New Dislocation Etchant for Zinc

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A new dislocation etchant for zinc reliably reveals etch pits at both grown-in and fresh dislocations without decoration treatments. The strongest proof that the etch pits are formed where dislocation lines cut the surface is provided by (1) the characteristic etch pattern formed after indentation; (2) polygonization walls; (3) the coincidence of etch pits. Various other observations support the main evidence. This etchant produces rectangular-shape etch pits.

Introduction

A dislocation etch pits on $(11\bar{2}0)$ surfaces of zinc crystals was reported by Mikuriya and Ohkohchi[1]. Their etchant distinguishes dark and light pits in the form of rhombic etch pits on $(11\bar{2}0)$ surfaces of zinc crystals.

The purpose of this paper is to describe the characteristics of a new dislocation etchant for zinc and to establish the reliability of the etchant. This etchant is substantially different from the Mikuriya-Ohkohchi etchant in that it produces rectangular rather than rhombic pits.

Experimental Procedure

Zinc single crystals with 99.999% purity were grown at a rate of 12 mm per hour using a Bridgman type furnace in a nitrogen atmosphere. Some section of crystals were cut into parallelepipeds measuring $10\times5\times15$mm using an etching-cutter; one set of parallel surfaces of parallelepiped contained $(11\bar{2}0)$ planes of the crystal and the long axis was parallel to a $\langle0001\rangle$ direction. The parallelepiped specimens were polished by chemical methods to remove the deformed surfaces resulting from etch cutting. Prior to the polishing operation the specimens were cleaned with 50% HNO_3, and then were first chemically polished by letting them move slowly on a cotton saturated with a solution of 50% HNO_3. Surface strains that may have been introduced by this polishing were removed by immersing the specimens into a solution containing 32 g CrO_3, 4 g Na_2SO_4, 2 g $Cu(NO_3)_2\cdot3H_2O$ and 100cc deionized water for 1 to 5 minutes at room temperature. After polishing, the specimens were rinsed in flowing water. During the chemical polishing in this solution, a yellow-brown chromate film was generally formed on the surface. This film was removed by letting the specimens move slowly into a solution[2] containing 50cc ethyl alcohol, 20cc 30% H_2O_2 and 5 cc concentrated HNO_3 for about 10 seconds. After polishing, the specimens were rinsed in flowing water. The sequence chemical polishing removed the surface strains resulting from polishing and provided a smooth $(11\bar{2}0)$ surface of zinc crystals. Then they were etched in the solution which consisted of 2 cc concentrated HNO_3, 6 g NH_4Cl, 8 cc concentrated HCl and 200cc deionized water. The etching was performed at room temperature with mild agitation; pits were produced in about 10 seconds. Straight after etching, as-etched surfaces were rinsed in flowing water, ethyl alcohol, methyl alcohol and then dried in a stream of air. Best results are obtained when the polishing procedure is immediately followed by the etching procedure.

Results and Discussions

Figure 1 shows the etch pits which were formed. The pits are rectangular in shape and randomly distributed on the $(11\bar{2}0)$ surface. Rows of closely spaced etch pits and branching

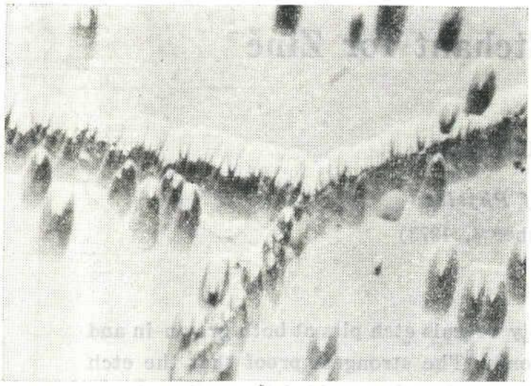
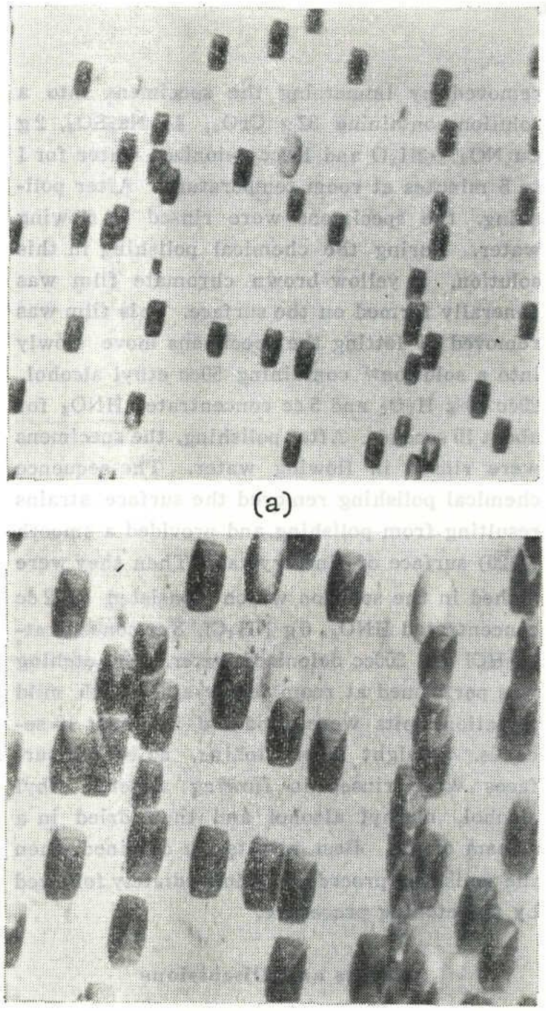


Fig. 1. Etch pits produced on a $(11\bar{2}0)$ surface of a zinc single crystal. ×660.



(a)

(b)

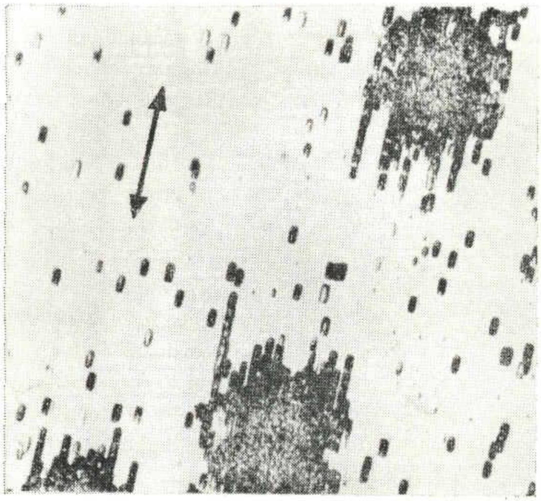
Fig. 2. Pit size as a function of etching time on the same area of $(11\bar{2}0)$ surface. (a) 10 sec etch, (b) 20 sec etch.

rows of etch pits resembling low-angle tilt boundaries were observed. This arrangement of etch pits and the regular rectangular shape of them suggests that the etch pits are the sites of dislocations.

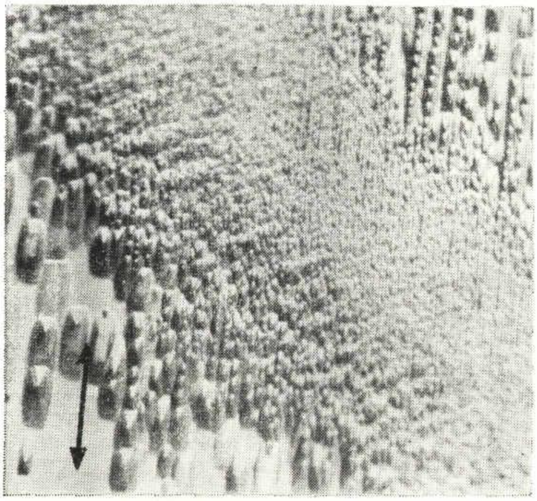
Dislocation lines have appreciable lengths so progressive etching must increase the size of well-defined rectangular etch pits on $(11\bar{2}0)$ surfaces without changing the grown-in dislocation density. This behavior is illustrated in Figs. 2 (a) and (b). The crystal surface was recorded after etching for 10 seconds and the same area was photographed again after etching for an additional 10 seconds. The dislocation density allows association of the individual etch pits in Fig. 2 (b) with those in Fig. 2 (a). The fact that the etch pits remain essentially constant in number and retain their sharpness while getting broader with progressive etching strongly indicates that the etch pits are the sites of dislocations.

Indentation of a crystal surface should produce dislocation patterns near indentations. Examination of these dislocation distribution patterns can be used to confirm the reliability of the etchant in revealing fresh dislocations. Dislocation patterns around indentations were observed on $(10\bar{1}0)$ surfaces in zinc[3] and a (111) surface in silver[4]. The technique of producing patterns from indentation of zinc crystal surfaces was developed in the present study. A specimen was chemically polished, indented with a Vickers indenter, and etched for about 10 seconds. Figure 3 (a) shows complex pip patterns produced by local indentations. The arrangement of etch pits along slip traces suggests that this etchant is capable of producing etch pits at fresh dislocations. A study of dislocation etch-pit patterns around surface scratches yields similar confirmation. Figure 3 (b) shows that many fresh dislocation etch pits are formed near the scratch as a result of moving a Vickers indenter slowly across the crystal surface.

One of the interesting observations relating to deformed crystals is the occurrence of glide polygonization. By annealing the deformed crystals for about 720 minutes at 170°C in a nitrogen atmosphere, the polygonized dislocations were revealed with etch pits as shown in Fig. 4. The etch pits seen are found to be aligned along slip planes. They also show a-



(a)



(b)

Fig. 3. (a) Complex pip patterns produced by local indentations. (b) Arrays of dislocation etch pits due to a scratch. Slip-plane trace parallel to arrow.

lignments in a direction perpendicular to the slip-plane trace. The occurrence of such pattern seems to be a strong evidence that etch pits are edge dislocations.

Fig. 4. Polygon boundaries formed by annealing for 720 min at 170°C in a nitrogen atmosphere. Slip-plane trace parallel to arrow. ×90.

Summary

Evidence has shown that the HCl-NH_4Cl-HNO_3 solution is capable of revealing etch pits at both grown-in and fresh dislocations on the $(11\bar{2}0)$ surfaces of zinc without decoration treatments. Unlike the Mikuriya- Ohkohchi etchant, this etchant produces rectangular pits.

Acknowledgment

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