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ELECTRON MICROSCOPE STUDIES OF THE MECHANISM OF NUCLEATION AND GROWTH OF Cu Au II FROM THE DISORDERED STATE

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Résumé. — Des monocristaux minces de Cu Au préparés par évaporation ont été étudiés à chaud au microscope électronique. Par recuit à 450 °C l'alliage est désordonné. La germination et la croissance des régions ordonnées est étudiée dans le domaine 380-400 °C. Par microscopie à fond noir sur les raies de surstructure, on étudie en détail la distribution des germes ordonnés et leur répartition en orientation. Celle-ci est expliquée par la présence de mâcles dans le plan (101) de l'alliage. Il semble que la croissance de la phase ordonnée soit modifiée près des dislocations. Dans certains cas la germination a lieu de préférence sur les dislocations. Ces observations sont comparées aux études de germination de la phase ordonnée dans des alliages massifs amincis après le traitement thermique.

Abstract. — Thin single crystal films of Cu Au prepared by evaporation have been studied on a hot stage inside the electron microscope. The alloy is disordered by annealing at 450 °C, and the nucleation and growth of ordered regions is studied as the temperature is lowered to some value in the range 380-400 °C. By use of dark field microscopy on superlattice reflections, the distribution of ordered nuclei within a disordered matrix is studied in detail, as well as the orientation distribution within the ordered nuclei. This latter distribution is explained in terms of (101) twinning of the Cu Au. Evidence is obtained that dislocations modify the growth of the ordered phase in their vicinity, and that in some circumstances preferential nucleation of order occurs on the dislocations. These observations are being compared with studies of the nucleation of order produced in bulk alloy which is thinned after the heat treatment.

1. Introduction. — The alloy Cu Au exhibits two ordered superlattices known as Cu Au I and Cu Au II. Cu Au I exists below 380 °C, and consists of a tetragonal structure ($c/a \sim 0.92$) which is a distortion of the face-centred cubic structure of the disordered phase. The (002) planes of Cu Au I contain alternately all gold and all copper atoms. Cu Au II exists between 380 °C and 415 °C, and is orthorhombic in structure. The crystallographic unit cell of Cu Au II contains ten of the Cu Au I tetragonal cells aligned along the

a-axis, as shown in figure 1, with an antiphase boundary (APB) half way along the cell.

The structure of Cu Au II was first examined with the electron microscope by Ogawa and al. [1], and subsequently by Pashley and co-workers [2], [3], [4]. In these experiments, evaporated thin films were first annealed at a temperature below 380 °C to form Cu Au I, which was then transformed to Cu Au II by further annealing at about 390 °C. The detailed periodic APB structure of Cu Au II was revealed on the electron micrographs,

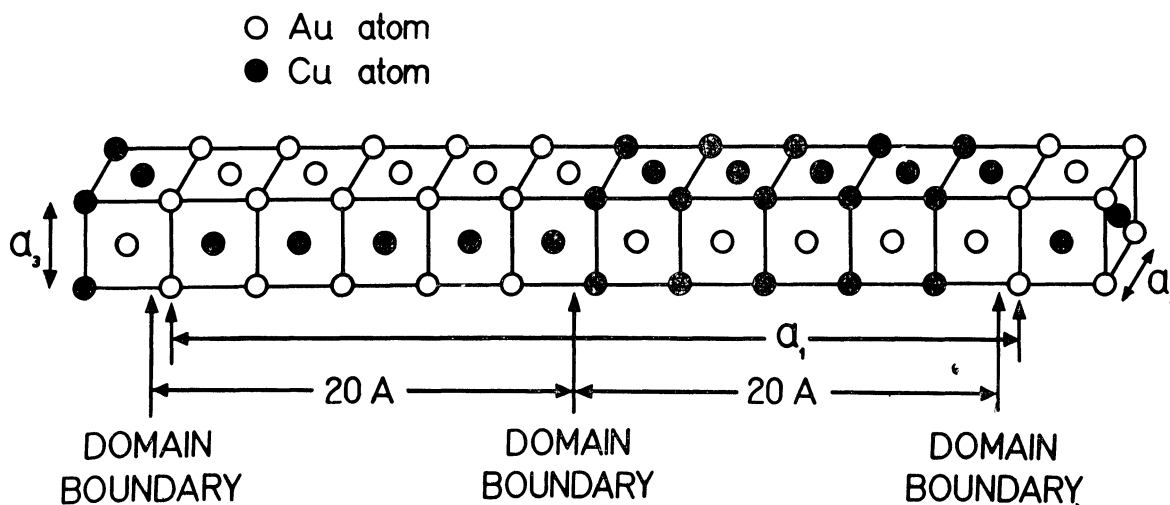


FIG. 1. — The unit cell of Cu Au II.

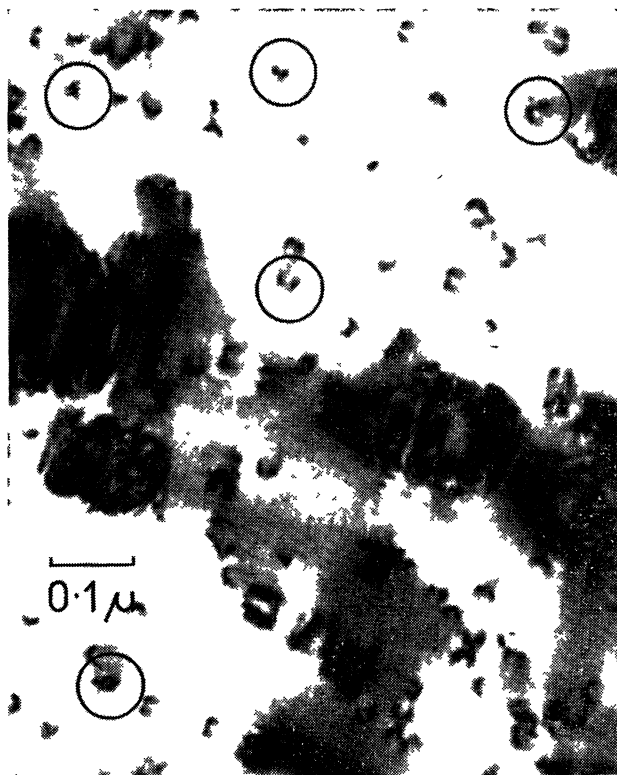
confirming the original determination of the structure by Johansson and Linde [5], who used X-ray powder diffraction techniques. The detailed mode of transformation from Cu Au *I* to Cu Au *II* has been studied by annealing Cu Au *I* at about 390 °C inside the electron microscope [3], [4]. These observations show that the transformation occurs by the nucleation of periodic arrays of antiphase domains in the form of platelets on the (100) and (010) planes of Cu Au *I*. From the earliest observable stage these platelets are 20 Å thick and 20 Å apart. The final Cu Au *II* structure is produced by the intergrowth of these nucleated platelets, and this was observed as it took place inside the electron microscope. The work described here concerns an extension of this study to the case where the Cu Au *II* is produced directly from the disordered phase, as the temperature is lowered through the critical temperature of 415 °C.

A study of the disorder \rightarrow Cu Au *II* transition which occurs in this way has already been made by Smith and Bowles [6] who employed X-ray diffraction and optical metallographic techniques on the bulk alloy. They showed that the order is initiated by the formation of ordered nuclei within the disordered matrix, and that further ordering proceeds by growth of these ordered nuclei at the

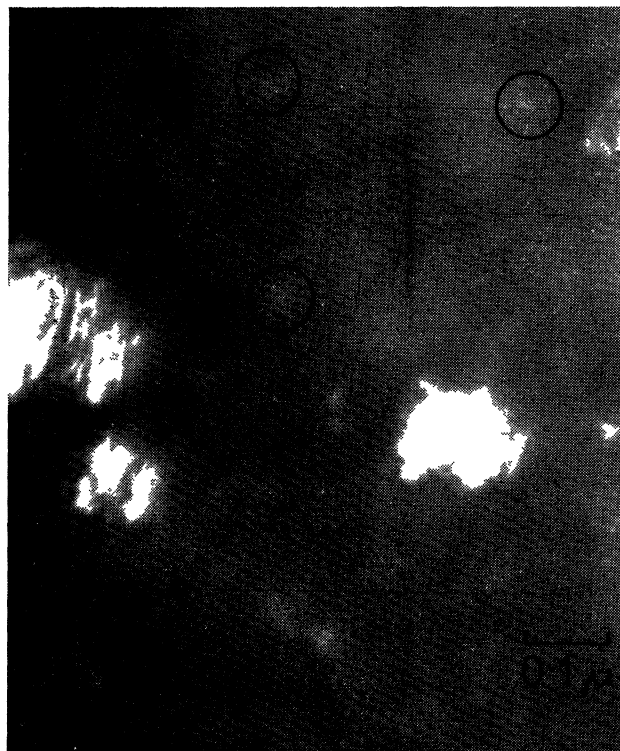
expense of the disordered matrix. The rate of nucleation and the rate of growth of the nuclei is very temperature-dependent. At 400 °C the transformation is completed only after about 25 hours, whereas at 380 °C the transformation is complete within 20 minutes. Smith and Bowles describe the crystallography of the transformation, and show that it is equivalent to a martensitic transformation.

We are studying the same transformation with thin films heat treated inside the electron microscope, in order to obtain more detailed information on the nucleation and growth of the Cu Au *II*. These results are being correlated with observations made on specimens prepared by the electrothinning of previously heat treated 0.001" foils of the alloy.

2. **Experimental technique.** — The single crystal evaporated films of Cu Au, about 400 Å in thickness were prepared in (001) orientation by the technique described previously [2]. They were placed in the electron microscope on the hot stage used for the previous work [3], and disordered by raising the temperature to about 450 °C. The temperature was then lowered slowly to about 400 °C, and finally to various temperatures in the range 380-



a



b

FIG. 2. — Ordered nuclei produced by annealing in the high temperature region of the 380-400 °C range: (a) bright field; (b) dark field on (110) of same area as (a). Magnification $\times 180,000$ (printed $\times 0.6$).

400 °C. Because the accuracy of temperature calibration of the furnace was insufficient, the effect of the temperature on the transformation has been studied in only a qualitative manner so far. All micrographs were recorded whilst the specimen was hot, during the course of the transformation.

In addition to normal bright field micrographs, selected area electron diffraction patterns and dark field micrographs were recorded. In particular, dark field micrographs formed by superlattice reflections were included. These have two important properties. Firstly they readily distinguish ordered regions from disordered regions, since only ordered regions appear bright; secondly they distinguish the three basic orientations of the ordered phase. The [001] axis of Cu Au II can form parallel to any of the three original cube axes of the disordered phase. (110) superlattice reflections (all indices are given in terms of the equivalent Cu Au I tetragonal unit cell) arise from the orientation with the [001] axis normal to the film plane (*N*-orientation), and the two (001) superlattice reflections which occur arise from the two orientations with the [001] axis in the film plane (the *P*-orientations). Correlation between the various dark field micrographs therefore reveals the distribution of the ordered material throughout the specimen, and also reveals the distribution of the [001] axis within the ordered regions:

The 0.001" foils of Cu Au were annealed at 450 °C, then lowered in temperature and held at 380-400 °C for various times, before being rapidly quenched in water. Thus the order-disorder distribution in the specimen was maintained, and could be examined in detail after subsequent thinning of the specimen in a chromic oxide-acetic acid bath.

3. Observations on ordering produced inside the electron microscope. — The disordered single crystal films, when examined at 450 °C, showed a high density (approximately $2 \cdot 10^{10}/\text{cm}^2$) of dislocations in very good contrast. These dislocations pass from one side of the film to the other and appear on the image as short lines which are largely parallel to [100] and [010] directions in the film plane. These are the directions along which images of all the screw dislocations would appear. It is therefore tentatively concluded that the majority of the dislocations are screws with all possible $\langle \frac{1}{2} \frac{1}{2} 0 \rangle$ Burgers vectors other than those which lie parallel to the film plane. Two qualitatively different modes of ordering have been studied. When ordering was carried out at high temperatures in the range 380-400 °C, a very slow rate of nucleation and growth of the ordered phase took place. At low temperatures within the same

approximate range, the rate of nucleation was much faster, and large ordered regions surrounded by a disordered matrix were not obtained. These two different modes are now considered separately.

(a) HIGH TEMPERATURE ORDERING. — Periods of up to about two hours were involved before nuclei were observed. The most sensitive technique for detecting the ordered nuclei was dark field observation with a (110) superlattice reflection, since the initial ordered nuclei appeared to be entirely in the *N*-orientation. They could be detected initially as regions no more than about 100A across. As they grew to several hundred A and more, they assumed a roughly rectangular shape on the image, bounded by $\langle 100 \rangle$ directions. Figure 2*a* shows a bright field image of the nuclei, and figure 2*b* the corresponding (110) dark field image. Dislocations are shown in good contrast on figure 2*a*, but this contrast is largely absent once ordering has taken place. The corresponding ringed areas on the two micrographs reveal that some of the very small ordered nuclei coincide with dislocation sites in the alloy. Careful correlation between images of this type leave no doubt that the dislocations act as preferential sites for the ordering which takes place under these conditions.

Figure 3 shows one of the nuclei at higher magnification; the periodic APB structure of the Cu Au II is clearly resolved. Figure 4 shows a similar image for part of a larger ordered region. The very elongated shape with fairly straight diffuse sides is consistent with a (101) habit plane for the ordered phase. This is the equivalent of a (101) plate of Cu Au II in a bulk specimen, the habit plane in this case being at 45° to the film plane. The two directions of the periodic APB's, corresponding to the unidirectional zones described by Glossop and Pashley [2], are visible on figure 4. The diffuse bands crossing the ordered regions along [100] are due to very thin regions of Cu Au II in the *P*-orientations. These are consistent with twinning of the Cu Au II on (101) planes, as already observed on a much coarser scale by Smith and Bowles [6]. The distribution of the *N* and *P*-orientations is revealed in figure 5*a, b, c*, which shows bright field and (110) and (001) dark field micrographs from the same area. The shape of the region in the *P*-orientations is consistent with their being twins of the *N*-orientation on (101) planes which are at 45° to the film plane. The width of the images of the majority of these twins is very narrow, suggesting that they do not extend completely through the film thickness.

(b) LOW TEMPERATURE ORDERING. — Preliminary observations reveal the following behaviour. The first observable sign on the bright field image that any change is taking place in the specimen is

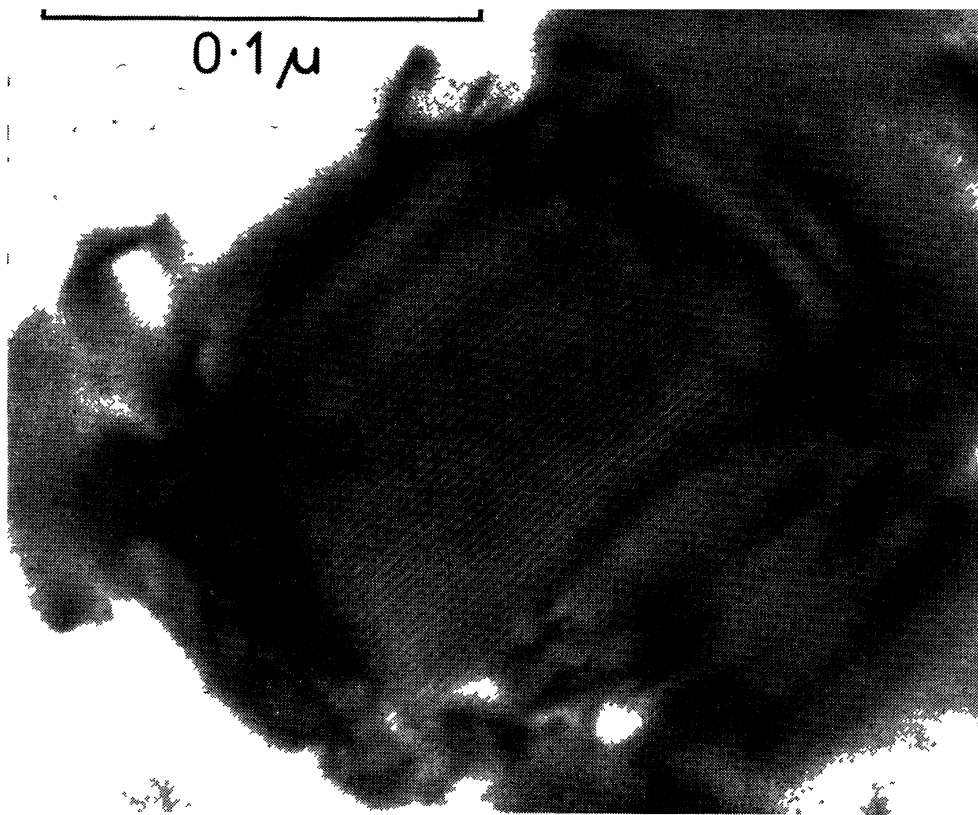


FIG. 3. — An ordered nucleus as for figure 2. Bright field. Magnification $\times 720,000$ (printed $\times 0.8$).

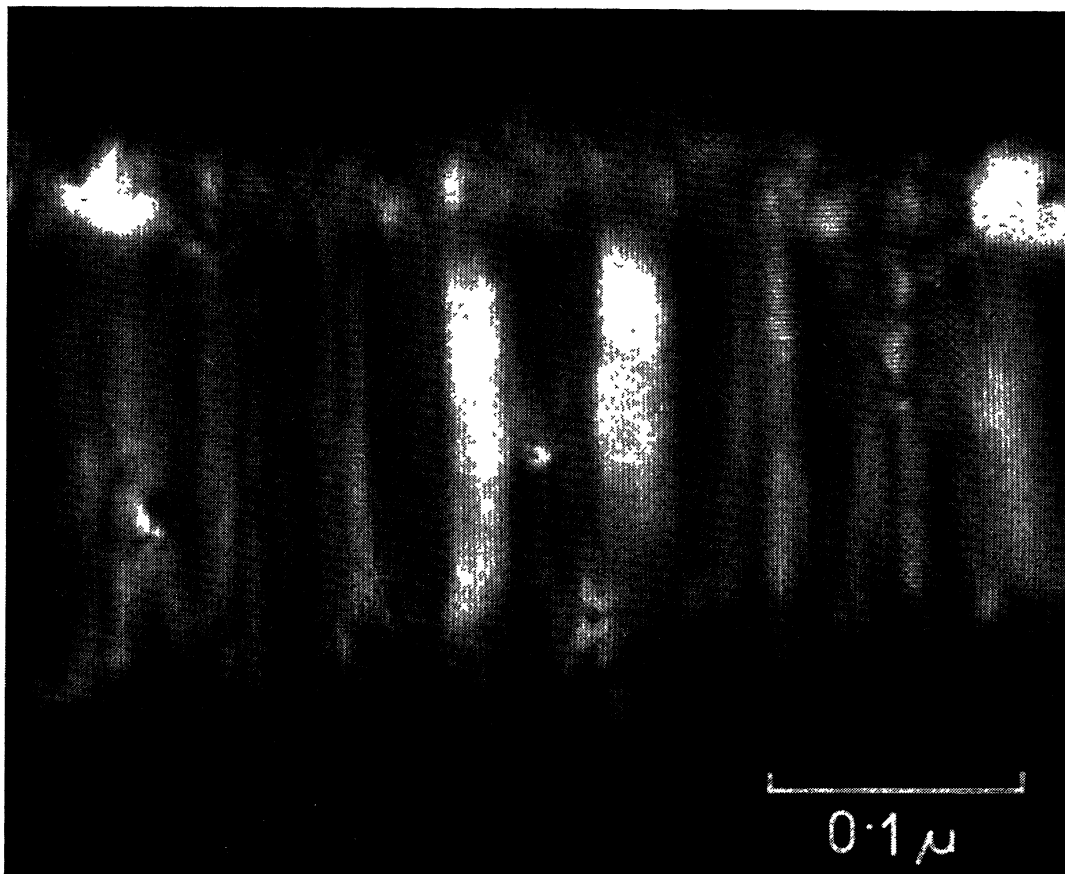
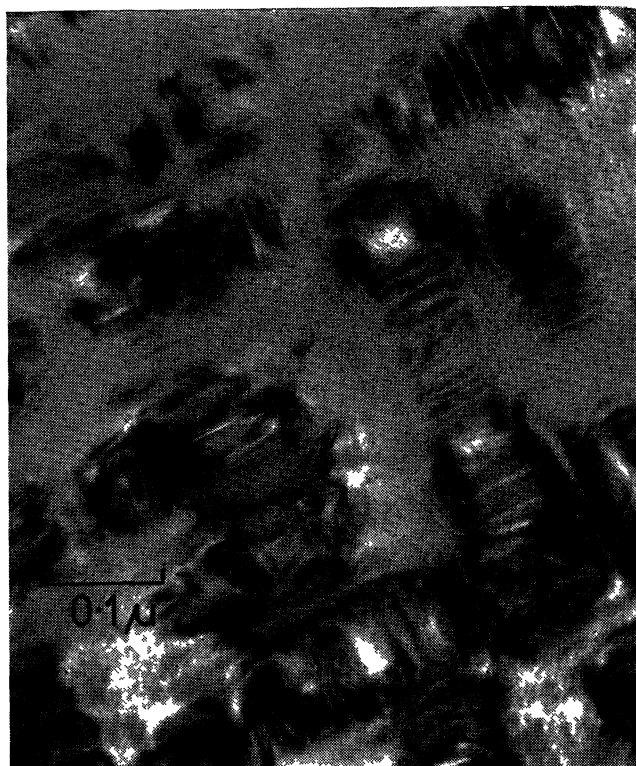


FIG. 4. — A later stage of the growth of an ordered nucleus similar to that of figure 3. Dark field on (110) with tilted illumination. Magnification $\times 420,000$ (printed $\times 0.8$).

*a*

the occurrence of streaming, as illustrated in figure 6*a*. This consists of a cross-textured appearance, with the $\langle 100 \rangle$ directions in the film plane being brought in to prominence. The image shimmers continuously, giving the impression of some kind of flow along the $\langle 100 \rangle$ directions. The influence of dislocations on this behaviour is most striking, and was first noticed by Pashley and Presland in 1959 (unpublished). The streaming effect is enhanced in the vicinity of the dislocation, so that pronounced streaming seems to occur preferentially away from one side of the dislocation. This leads to various contrast modifications around the dislocation such as shown, for example, in figure 7. In effect, the contrast due to the dislocation becomes elongated along a $\langle 100 \rangle$ direction, and this elongation continues until the dislocation is no longer detectable as such. It is not yet clear to what extent the effect is due purely to the influence of the strain field of the dislocation on the contrast of the streaming resulting from ordering, and to what extent the dislocation actually modifies the local ordering conditions. In view of the preferred ordering at dislocations revealed in figure 2, it seems probable that the latter possibility is at least in part responsible for the effect. More detailed studies of the contrast changes are in progress. It is possible that the

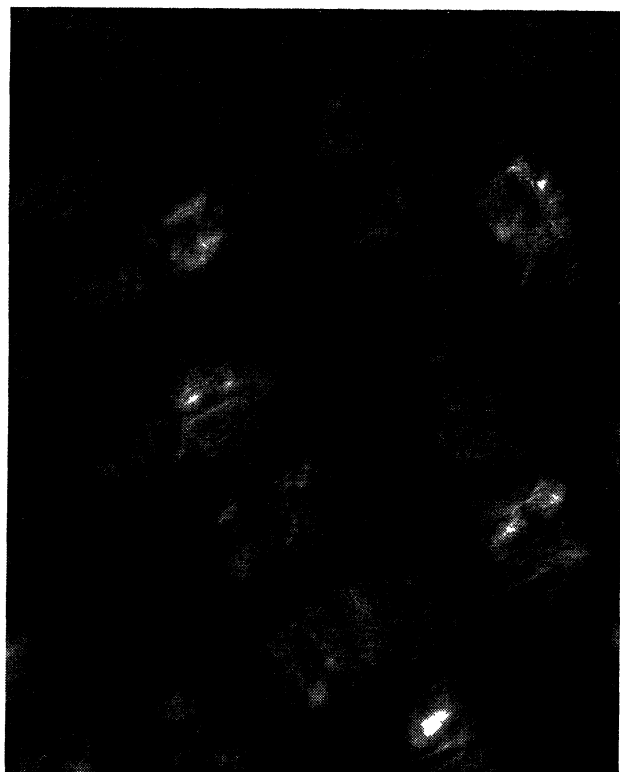
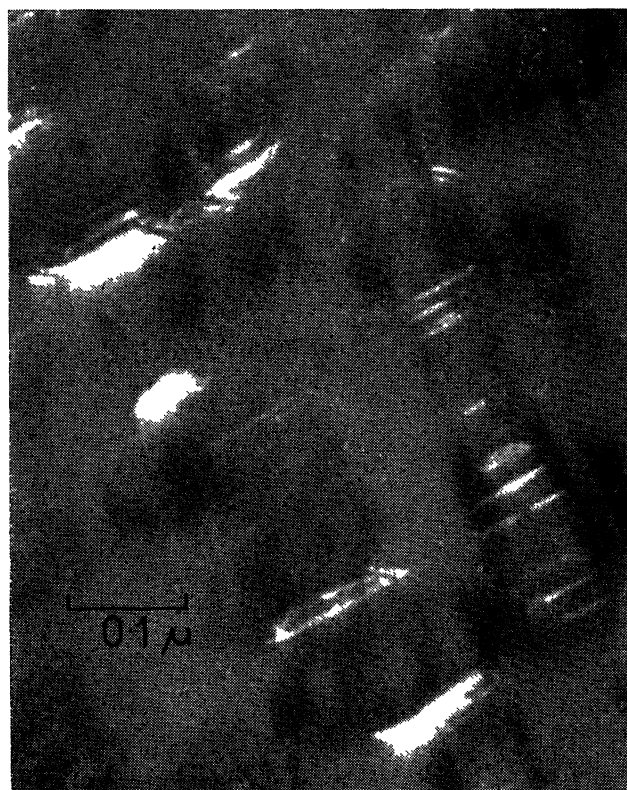
*b**c*

FIG. 5. — The [001] axis distribution which occurs during the growth of ordered nuclei : (a) bright field ; (b) dark field on (110) ; (c) dark field on (001), all from same area. Magnification $\times 260,000$ (printed $\times 0.6$).

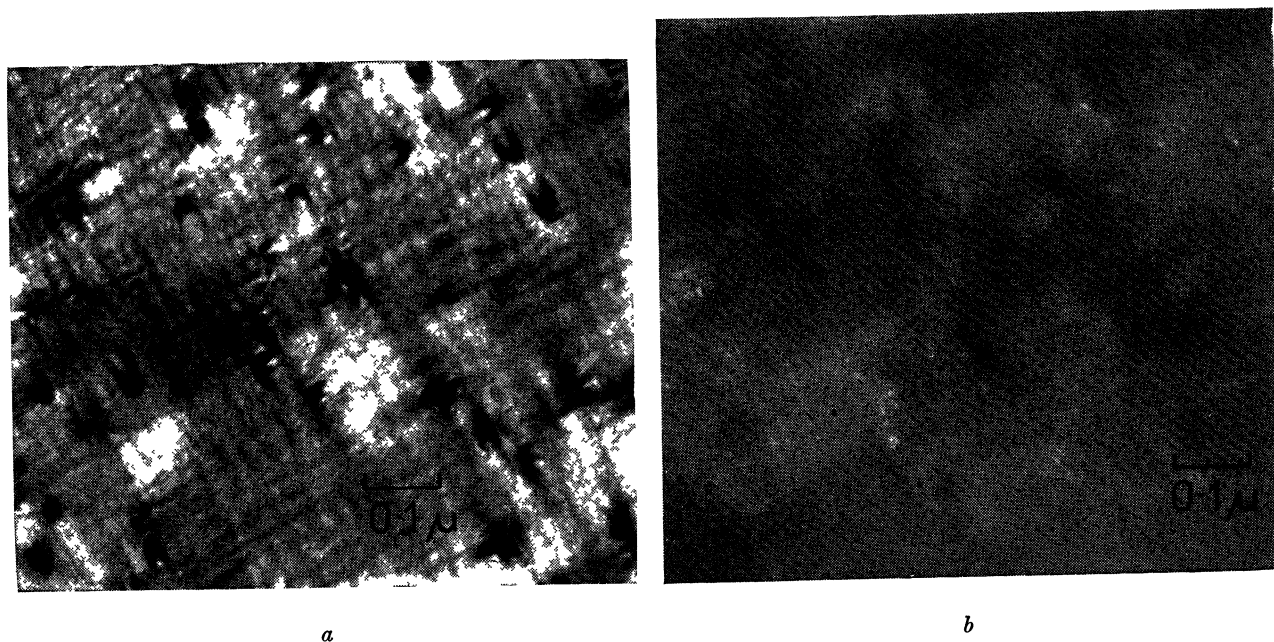


FIG. 6. — The streaming effect produced during ordering in the low temperature region of the 380-400 °C range : (a) bright field ; (b) dark field on (110) from same area as (a). Magnification $\times 164,000$ (printed $\times 0.6$).

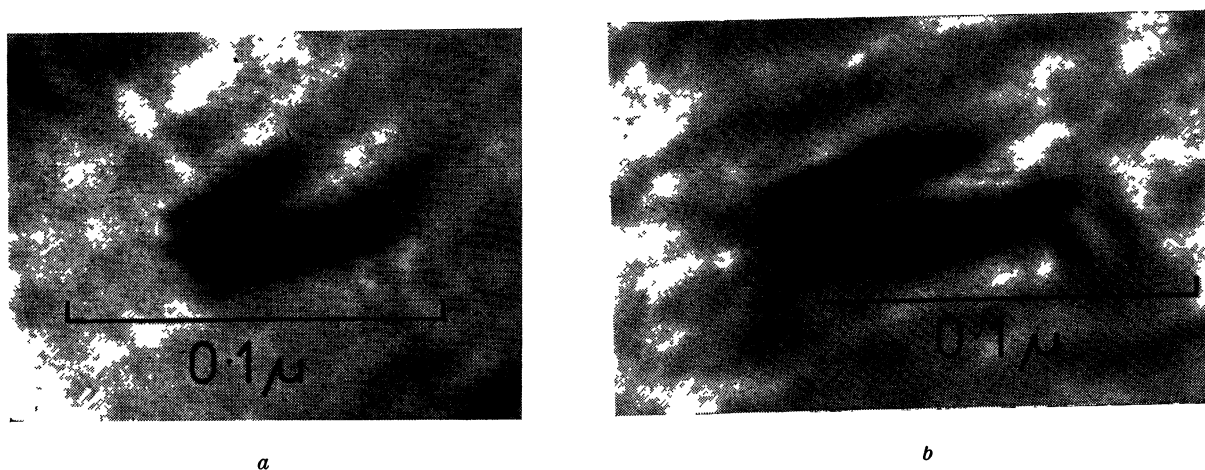


FIG. 7a, b — Enlarged images of two dislocations from the same micrograph as for figure 6a. The characteristic elongation of the contrast along $\langle 100 \rangle$, with doubled appearance, is shown. The dislocations are at the left-hand end of the region of black contrast. Magnification $\times 615,000$ (printed $\times 0.8$).

contrast is in part due to a very fine scale distribution of the N and P -orientations. A dark field micrograph of the specimen area of figure 6a is shown in figure 6b. The apparently small ordered regions shown on this dark field image might well be due to such a fine scale orientation distribution.

The streaming effect eventually "solidifies", at which stage the order is complete; $[001]$ axis distribution is then certainly present in the form of very fine intersecting or overlapping twins. The extended dislocation contrast described above

seems to develop gradually in to the contrast resulting from these fine twins. A very regular cellular arrangement of twins produced in this way is shown in figure 8.

4. Observations on specimens ordered before thinning. — The main purpose of this part of the work has been to obtain information on the shape of the ordered regions, their crystallographic relationship with the disordered matrix, and their internal structure (twinning). No systematic study of the effect of ordering temperature on these pro-

perties has yet been started, due to inadequate temperature control of the annealing furnace. Ordering has been carried out for various periods in the approximate temperature range 380-400 °C, so

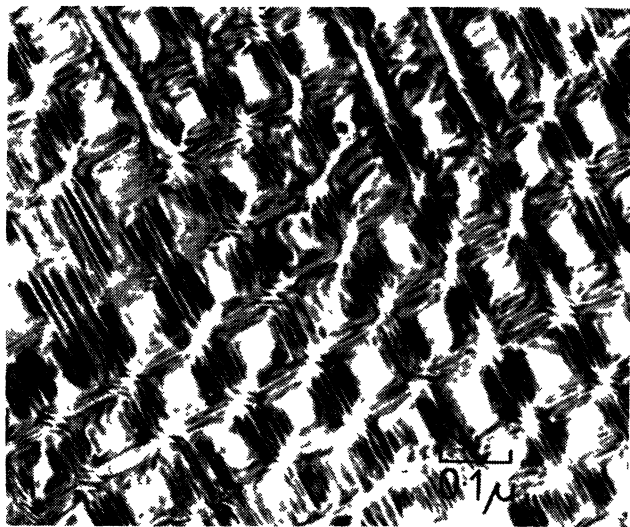


FIG. 8. — Fine scale [001] axis distribution produced by growth of order in the low temperature region of the 380-400 °C range. Bright field. Magnification $\times 164,000$ (printed $\times 0.6$).

that the specimens have varied in structure from completely ordered to largely disordered, but containing a few widely separated ordered regions. Figure 9 shows an example of the latter case. The fundamental ordered regions seem to consist of platelets which are parallel, or nearly parallel to the

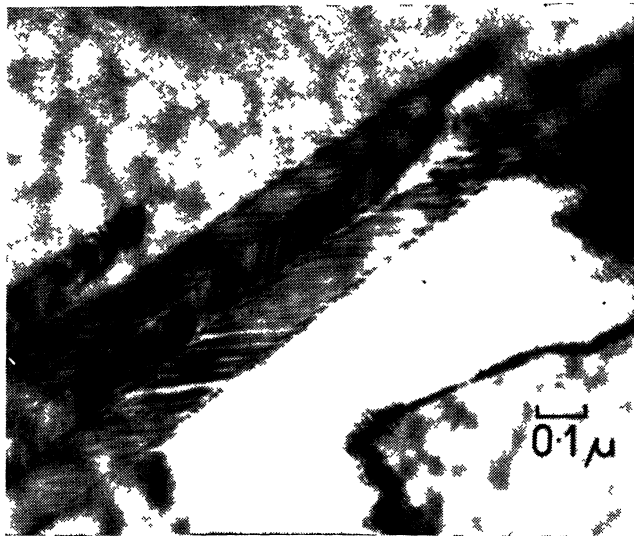


FIG. 9. — Ordered platelets of Cu Au II produced in bulk Cu Au by annealing disordered alloy at about 390 °C. Bright field. Magnification $\times 100,000$ (printed $\times 0.6$).

{110} planes in the disordered matrix. In all cases these platelets are twinned, and this twinning is commonly on a very fine scale, which is well below the resolution of the optical techniques used by Smith and Bowles [6]. The detailed crystallography of the ordering and twinning will be published elsewhere.

5. Discussion. — We have revealed, by means of high resolution electron microscopy, the early stages of nucleation and growth of Cu Au II within a disordered matrix. Although it is clear that dislocations can act as preferential nucleation sites, no direct evidence has been obtained to support a dislocation mechanism, such as discussed by Smith and Bowles [6], for the growth of these ordered nuclei. However, insufficient evidence has been obtained to rule out this possibility completely.

The mechanism by which preferential ordering occurs at a dislocation is not known, but there are at least two possibilities. Firstly since the formation of Cu Au II nuclei involves local changes in lattice parameters, it could be that the ordering occurs more readily in the vicinity of a dislocation because the strain field of the dislocation allows these changes to be accommodated more readily. This is equivalent to a kind of stress ordering mechanism. It would be interesting to carry out similar observations on a cubic ordered structure (e.g. Cu₃Au), to find out whether dislocations can still act as sites for preferential ordering in the absence of any strain effect. Secondly, if any local composition change were to occur in the vicinity of a dislocation, in analogy with the segregation effects which are believed to occur with more dilute solid solution alloys [7], the critical ordering temperature would be changed locally. For an alloy at the exact Cu Au composition this effect could only lower the ordering temperature, so that the ordering would then occur less readily at the dislocations. If, however, the specimen were off the exact composition, which is a possibility with the evaporated thin films, the situation might be reversed so that ordering would occur more readily at the dislocations. This possibility requires further investigation.

The results indicate that the initial ordered nuclei of Cu Au II occur more readily in the *N*-orientation, than in either of the *P*-orientations. This is consistent with the orientation of Cu Au II produced with specimens prepared by annealing of quenched disordered single crystal films [2], [3]. The reason for this orientation preference is believed to be that the normal orientation leads to contraction in a direction normal to the film plane, and expansion in all directions lying in the film plane. This situation is more readily accommodated than any contraction in the film plane, since

the latter would lead to high stresses. Nevertheless, the evidence shows that subsequent growth of the Cu Au *II* nuclei involves the formation of regions with one of the *P*-orientations. These regions appear to correspond with very narrow twin lamellae on {101} planes. This supports the hypothesis that the growth of a nucleus can only proceed if it is accompanied by twinning. Such twinning is a common feature of martensitic transformations, and is observed with a shear transformation in the indium-thallium system [8], [9], where the crystallography is equivalent to that of the Cu Au ordering. We find it present with both kinds of specimen used, and it is interesting that the scale of the twinning is much finer than that observed by Smith and Bowles [6]. Possibly the twin bands observed by the latter authors were further subdivided in to finer twin

lamellae which were beyond the resolving power of their optical microscope technique.

As far as can be judged the earliest observable Cu Au *II* nuclei (smaller than 100Å across) contain the normal periodic APB structure. Unidirectional zones (see reference [2]) occur, within a region of unique [001] axis orientation, and numerous examples of overlapping unidirectional zones have been found in the Cu Au *II* nuclei formed in the single crystal film specimens. Thus the APB structure of thin films of Cu Au *II* produced directly from the disordered state appears to be similar to that of Cu Au *II* formed by the Cu Au *I*-Cu Au *II* transition [3].

6. Acknowledgement. — This paper is published by permission of the Chairman of Tube Investments Limited.

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