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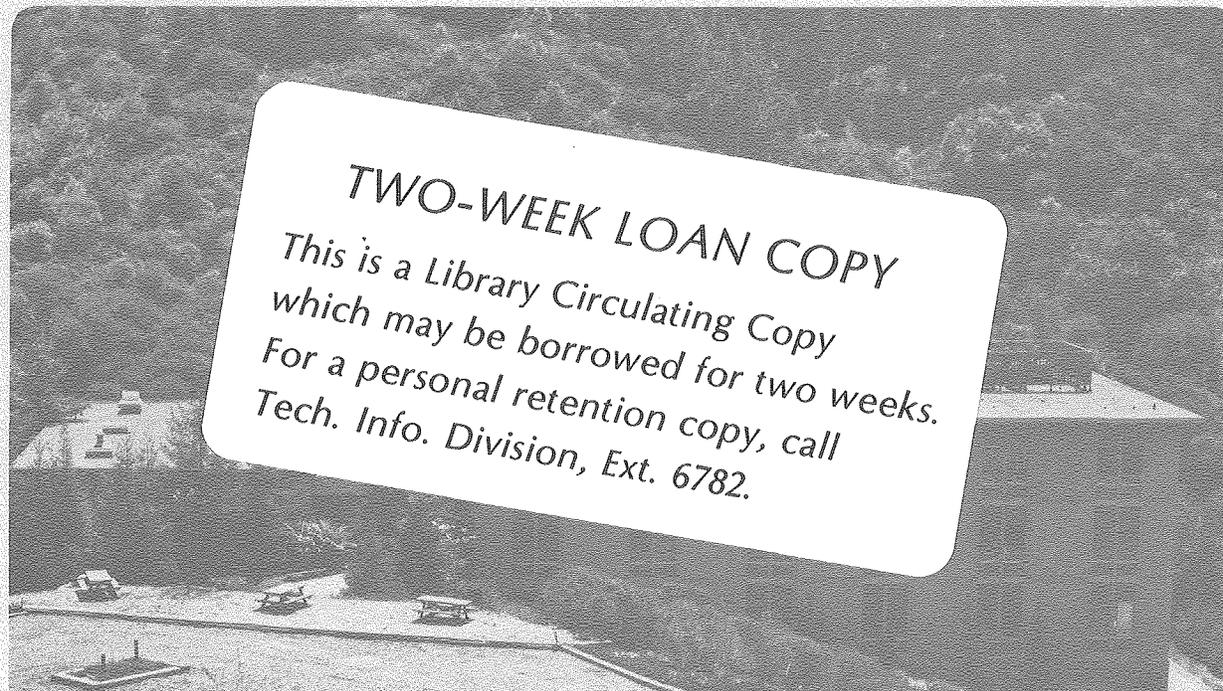
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THE ORIGIN OF UNUSUAL DISLOCATION STRUCTURES
OBSERVED IN ION-THINNED NICKEL OXIDE

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ABSTRACT

Ion-thinned single crystals of nickel oxide were examined and found to contain some unusual dislocation configurations showing anomalous contrast under certain diffracting conditions. These configurations took the form of glissile dislocations threading the foil but leaving long trailing dislocations in the near surface region at both top and bottom surfaces. The Burgers vector of the dislocations was identified as $\frac{a}{2} \langle 110 \rangle$ as expected for nickel oxide, and the contrast anomalies were ascribed to certain surface effects. The dislocations themselves were thought to have arisen as a result of cleavage processes in the crystal, and their retention in the foil is attributed to the formation of reduced surface layers during the ion thinning.

INTRODUCTION

During the course of two independent investigations of nickel oxide single crystals, some unusual dislocation configurations were observed which showed an anomalous contrast under certain diffracting conditions. In both studies transmission electron microscopy was being used to characterize the types of dislocation and their associated Burgers vectors in as-prepared specimens as part of a sub-grain boundary structure characterization (1), or prior to further in-situ reduction experiments (2).

EXPERIMENTAL

Materials from two different sources were studied but both the material and preparation techniques were essentially similar. In Berkeley, nickel oxide single crystal boules with $\langle 001 \rangle$ growth directions were used from a batch supplied by the Marubeni-Iida Co. Ltd. of Osaka, Japan (crystal growth

method unknown). Circular discs were cut from the boules perpendicular to this $\langle 001 \rangle$ direction and then mounted and smaller 3 mm discs cut using an ultrasonic cutting machine. Nickel oxide is a p-type semiconductor containing an oxygen excess and so to minimize this deviation from stoichiometry and equilibrate the sample, the discs were annealed in air at 1350°C for 24 hours. After annealing, the discs were hard ground using silicon carbide and diamond paste to approximately $50\ \mu\text{m}$. This process of mechanical deformation by grinding after an annealing process has been reported (3) to increase the dislocation density over unannealed specimens and to produce long straight dislocation lines. The specimens were then thinned in an ion-beam thinner at an angle of incidence of $20\text{-}25^{\circ}$ using 7 - 8 kV initially and $10\text{-}15^{\circ}$ and 4 - 5 kV in the final stages. Specimens were examined in a Phillips 301 at 100 kV and an AEI-EM7 microscope at 1 MV.

RESULTS AND DISCUSSION

The new features of interest were pronounced traces resulting from strongly diffracting slip dislocations retained at the foil surfaces. This phenomenon is strikingly similar to that observed in the early days of transmission microscopy in certain metals (4) and attributed to the presence of oxide films on the surface of the metals. In these observations, the dislocation traces, which arose from stress-induced dislocation motion in the foils, remained almost indefinitely in stainless steel, but lasted only a few seconds in aluminum. In the present work evidence indicates that dislocation activity had occurred either during thinning or during subsequent specimen handling. The dislocation configurations, consisting of a leading glissile segment threading the foil and a pair of trailing dislocations,

were observed distributed non-uniformly throughout the foil (see Fig. 1). In all cases the dislocations lay on the expected $\{110\}$ slip plane and had $\frac{a}{2} \langle 110 \rangle$ type Burgers vectors. During prolonged observation in the microscope, the near-surface dislocations were observed to slowly slip out of the foil surface leaving discontinuous segments (see Fig. 2) which continued to diffract strongly, interspersed with regions with the more usual low residual contrast. Analysis of the end and near-surface dislocation contrast indicated that each had the same Burgers vector, but under some diffracting conditions anomalous behavior was seen, e.g. under weak beam conditions, much stronger contrast was seen from the near-surface dislocations, while the end dislocations appeared in true weak-beam contrast (Fig. 3). The end dislocation was also often observed to be in well-defined crystallographic directions within the plane with segments parallel to the $\langle 111 \rangle$ directions thus giving rise to the arrowhead type of configuration seen in Figs. (1-3). If the end dislocations were straight they would be of pure screw character and be along $\langle 110 \rangle$ directions with this foil geometry and their apparent reluctance to do so may be related to the ionic structure of nickel oxide. Although the core structure of a screw dislocation in ionic crystals is not understood, in the perfect crystal the signs of the ionic charges in a $\langle 110 \rangle$ direction are all the same whereas they alternate along a $\langle 111 \rangle$ direction.

Discussion of these dislocation structures is split into two sections: the origin of the dislocations and the reasons for the dislocation retention close to the surface. As analogous examples of this latter effect have been previously reported (2), we will deal with this question first. Three cases may be considered corresponding to pure edge, mixed surface dislocations and pure screw.

If a dislocation of screw or mixed character and Burgers vector $b = \frac{a}{2}$ (110) glides in a foil with surfaces parallel to the (010) plane, the trailing dislocations would be of pure edge character. The energy of such a dislocation may be sufficient to induce it to slip through the surface (even in the presence of a surface layer) and leave merely a slip step showing very weak contrast rather than the strong contrast left by near-surface dislocations. Such cases are observed (Fig. 4).

A second case concerns the effect of charge neutrality effects for a foil with surfaces not parallel to a {100} type plane. The example analyzed in detail concerns foils oriented parallel to (01 $\bar{2}$) so that the intersection of glide plane and foil surface is oriented parallel to (121) and slip steps are also oriented parallel to the (121) direction. In the {110} planes there are rows of equally charged ions oriented parallel to the $\langle 121 \rangle$ directions and so the production of a surface step is extremely unfavorable*. Thus a trailing dislocation would be retained very close to the surface unable to slip out due to these ionic charge effects.

The third case can be understood if the dislocation is located at the interface between the nickel oxide crystal and a thin surface layer with a structure different from that in the bulk and lies within about 1/10 of an extinction distance from the foil surface. In the first case it was postulated that an edge dislocation may be able to slip through such a surface layer but this may not always be possible and if the foil surfaces are oriented parallel to (001) then a lower energy pure screw dislocation will result which will be more easily impeded by the surface layer (5). Such a change in the

* A charge effect is produced on surface steps at every surface not parallel to a {100} plane, but {121} surfaces give the strongest effect.

structure of the surface layers of the specimen may occur during the specimen preparation. Theoretically, the contrast expected from such a near surface dislocation is difficult to predict (6,7) so anomalous effects are not unexpected. However, in these examples the surface layer was postulated to be a surface oxide on a metal whereas in the present case we are dealing with an initial nickel oxide substrate. Consequently, we may postulate either a heavy carbon layer deposited on the surface or a reduced surface consisting of some type of nickel-rich layer. A carbon layer is discounted since its presence would be obvious in the freshly prepared sample. It is possible, however, that the surface layers of the nickel oxide were in a slightly reduced form due to interaction with the ion beam and/or environment in the ion-thinning procedure. At room temperature the equilibrium ratio of hydrogen to water vapor in the nickel/nickel oxide system is approximately 1:30 (8) and so any less water than this tends to give a reducing environment. For the ion thinner, a reducing atmosphere is quite likely since there are great numbers of residual reducing species and very little water in the vacuum system. Moreover, the process involved may not be a true equilibrium process. For example, the surface may be a modified nickel oxide layer if the oxygen excess present is merely reduced to stoichiometric levels or below. Such processes are obviously very dependent on kinetic as well as thermodynamic effects and are thus temperature dependent. Significantly the specimen holder was found to get quite hot during the thinning process. Indeed, temperature rises of 100-200°C have been measured during ion-beam thinning of certain metallic alloys (9) and higher temperatures may be expected in the less conductive oxides.

The observation that the dislocations disappear slowly under the influence of the electron beam in the electron microscope atmosphere further supports this interpretation. As stated previously, the equilibrium hydrogen/water vapor atmosphere at room temperature in the nickel/nickel oxide system is approximately 1:30 and so higher levels of water vapor than this would tend to give an oxidizing atmosphere. Measurements of this ratio in the Phillips 301 under ordinary everyday running conditions (10) have indicated that the ratio is approximately 1:20 and may be considerably higher under conditions when new film has just been admitted to the camera chamber and is still outgassing. Thus, it seems possible that any reduced layer, amorphous or crystalline, on the surface of the nickel oxide could reoxidize in the microscope when heated under the influence of the electron beam and could thus allow the dislocations to slip out of the surface in agreement with the observations. The idea of a reduced surface layer has also been used by other workers (11,12) to explain observations in molybdenum trioxide although the dislocations there are believed to be partial screw dislocations. Further agreement with these hypotheses came from an attempt to observe similar dislocation structures in magnesium oxide samples prepared by the same route. Since no such dislocations were observed, even in specimens containing cleavage edges, this may be attributed to lack of similar reduced surface layers. The equilibrium hydrogen/water vapor ratio for this system at room temperature is approximately 10^{20} :1; reduction is extremely unlikely and thus dislocation egress from the surface will not be impeded. Only {100} sections of MgO were studied and thus the absence of dislocation retention due to the charged slip step mechanism may be attributed to incorrect geometries.

The second main question concerns the origin of the dislocations. There is a non-random distribution of areas within the foil where the dislocations are found to occur and in the examples studied these are adjacent to cleavage edges or possible cleavage cracks in the specimen. Dislocations run both parallel and perpendicular to these edges but are mainly parallel. Thus it is likely that they arise from processes occurring during cleavage, directly as a result of the cleavage process, or from cleavage induced motion of grown-in dislocations. Support for this idea was found in specimens ion-thinned until the foil just perforated. The edges of such a specimen were rounded with little evidence of the long straight cleavage edges found when the hole was allowed to become enlarged. Such specimens contained none of the dislocation structures previously observed again suggesting a causal relationship with cleavage. In general the active $\{110\}$ planes appear to be those at 45° to the $\{100\}$ type cleavage planes and resulting dislocation motion may contribute to stress relief during cleavage.

As the dislocations glide in the foil further interaction becomes apparent (Fig. 5). The dislocation at A acquires a small segment at the tip of the arrowhead and this may result from dislocation interaction on two different slip planes although the precise mechanism of such an interaction is unclear.

CONCLUSIONS

Handling of fragile ion-thinned nickel oxide single crystal TEM specimens can result in cleavage cracking and associated dislocation activity. A striking visual record of this activity is produced by retention of the slipping dislocations at the foil surface. This retention is attributed to a combination of directional, charged slip-step effects, the dislocation

character and the presence of modified (reduced) surface layers.

The secondary importance of these observations lies in the fact that the preparation of ceramic foils for TEM by ion-beam thinning results in the formation of surface layers which are different from the bulk. Such compositional differences could affect other properties and should always be born in mind when examining similar crystal structures.

ACKNOWLEDGEMENT

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Figure Captions

Fig 1 Bright-field micrograph showing general appearance of the dislocations.

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Fig 2 Bright field micrographs showing the appearance of the dislocations as they slip to the surface under the influence of the electron beam.

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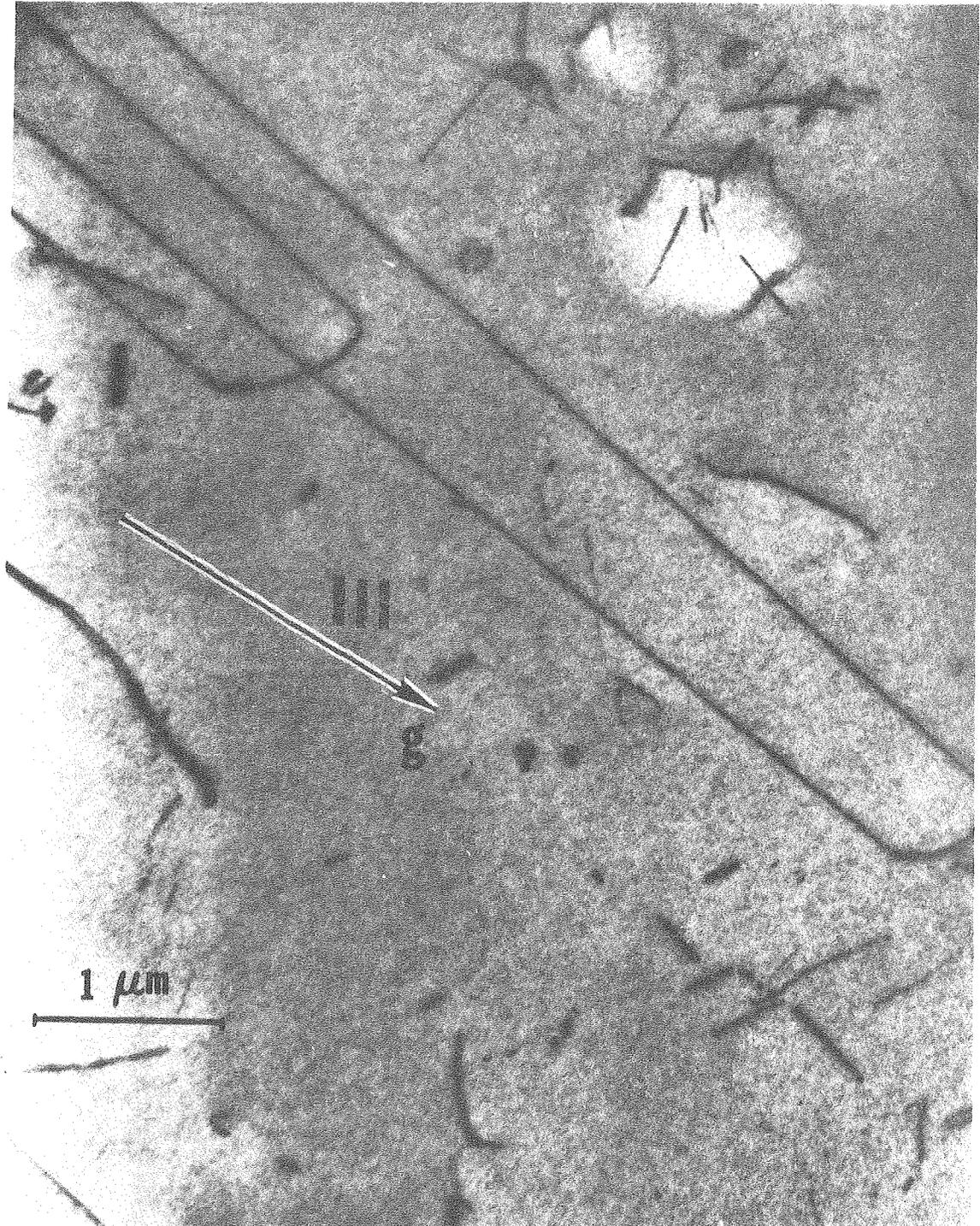
Fig 3 Dislocations viewed under weak beam conditions (same area as in Fig 1).

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Fig 4 Bright field micrograph showing faint slip step traces produced by some dislocations. XBB 805 5930

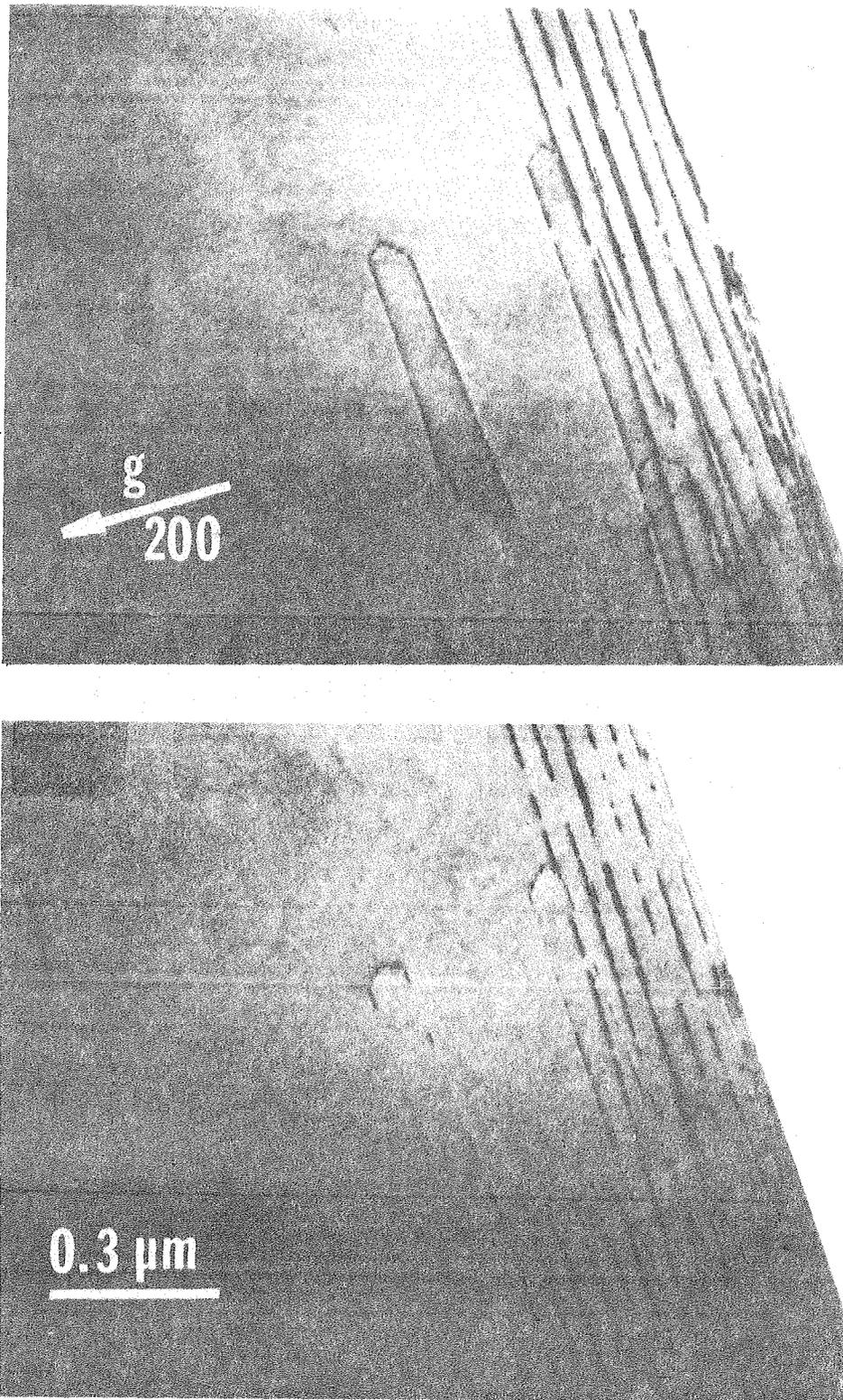
Fig 5 Dislocation interaction results in a cusp on the glissile dislocation.

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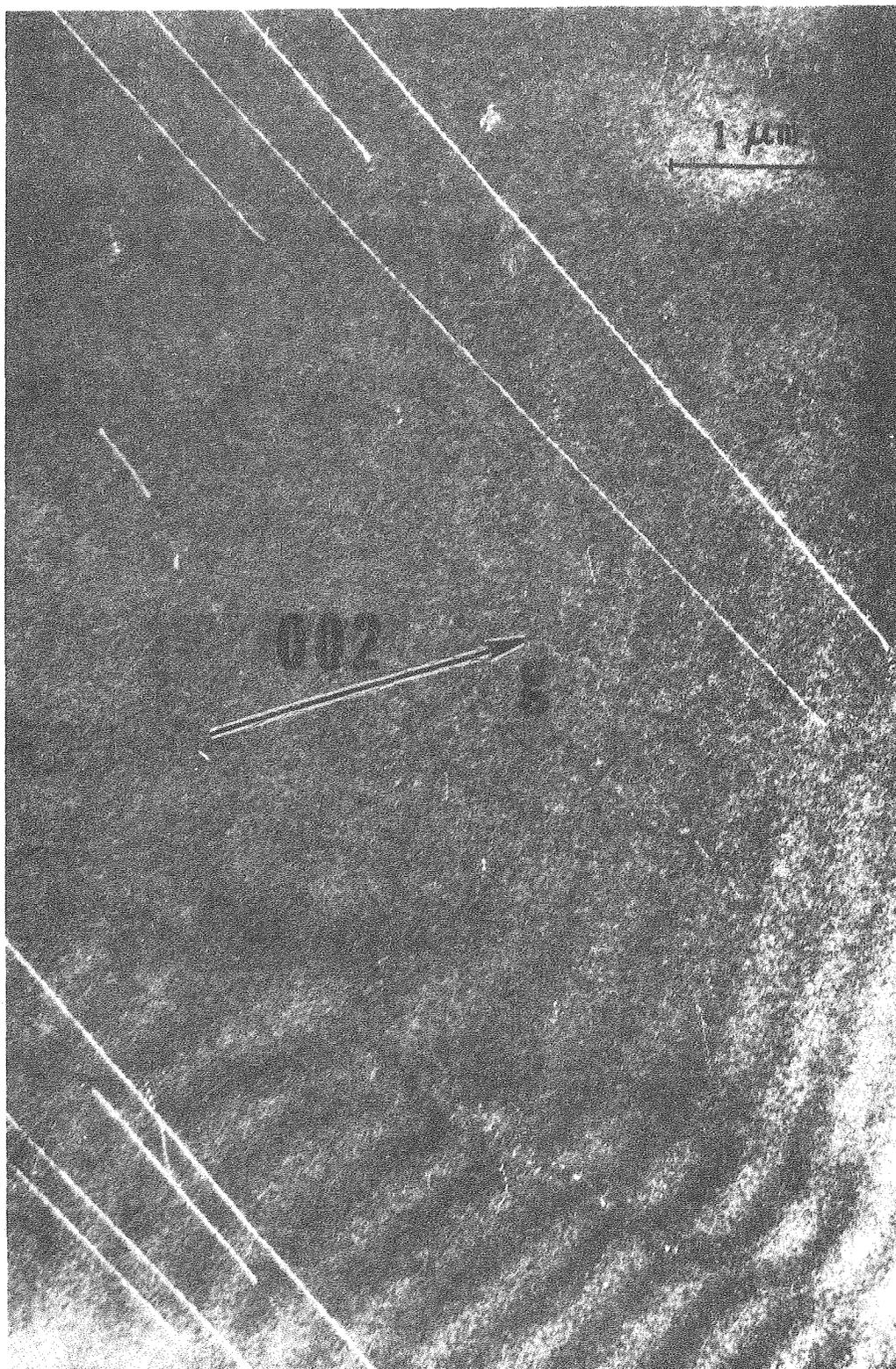
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Fig 1 Bright-field micrograph showing general appearance of the dislocations.



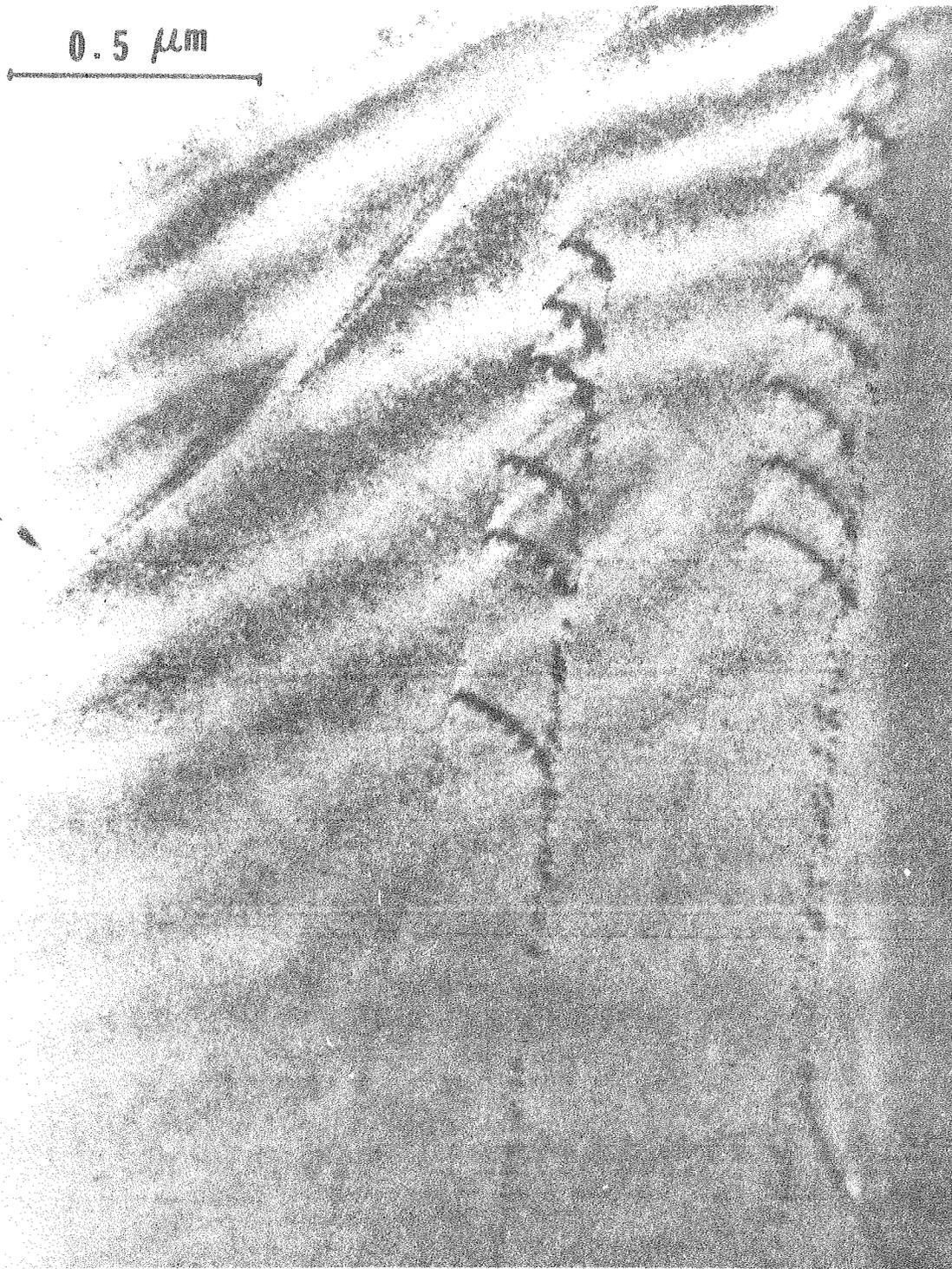
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Fig 2 Bright field micrographs showing the appearance of the dislocations as they slip to the surface under the influence of the electron beam.



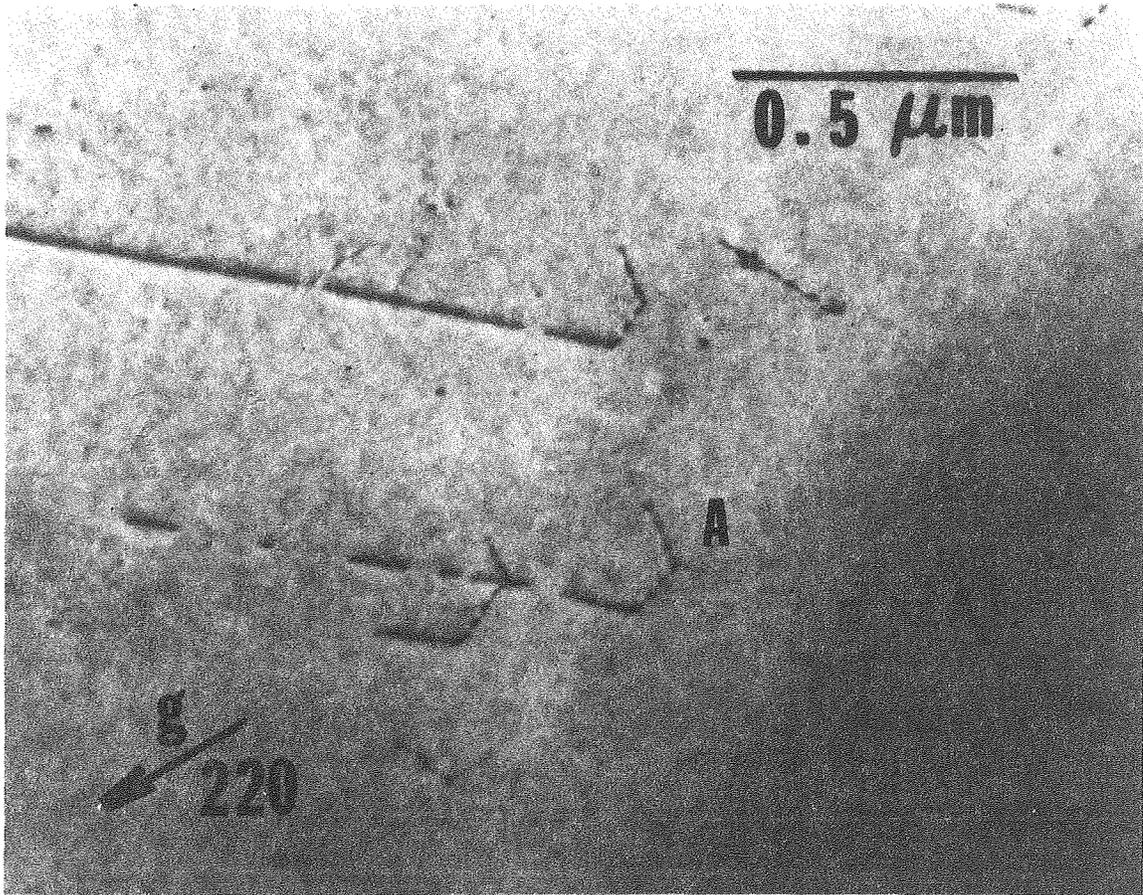
XBB 305 5928

Fig 3 Dislocations viewed under weak beam conditions (same area as in Fig 1).



XBB 805 5930

Fig 4 Bright Field micrograph showing faint slip step traces produced by some dislocations.



XBB 805 5931

Fig 5 Dislocation interaction results in a cusp on the glissile dislocation.

