Clearly, this model represents an idealized case in the sense that the forces acting on the climbing dislocation loop are assumed to be constant. Due to internal stress fluctuations in the material, this is not the case. If a high local stress acts on the climbing dislocation, it may locally break away from the small precipitates. A situation of this type may be seen in Fig. 1 where the dislocation has locally separated from the precipitates. Hence, in addition to the rod-like precipitates small silver particles may exist in the colonies as was observed. Clearly, the colony growth processes described above are not limited to an expanding prismatic dislocation. In principle, any climbing edge dislocation should permit colony growth. This conclusion seems to be consistent with the results reported in the literature [7, 8] and with the experimental observations. In addition to the radially growing colonies, elongated precipitate colonies were observed showing the features expected for a colony growing behind a climbing straight edge dislocation.

In the above model, colony growth occurs essentially by a vacancy enhanced lattice diffusion process. Hence the apparent activation energy for colony growth should be comparable to the value obtained for lattice diffusion. Alternatively to the colony growth, the decomposition of the supersaturated solid solution may also occur by a discontinuous precipitation reaction, the activation energy of lattice diffusion. Hence, at high temperatures decomposition by colony growth and at low temperatures decomposition by discontinuous precipitation, may be expected, as was observed. The temperatures decomposition by discontinuous precipitation, may be expected as was observed. The interpretations proposed for the experimental observations coincide in various aspects with the models put forward in the literature for the growth of precipitate colonies. The significance of the vacancy generation by the climbing dislocation surrounding the precipitate colony has already been emphasized by Räty and Miekk-Oja [7, 8]. However in the model used by these authors the vacancies are assumed to be required primarily to relax the lattice misfit between the silver precipitates and the surrounding copper matrix. Similarly, in the model of Nes [2], repeated precipitation is analysed in terms of balancing the rate at which vacancies (generated by a climbing dislocation) are being absorbed by the growing particles to the dislocation climb rate. Diffusion enhancement by the lattice misfit between the phases involved was considered in Hornbogen's model [1] as a critical factor. Hornbogen concluded that precipitate colonies can only form if the lattice constant of the supersaturated solid solution is reduced during precipitation, as was observed.

The growth of precipitate colonies from a super-saturated copper–silver solid solution occurs by climb of a prismatic dislocation which emits vacancies and thus generates a region of enhanced diffusivity at the growing edge of the colony. Precipitation of the silver atoms occurs preferentially at the climbing dislocation and the subsequent Ostwald ripening results in rod-shaped particles arranged in a spoke-like fashion in the interior of the colony with a constant spacing controlled by interfacial energy and lattice diffusion of the silver atoms.

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