ing angular dispersion when the strain-induced anisotropy is small.

ACKNOWLEDGMENTS

Etching of High Purity Zinc*

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A method of etching high purity zinc to reveal various etch figures on {10$\bar{1}$0} planes is presented in this paper. Etch figures are formed by polishing in a dichromic acid solution after the introduction of mercury to the crystal surface. No measurable aging time is required to form etch figures at newly formed dislocation sites whem mercury is on the surface prior to deformation. The mercury concentrates at the sites where etch figures form and may be removed by vacuum distillation and chemical polishing before it appreciably affects the purity of the bulk of the crystal.

INTRODUCTION

CHEMICAL etching to reveal dislocations in crystals has been recognized by many investigators as a valuable tool for the study of dislocation configurations and interactions. Several reports have been made of etching procedures that reveal etch pits in zinc single crystals containing relatively high concentrations of various solute impurities such as cadmium,[1] iron,[2] and tin.[3] Techniques that rely on the presence of impurities precipitated on dislocations usually present several distinct disadvantages. First, the mechanics of dislocation motion are changed when impurities are present because of interactions between dislocations and impurity atoms; and second, an aging treatment must follow any experiments in order to allow bulk diffusion of the impurities to dislocations. Aging treatments following deformation are undesirable in zinc because the dislocation configuration can change appreciably during the aging. Hence, a technique is desired that does not require bulk doping and that will permit observation of dislocation configurations immediately after deformation takes place.

George[4] and Rosenbaum[5] have reported techniques for revealing dislocations on (0001) faces of high purity zinc. Dislocations that lie on the (0001) basal planes cannot be revealed by these techniques. Sinha and Beck[6] have recently reported a technique for revealing dislocations on {10$\bar{1}$0} surfaces of zinc. This technique did not produce etch figures at dislocations in the high purity crystals used in the present study. The difference in etching behavior may be attributed to differences in the impurities in the crystals or the composition of the chemical reagents used.

In view of the fact that a technique for revealing basal dislocations in high purity zinc without the addition of impurities to the bulk material was not available, an experimental study of chemical etching was made.

EXPERIMENTAL TECHNIQUES

Specimen Preparation

Zinc of 99.999% purity was further purified by zone refining in a helium atmosphere. Two separate molten zones were passed along a charge six feet in length at the rate of 2 in./h. A total of twenty single zones were passed through the charge. The zinc in the first one third of the total charge length was used for growth of the crystals designated as zone-refined. Single crystals of both 99.999% purity and zone-refined zinc were grown by the Bridgeman technique in graphite coated molds of Pyrex.

Specimens were prepared by acid sawing the as-grown crystals with 8N nitric acid on stainless steel wire, and by cleaving on (0001) planes after the crystals had been slowly cooled to the temperature of liquid nitrogen. The acid-sawed surfaces were chemically

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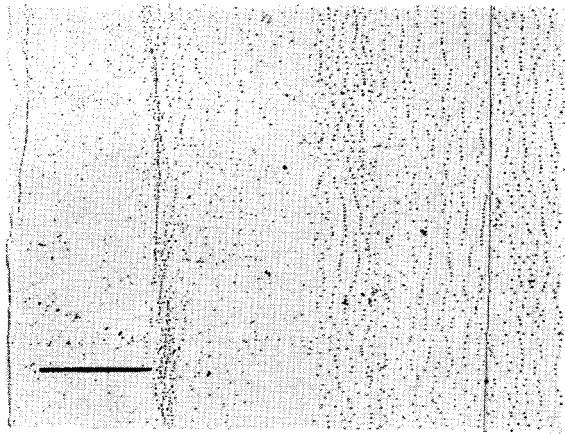[6] R. P. Sinha and P. A. Beck, J. Appl. Phys. 32, 1222 (1961).

Fig. 1. Etch figures revealed on a $(10\bar{1}0)$ prism plane. Line indicates $[\bar{1}2\bar{1}0]$ direction. Magnification ×100.

lapped flat on a slowly turning Lucite disk covered with a thin film of 8N nitric acid.

Polishing and Etching

Etch figures were produced with the four solutions listed below:

P-1   160 g CrO_3
       20 g Na_2SO_4
       500 ml distilled water
P-2   Equal parts of: Methanol
                        30% H_2O_2
                        16N HNO_3
P-3   160 g CrO_3
       500 ml distilled water
E   One part: 1 g $Hg(NO_3)_2$
                    1 ml 16N HNO_3
                    500 ml distilled water
       Two parts: distilled water.

The crystals were polished by dipping in solution P–1 for 20 to 100 sec with mild agitation. The crystals were occasionally dipped in solution P–2 to accelerate the polishing process. This solution removes the CrO_3 film that builds up on the surface. The last step in the polishing procedure consisted of dipping the crystals in solution P–2. Relatively rapid corrosion of crystals was noted when the CrO_3 film was not removed. After polishing, the crystals were rinsed in distilled water and dried in an air blast.

The etching procedure follows the steps listed below:

1. Dip with mild agitation in solution E, 5–6 sec.
2. Dip with mild agitation in solution P–1, 5–6 sec.
3. Dip with mild agitation in solution P–3, 2–3 sec.
4. Rinse in running tap water.
5. Rinse in running distilled water.
6. Dry in an air blast.

Best results are obtained when the polishing procedure is immediately followed by the etching procedure.

A typical example of the result obtained on a $(10\bar{1}0)$ crystal face is illustrated in Fig. 1. It is shown in the accompanying paper[7] that the individual etch figures represent dislocation intersections with the crystal surface.

OBSERVATIONS

Several characteristics of the etching procedure were observed that are relevant to an explanation of the etching mechanism.

(1) Etch figures consist of small hillocks or pips rather than etch pits as determined by microscopic examination with side illumination. The size of these pips is a function of the time the specimen is immersed in solution E. Larger pips are formed if the specimen is immersed for a longer time in solution E.

(2) The presence of mercury introduced by solution E has virtually no effect on the rate at which material is removed from prism surfaces by the P–1 polish with
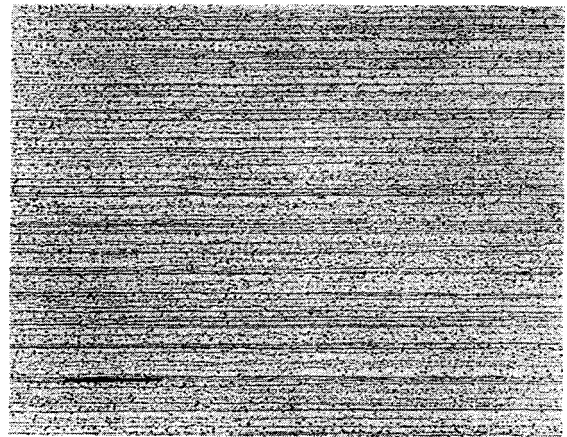
(a)
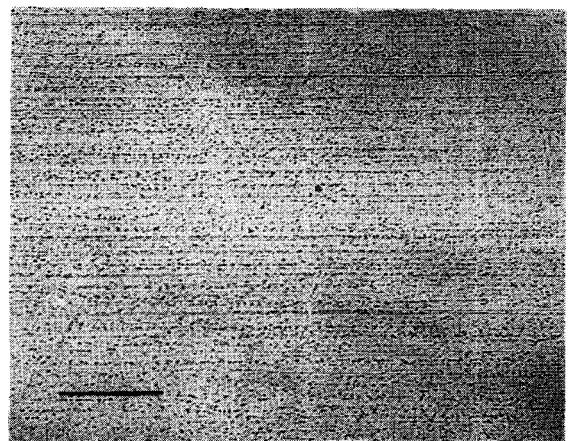
(b)

Fig. 2. Variation of etch figure densities with prism plane orientation. Twisted specimen. (a) Prism plane. (b) 5.5° from a prism plane. Magnification ×150.

[7] R. C. Brandt, K. H. Adams, and T. Vreeland, Jr., J. Appl. Phys. **34**, 591 (1963), following paper.

intermittant rinses in P–2. With or without prior treatment with the E solution the polishing rate was found to be 0.25 μ/sec as determined with the fine focus scale on a microscope after a 100-sec polish treatment.

(3) In specimens that have previously been etched, new etch pips form at areas of new deformation upon immersion in the polishing solutions P–1 and P–3. This will occur even if the mercury was introduced several weeks previous to the deformation.

(4) A specimen was bent while it was in solution P–1 during step 3 of the etching procedure. The succeeding steps of the etching were then taken as usual. Examination of the surface showed a pip density considerably
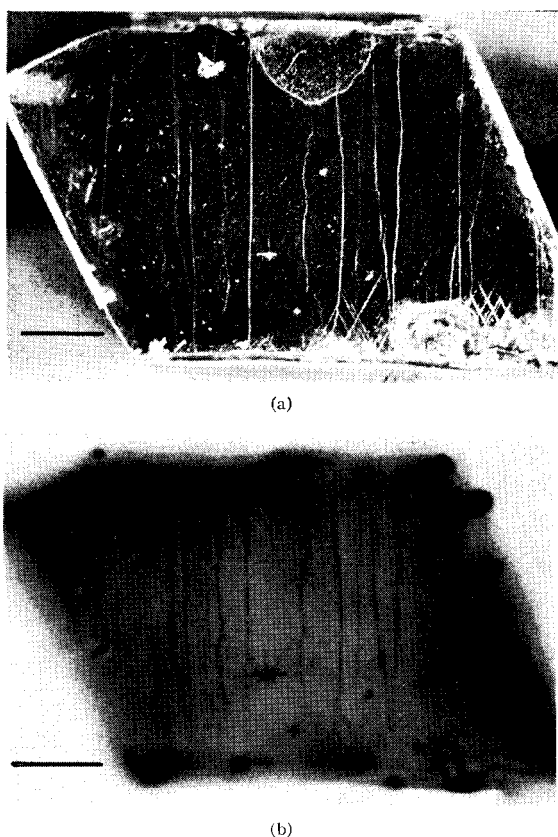

(a)

(b)

Fig. 3. (a) Prism plane of specimen etched with radioactive Hg. (b) Autoradiogram of corresponding surface. Magnification ×5.

in excess of the initial density. The majority of the pips could be associated only with dislocations formed during the deformation.

(5) A grid of gold electrodes, 0.2 mm in diameter, was vacuum deposited on polished prism surfaces of several specimens. Measurement of capacitance on unetched specimens indicated a coherent oxide layer of around 50 Å thickness. Etched specimens had electrical shorts between the electrodes and specimen.

(6) Etching is sensitive to the crystallographic orientation of crystal surfaces that are perpendicular to the (0001) basal plane. Good etch figures can be obtained on surfaces oriented within about 5° of the {10$\bar{1}$0} prism
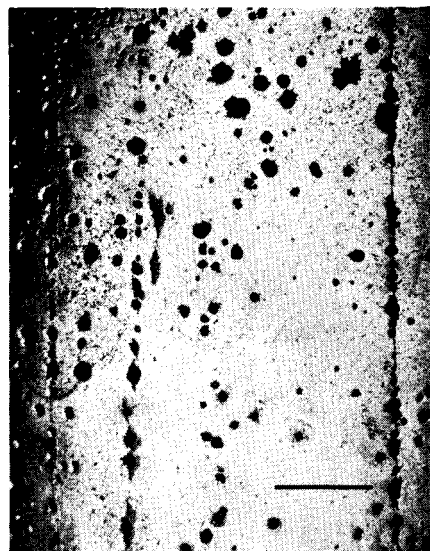

Fig. 4. Autoradiogram of a cylindrical specimen etched with radioactive Hg. Magnification ×50.

planes. Figure 2(a) shows a region of the prism surface of a crystal twisted about the c axis. Figure 2(b) shows a region which is oriented approximately 5.5° from the prism plane. A lower density of pips is observed in Fig. 2(b) as compared to Fig. 2(a). At angles greater than 5° from prism surfaces the etch pip density is observed to be lower while the surface becomes relatively rough as compared to prism surfaces. No pips can be observed on surfaces at angles greater than 15° from prism surfaces.

(7) A cylindrical specimen oriented with the c axis of the crystal along the cylindrical axis was etched and then placed in an 8.N HNO$_3$ solution saturated with H$_2$S. Dark bands of HgS formed on the specimen surface within 15° of {1$\bar{2}$10} planes. No HgS was observed on {10$\bar{1}$0} surfaces. This indicates a relatively low concentration of Hg on prism surfaces.

(8) Repolishing after etching is greatly facilitated by placing the specimens in a high vacuum for 12 h or

Fig. 5. Autoradiogram of a twisted and twinned specimen etched with radioactive Hg. Magnification ×50.

more. After the vacuum treatment, a good polish can be obtained by removing as little as 50 μ of the crystal surface. Without the vacuum treatment, several thousand μ must be removed to obtain a good polish.

(9) Several specimens were etched by an E solution containing 97% natural mercury and 3% Hg^{197} (a γ emitter). Measurements were made of the gamma activity of prism surfaces of the specimens and of control solutions. The following results were obtained.

(a) 65±6 $\mu g/cm^2$ of mercury were deposited on the specimens in the standard etching procedure.

(b) A vacuum treatment at 2×10^{-5} mm Hg for $10\frac{1}{2}$ h at 25°C removed 57% of the mercury originally on a prism surface.

(c) After the vacuum treatment, 3 min of polishing (30 sec in P–1, 2 sec in P–2, repeated) removed 50% of the mercury remaining on a prism surface.

(10) Autoradiograms were made of specimen surfaces after the etching procedure was carried out using the radioactive E solution. Figure 3(a) shows a specimen containing a number of subboundaries and twins. The autoradiogram of this specimen, a Kodak lantern slide plate, is shown in Fig. 3(b) (reversed in printing). Both the subboundaries and twins are revealed in the autoradiogram, indicating that mercury concentrates at these sites. Figure 4 shows the surface of a cylindrical crystal coated with an exposed and developed emulsion. The dark spots in the emulsion correspond to subboundaries and isolated etch figures on the specimen. Figure 5 shows a prism surface of a crystal which has been twisted about the c axis and twinned in handling. The emulsion was exposed by γ rays eminating from twin boundaries and isolated etch figures.

DISCUSSION

The autoradiograms show that mercury concentrates at etch figures on prism surfaces of the zinc crystals. We may assume, as is shown in the following paper,[7] that these etch figures correspond to dislocation intersections with the surface. The very rapid formation of etch figures at freshly formed dislocation sites indicates that the mercury moves to these sites by surface diffusion over the coherent oxide layer. The attraction between mercury and dislocations may arise from a strain field in the oxide at the dislocation sites or from a perturbation of the electric field,[8] or both. The concentration of mercury at these sites is great enough to

make an electrical short between deposited gold electrodes on the oxide and the zinc substrate. The mercury lowers the rate of chemical attack at dislocation sites on subsequent polishing in the dichromic acid solution, causing hillocks to form. Observation 3 indicates that surface diffusion of the mercury is rapid while diffusion of mercury into the bulk of the crystal is relatively slow.

The orientation dependence of the etching on surfaces perpendicular to (0001) may be explained if we assume that mercury also concentrates at monatomic steps and larger terraces on the crystal surface. The surfaces near the prism planes should have a low density of terraces, while $\{1\bar{2}10\}$ surfaces could be highly terraced, and attract a relatively high concentration of mercury. This is evidenced by the formation of HgS near $\{1\bar{2}10\}$ planes upon polishing in the HNO_3 solution saturated with H_2S, and could account for the relatively rough surface produced by the polish on surfaces not near $\{10\bar{1}0\}$.

Masking of all surfaces other than the prism surface to be examined will reduce the total concentration of mercury introduced by the etching procedure. A masked specimen of 1 cm^3 with a 1-cm^2 prism surface will pick up a total atomic ratio of approximately 3×10^{-7} of mercury. The majority of this mercury can be removed by vacuum distillation and chemical polishing before an appreciable concentration diffuses into the bulk of the crystal, as may be deduced from observations 3, 8, 9(b), and 9(c) above. The removal of mercury will be considerably accelerated by elevating the temperature of the specimen during the vacuum treatment.

SUMMARY AND CONCLUSIONS

Surface doping of high purity zinc crystals with mercury followed by polishing in a dichromic acid solution causes etch figures to form at dislocation sites on $\{10\bar{1}0\}$ surfaces. The etch figures form at dislocations produced by deformation without an aging treatment. This implies that mercury moves to the fresh dislocations by surface diffusion. Subsequent removal of mercury by vacuum distillation and chemical polishing permits a good polish to be produced, so that the crystal can be annealed and retested without appreciably affecting its purity.

ACKNOWLEDGMENTS

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