

Transmission electron microscopy of dislocations in nickel oxide single crystals

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The dislocation structure of NiO single crystals used in diffusion studies has been examined by transmission electron microscopy. The crystals contain dislocations (the dislocation density being $4 \times 10^{12} \text{ m}^{-2}$) that are probably a result of the growth process. The dislocations have a Burgers vector of $a/2 \langle 110 \rangle$. On annealing at temperatures above 1400°C the density is reduced to $\sim 7 \times 10^{11} \text{ m}^{-2}$, most of the dislocations forming low angle boundary arrays. The dislocation density was found to be much greater in the vicinity (within $1 \mu\text{m}$) of a mechanically polished surface.

1. Introduction

There is a large volume of experimental work documenting diffusion along grain boundaries and dislocations in metals. This short-circuit diffusion becomes much more rapid than lattice diffusion at temperatures below about half the melting temperature of the metal. It is widely believed that the situation is similar in oxides, but as yet there have been only a few investigations of the phenomenon. Diffusion in oxides is particularly relevant to the oxidation of metals and alloys and therefore knowledge of short-circuit diffusion is important in considering oxidation at temperatures below half the melting temperature of the oxides formed in the protective scale. In service use, most "corrosion-resistant" alloys would be oxidizing in this temperature range.

We are carrying out research to assess the importance of various diffusion mechanisms contributing to the oxidation of Ni and part of this research has been a study of ^{63}Ni tracer diffusion in NiO single crystals. Analysis of the diffusion profiles has shown [1] a contribution from diffusion along dislocations in the temperature range 500 to 900°C and therefore the dislocation structures of similar NiO crystals have been studied by transmission electron microscopy in order to provide the following information:

(i) The Burgers vector of the dislocation.

(ii) The dislocation density in a typical diffusion specimen.

(iii) Whether the dislocations are in random orientations, or in ordered arrays.

(iv) Whether the dislocation density and arrangement is significantly different close to the crystal surface (where the tracer profiling was performed).

(v) Whether the dislocations are a result of the crystal growth process, or arise from mechanical damage during sample preparation.

(vi) The efficacy of various annealing treatments in reducing the dislocation density.

2. Experimental

Nickel oxide single crystals grown by flame fusion were supplied by Cristal Tec (Grenoble) in the form of discs, about 10 mm in diameter and 3 mm thick, with flat faces in the (111) plane.

Slices of NiO ~ 0.5 mm thick were cut parallel to the (111) plane with a diamond saw and ground to less than half that thickness using $14 \mu\text{m}$ diamond paste on a glass plate. These slices were cut into roughly square pieces with a minimum dimension of 3 mm and each piece was then ground to give a 2.9 mm diameter disc approximately $200 \mu\text{m}$ thick. The discs were thinned mechanically to $\sim 25 \mu\text{m}$ as described by Fynn *et al.* [2] using a precision polishing jig (Metals Research Ltd, Royston, UK) with $6 \mu\text{m}$ diamond paste on cast iron and tin/lead laps for grinding and polishing respectively.

To determine the effect of annealing on the dislocation density, some specimen discs were annealed for 24 h in air, at temperatures ranging from 1000 to 1600° C before thinning to electron-transparency.

Electron-transparent foils were produced in an ion beam thinning unit (Ion Tech Ltd, Teddington, UK) using two beams of 5 to 6 keV argon ions, impinging, one on each side of the sample, at an angle of $\sim 20^\circ$ to the surfaces of the disc. The specimens were rotated during the thinning process which progressed at an approximate rate of $0.5 \mu\text{m h}^{-1}$ per side. Ion beam thinning was chosen as the final thinning technique after unsuccessful attempts to discover a suitable chemical jetting process using orthophosphoric acid at temperatures up to 300° C [3].

The two ion sources of the ion beam thinning unit can be operated independently. It was therefore possible to remove different amounts of material from each side of a specimen, thus allowing observation of the dislocation structure at any depth below the surface of the mechanically polished disc. Most of the specimens produced for this work were ion beam thinned by the same amount from each side of the $25 \mu\text{m}$ thick disc, and hence the electron micrographs show the dislocation structure that was $\sim 12 \mu\text{m}$ below the mechanically polished surfaces. Electron micrographs appropriate to other depths are marked as such in the figure captions. Ion beam thinning was stopped when a hole formed in the disc and the thin foils were examined in a Siemens Elmiskop I 100 kV electron microscope. Ample electron-transparent material was found around the edge of the hole in specimens with a hole of $\sim 100 \mu\text{m}$ in diameter.

To observe the dislocation structure of a NiO sample that had not been mechanically polished it was necessary to cleave a crystal, hoping that some fragments that were produced had edges thin enough for electron transmission. However, samples produced in this way had too little thin area. Therefore, two of the most promising cleaved fragments were selected for further thinning. The fragments were fixed with colloidal silver to a copper grid with a 1 mm diameter hole, in such a way that their thinnest regions protruded across the hole. Mounted in this way the NiO fragments were ion beam thinned for ~ 4 h to obtain a reasonable area of electron-transparent material.

Dislocation densities were measured by two methods:

(i) By counting the number of dislocations intersecting unit area of specimen surface (number per m^2). This method of counting was possible since all single dislocation lines intersected both surfaces of the foil. (Dislocations can never end inside a crystal but must end either at the surface of the crystal or at a grain boundary, form closed loops or branch into other dislocations.) Specimens showing extensive dislocation networks (e.g. Fig. 5) could not be characterized by this method since the number of dislocations intersecting a plane is a function of the relative orientation of the network and the plane.

(ii) By measuring the total length of the dislocations projected onto a plane perpendicular to the beam direction, observed in a given volume of specimen (m of dislocation per m^3 of material). For this second method, thickness fringes were used in the way described by Edington [4] to determine the thickness of the foil ($\sim 0.4 \mu\text{m}$) in the region of interest.

3. Results

3.1. Determination of the Burgers vector

Figs. 1a to c are typical micrographs of a NiO single crystal specimen that has had no annealing treatment following crystal growth, grinding, polishing and thinning. The Burgers vector, \mathbf{b} , of some of the dislocations was determined by the normal $\mathbf{g}\cdot\mathbf{b}$ analysis [4], where \mathbf{g} is the operative Bragg reflection.

For example, the dislocations labelled A and B in Fig. 1a ($\mathbf{g} = (\bar{2}\bar{2}0)$) are both invisible (i.e. $\mathbf{g}\cdot\mathbf{b} = 0$) in Fig. 1b ($\mathbf{g} = (02\bar{2})$) and Fig. 1c ($\mathbf{g} = (\bar{1}\bar{1}\bar{1})$). Hence the Burgers vectors for both dislocations are $a/2 [011]$ or $a/2 [0\bar{1}\bar{1}]$ where a is the lattice parameter. Similar analysis of other dislocations showed them all to be of this type, as expected in a fcc lattice and confirming the earlier determination on corrosion films by Hales [5].

3.2. Cleaved NiO single crystals

Figs. 2a and b illustrate the dislocation structure of a cleaved piece of NiO single crystal.

The average dislocation density was measured to be $\sim 4.3 \times 10^{12}$ m of dislocation per m^3 , but there were distinct bands of dislocation tangles $\sim 0.5 \mu\text{m}$ in width, running through the sample,

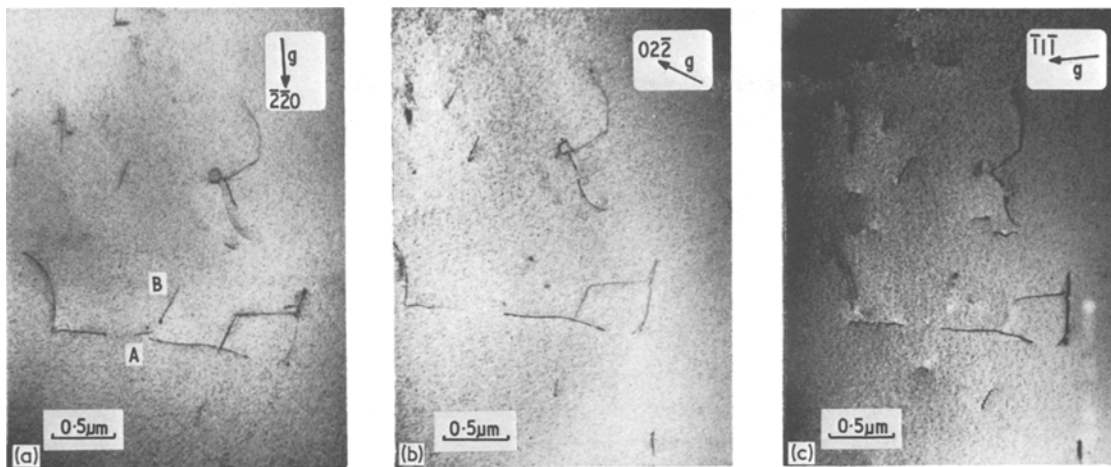


Figure 1 Burgers vector analysis of dislocations in NiO single crystal.

where the dislocation density was considerably higher; at times as high as 1.2×10^{13} m per m^3 . The bands of dislocation tangles were aligned along $\langle 100 \rangle$ directions and were often accompanied by a sudden change in the thickness of the foil (illustrated clearly in Fig. 2a). Besides these dense bands there were some small areas ($\sim 2 \mu\text{m} \times 2 \mu\text{m}$) where the dislocation density was as high as 3.6×10^{13} m per m^3 (see Fig. 2b).

These dislocation aggregations are the result of plastic deformation during cleavage and are similar to those observed in lightly deformed fcc metals [6].

3.3. The effect of annealing

Fig. 3b shows the change in dislocation density of a NiO single crystal sample as a function of annealing temperature.

At 1400°C some of the dislocations began to form networks (Fig. 4) and at 1600°C the networks had become much more extensive (Fig. 5), giving local dislocation densities as high as $\sim 1.3 \times 10^{13}$ m per m^3 , compared with a background dislocation density more than an order of magnitude lower. Because of these wide variations, the average density in this sample (Fig. 3b) is an estimate based on the average size and distance apart of the dislocation networks and the background dislocation density.

At 1600°C the dislocation networks frequently assumed a hexagonal configuration (Fig. 5). Frank [7] has shown that dislocation nets are equivalent to low angle grain boundaries. A regular, hexagonal pattern represents a twist boundary on the (111) plane with an angle of rotation of $\sim |b|/h$, where h is the distance between centres of adjacent hexa-

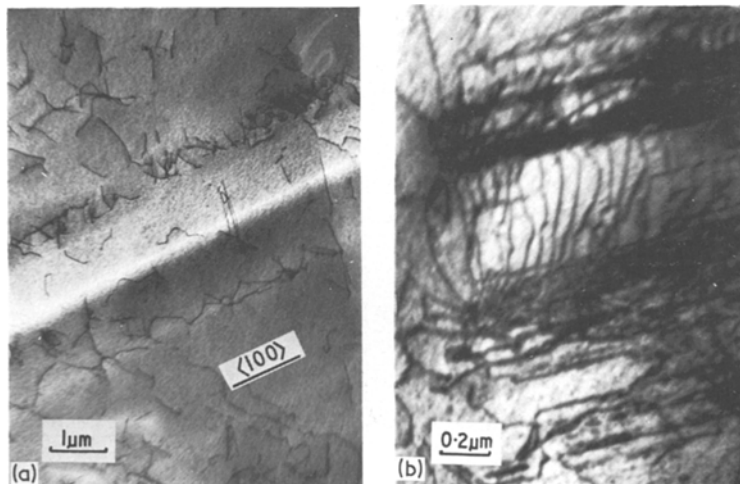


Figure 2 Dislocations in cleaved NiO.

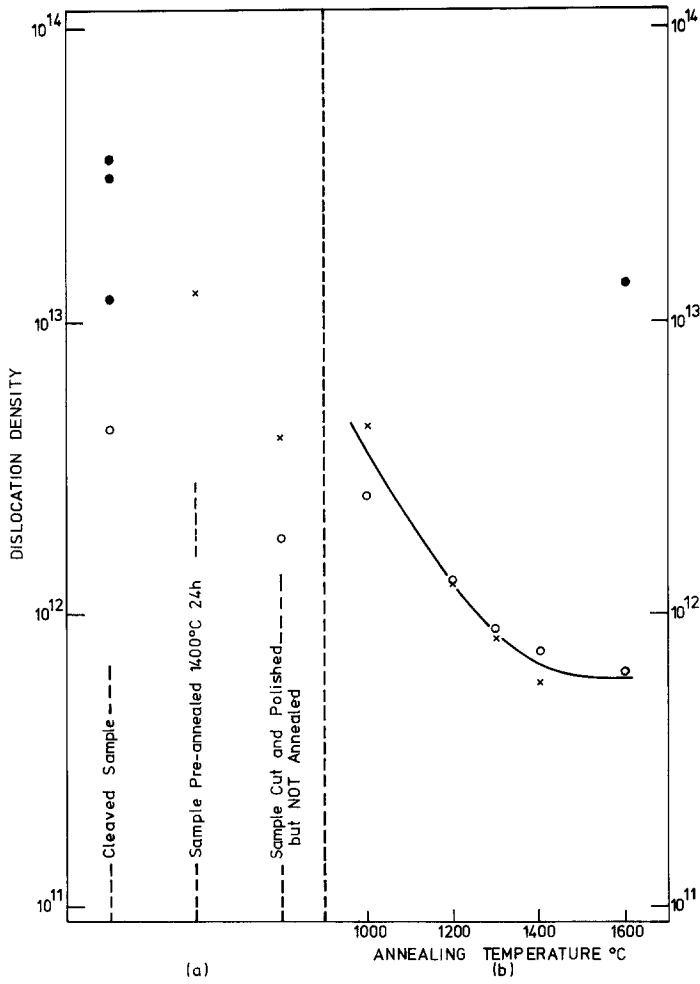


Figure 3 Dislocation densities in NiO. (a) The comparison of various samples. (b) The effect of annealing temperature. \circ average dislocation density, by measuring method (m per m³); \bullet dense regions, by measuring method (m per m³); \times average dislocation density, by counting method (per m²).

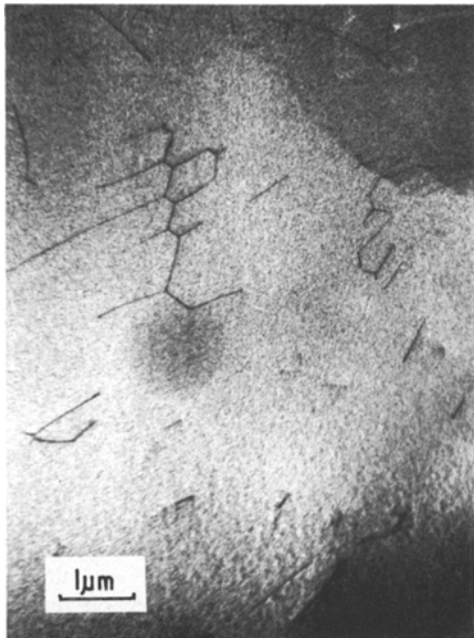


Figure 4 Dislocation structure of NiO, annealed in air at 1400°C for 24 h.

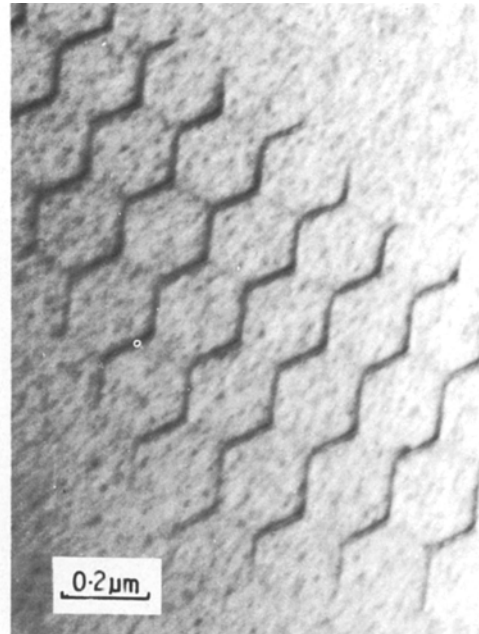


Figure 5 Hexagonal dislocation network formed in NiO, annealed at 1600°C for 24 h.

gons in the net and $|b|$ is the elementary Burgers vector length. In Fig. 5, the twist boundary has an angle of rotation of $\sim 8.5 \times 10^{-2}$ degrees. Frank [7] has shown that the Burgers vectors of the dislocations are parallel to the dislocation lines and therefore all the dislocations in the net are pure screws. If such a dislocation net lies in any plane other than the (111) plane, the regular hexagon structure must be modified to minimize long range stresses in the regions of crystal either side of the net.

3.4. Pre-annealed NiO

The isochronal anneals of Section 3.3 were performed on samples that had previously been cut, ground and polished to discs of $25 \mu\text{m}$ thickness. The observed dislocations could therefore have been introduced either during the growth process of the crystal or during the disc preparation.

To clarify this situation a slice of single crystal, almost 0.5 mm thick, was annealed in air at 1400°C for 24 h before the preparation of thin discs. The aim of the annealing treatment was to reduce the dislocation content of the bulk sample to as low a value as possible before grinding and polishing to produce the thin discs required. Annealing at 1600°C was avoided as the formation of twist boundaries in the sample was considered to be an unnecessary complication. No further annealing treatment was given after the disc preparation and the sample was ion beam thinned in the normal way.

Fig. 6 is a typical micrograph of the dislocations seen in this sample, $\sim 12 \mu\text{m}$ from the original polished surface. It is surprising that the average dislocation density ($\sim 1.3 \times 10^{13} \text{ m}^{-2}$) is higher than that of a sample that had no annealing treatment either before or after the preparation of the thin disc ($4 \times 10^{12} \text{ m}^{-2}$).

If it is assumed that annealing at 1400°C reduces the density to $\sim 8 \times 10^{11} \text{ m}^{-2}$ (see Fig. 3b) it can be concluded that it is easier to introduce dislocations into a crystal by mechanical grinding and polishing if the initial dislocation density is lower. This may indeed be possible since the geometry of the dislocations is different in the two specimens. Polishing after 1400°C annealing (Fig. 6) results in long straight dislocation lines with preferred directions whereas the un-annealed specimen (Fig. 1a) exhibits shorter, randomly arranged dislocations, many of which are curved. Because of this different geometry, it is probable

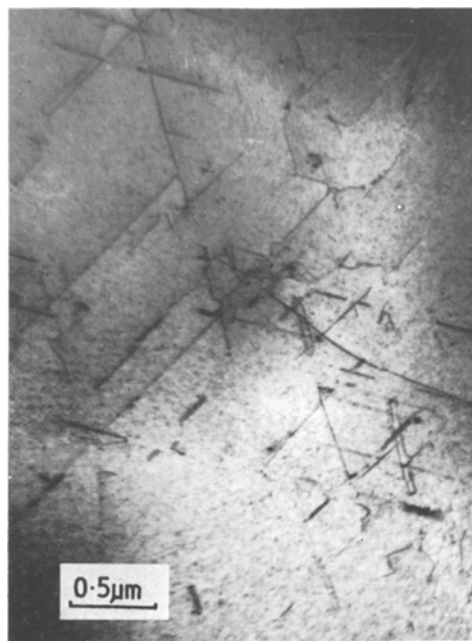


Figure 6 Dislocation structure of pre-annealed NiO.

that the dislocations observed $\sim 12 \mu\text{m}$ below the polished surface of an unannealed crystal result from the crystal growth process rather than from mechanical damage. It is difficult to be confident of this conclusion, however, since the different dislocation geometry might arise from a redistribution of impurity pinning centres during the annealing process.

3.5. The near-surface region

Since this work was carried out in support of a programme of work on diffusion in NiO, an attempt was made to ion beam thin a disc from one side only and thus observe the damage in the first $0.5 \mu\text{m}$ below a mechanically polished surface. This proved impossible as before the disc was sufficiently thin it cracked at the thinnest part and curled up, indicating that the mechanically polished surface was more highly strained than the bulk of the sample.

Similarly, Hockey [8] found that it was impossible to produce a thin foil of Al_2O_3 that included a mechanically polished surface. However, he did succeed in producing a thin foil close to the surface by removing only 2000 \AA of Al_2O_3 from the surface of interest using one ion source. The specimen was thinned to perforation using the second ion source operating on the other side of the sample.

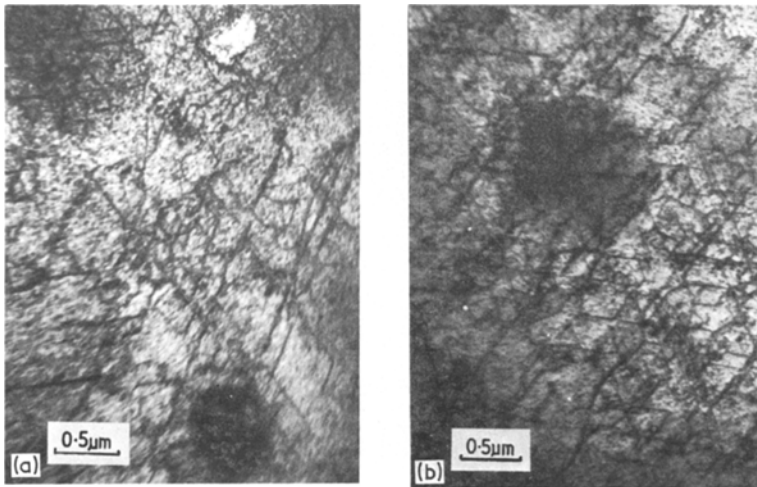


Figure 7 Dislocation structure in the near-surface region of a mechanically polished specimen. The foils were formed (a) ~ 1.5 to $1.9 \mu\text{m}$ and (b) ~ 0.3 to $0.7 \mu\text{m}$ below the polished surface.

Hockey's technique was applied here to NiO, using single crystals which had been pre-annealed at 1400°C as described in the previous section. Some difficulty was experienced in knowing how much material had been removed from the polished surface because the rate of removal of material by the ion beams varied from specimen to specimen, sometimes by as much as a factor of two. Despite these variations in rate of removal of material it was assumed that for any one specimen the rate of removal remained constant. It was also assumed that both ion beams removed material at the same rate.

Two specimens were produced; one in which the foil ($\sim 0.4 \mu\text{m}$ thick) was formed with its "top" and "bottom" surfaces at depths below the original surfaces of ~ 1.5 and $1.9 \mu\text{m}$ respectively (Fig. 7a) and the other with foil surfaces ~ 0.3 and $0.7 \mu\text{m}$ below the original surfaces (Fig. 7b).

The micrographs may be compared with that of the pre-annealed sample in Section 3.4 (Fig. 6) where the specimen had exactly the same annealing and polishing treatments, but the thin foil was ~ 12 to $15 \mu\text{m}$ below the polished surface. Note how the dislocation density becomes greater as the surface is approached and, in fact, is too high for an accurate determination, though in Fig. 7b the density has been estimated as $7 \times 10^{13} \text{m}^{-2}$. These dense dislocation tangles are similar to those reported by Hockey [8] in the near-surface regions of polished Al_2O_3 .

Neither specimen that had some material removed from its mechanically polished surface showed any tendency to crack or buckle and it is therefore concluded that the dislocation density

at the very surface must be even greater than that seen 0.3 to $0.7 \mu\text{m}$ below the surface.

4. Conclusions

(1) The Burgers vector of all dislocations analysed was $a/2 \langle 110 \rangle$.

(2) In a typical diffusion specimen the dislocation density, measured at a depth of about $12 \mu\text{m}$ below the mechanically polished surface was $\sim 4 \times 10^{12} \text{m}^{-2}$.

(3) The dislocations in samples annealed below 1400°C were in random orientations. At 1400°C some dislocations had begun to form hexagonal networks (twist boundaries) on the (111) plane and at 1600°C the networks were much more extensive.

(4) The dislocation density of a sample (pre-annealed at 1400°C) was $\sim 1.3 \times 10^{13} \text{m}^{-2}$ when measured at a depth of $\sim 12 \mu\text{m}$ below a mechanically polished surface (with no subsequent annealing). Close to the polished surface ($\sim 0.5 \mu\text{m}$ below) the dislocation density had risen by at least an order of magnitude. Bands of densely tangled dislocations, often difficult to resolve ($\sim 10^{15} \text{m}^{-2}$) were observed in specimens formed as close as possible to the polished surface.

(5) Dislocations in the near-surface regions of polished crystals were a result of mechanical damage during grinding and polishing. At greater depths below the polished surface (e.g. $12 \mu\text{m}$) the dislocations observed were probably a result of the crystal growth process, since their geometry is different from dislocations produced by polishing damage.

(6) To reduce the dislocation density of NiO by

a significant amount it was necessary to anneal a sample at a temperature higher than 1000° C. For maximum reduction in dislocation density an annealing temperature of at least 1400° C was required.

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