The Dislocation Etchant for β -CuZn Crystals

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A new dislocation etchant was found which developed etch pits on the {001} plane of β -CuZn single crystals. The most suitable composition of it is 20 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.8 cm³ of HCl and 100 cm³ of distilled water. Etch pits are ellipse or spindle-shaped with their major axis in the $\langle 001 \rangle$ direction. The correspondence of etch pits to emerging dislocations was examined and it was found that both aged and fresh dislocations could be observed as etch pits.

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I. Introduction

The etch pit technique is recognized as one of the significant methods in studying the dislocation behavior at a relatively early stage of deformation. The most important point in the use of this method is that etch pits should correspond one to one to dislocations emerging at the surface. Therefore, the study on the dislocation behavior with the etch pit technique is limited to several kinds of metals and alloys on which the correspondence between etch pits and dislocations has been confirmed.

Observation of etch pits has been reported on β -CuZn⁽¹⁾, but these etch pits do not seem to correspond to dislocations. In the present study, the possibility of developing etch pits on the {001}, {011} and {112} surfaces has been examined with several etching solutions. It was found that on the {001} surface an etchant composed of ammonium persulfate, hydrochloric acid and distilled water developed etch pits at both aged and fresh dislocations. The etchant found in the present study may be useful for studying the behavior and arrangement of dislocations in plastically deformed β -CuZn.

II. Experimental Procedure

An ingot of β -CuZn (48.9 at% Zn) was prepared from 99.99% copper and 99.9% zinc. Single crystals of $4 \times 3 \times 150$ mm³ were grown by the Bridgman method in argon gas atmosphere. After determining the orientation by the Laue back reflection method, crystals with the top surface within 0.070 rad from {001}, {011} and {112} were selected. Specimens 3 cm or 6 cm in length were cut from the central part of the crystals using an acid sawing machine. They were homogenized at 1073 K for 36 ks in a silica tube filled with argon gas to minimize the evaporation of zinc, and then furnace-cooled to room temperature.

Specimens were initially chemically polished in the solution composed of 30 cm³ of phosphoric acid, 30 cm³ of nitric acid, 40 cm³ of acetic acid and 0.1~0.2 cm³ of hydrochloric acid and electropolished in the solution composed of 90 cm³ of phosphoric acid and 10 cm³ of ethyl alcohol. They were then rinsed in distilled water and dried. After the etching by the testing solution, they were observed in an optical microscope with the interference contrast. Specimens 6 cm in length were stretched with a gauge length of 4 cm and a strain rate of $4.2 \times 10^{-4} \text{ s}^{-1}$ at room temperature.

III. Results and Discussion

1. Developing of etch pits

Bassi's solution⁽¹⁾ composed of $(\text{NH}_4)_6\text{Mo}_7$

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$O_{24} \cdot 4H_2O$ and HCl is the only etchant reported for β -CuZn. The correspondence of etch pits developed by this etchant to the emerging dislocations, however, does not seem satisfactory, because the observed etch pit density in the deformed specimen is far less than the estimated dislocation density. In the present experiment, Bassi's solution and its modified ones were tested to examine whether or not the correspondence of etch pits to the emerging dislocations could be obtained. However, on either planes the etch pits which appeared to correspond to dislocations were not developed. Next, the etchants used on the low index planes of copper single crystals reported by Lovell⁽²⁾, Livingston⁽³⁾ and Young⁽⁴⁾ were tested on the low index planes of β -CuZn, but etch pits did not appear on any crystallographic planes. It was found out, however, that solutions composed of $(NH_4)_2S_2O_8$ and a small amount of HCl developed etch pits on the $\{001\}$ plane. Hereafter, only etch pits on the $\{001\}$ plane will be described.

Photograph 1(a)~(j) were taken on the same

area of a specimen which were treated by repeating etching and electropolishing. Etchants were made of 100 g of distilled water and given amounts of $(NH_4)_2S_2O_8$ and HCl. In Photo. 1, pictures on the right side are taken by using the etchants with the higher volume of HCl, and those in the lower parts by using the etchants with larger amounts of $(NH_4)_2S_2O_8$. This increase of $(NH_4)_2S_2O_8$ and HCl tends to increase the rate of resolution and to make the surface faceted. The following solution was found to be most suitable for etch pitting; 20 g of $(NH_4)_2S_2O_8$, 0.8 cm³ of HCl and 100 cm³ of distilled water; the temperature of solution, 293 K. In Photo. 1 linear arrays and isolated etch pits in one picture correspond well with those in other pictures. Therefore, it is considered that these etch pits have been developed at line defects, i.e., dislocations, appearing on the surface. As the specimen is in the annealed condition, these etch pits correspond to the aged dislocations.

The shape of etch pits seems to be ellipse- or spindle-shaped with its major axis in the $\langle 001 \rangle$

Photo. 1 An area etched with the solution of $(NH_4)_2S_2O_8$ (g) and HCl (cm³) in 100 cm³ distilled water at 293 K for 60 s. The amounts of the constituents are varied. (a) (5 g, 0.08 cm³), (b) (20 g, 0.08 cm³), (c) (40 g, 0.08 cm³), (d) (5 g, 0.8 cm³), (e) (20 g, 0.8 cm³), (f) (40 g, 0.8 cm³), (g) (5 g, 1.6 cm³), (h) (20 g, 1.6 cm³), (i) (40 g, 1.6 cm³).

direction. Photograph 2 shows etch pits on the surface, parallel to $\{001\}$ plane, having a hollow at the center. Using an optical microscope equipped with a goniometer stage, the following was found: (1) At the bottom, where the surface was parallel to the $\{001\}$ plane, etch pits did not appear. (2) Etch pits appeared on the plane inclined by $0.0175 \sim 0.070$ rad from the $\{001\}$ plane. The size of etch pits became smaller as the inclination increased and they disappeared on the plane with deviations of more than 0.070 rad from the $\{001\}$ plane.

2. Correspondence of etch pits to dislocations

In β -CuZn it has been reported that even by rapid quenching the ordering reaction cannot be suppressed and the equilibrium degree of order is approximately attained⁽⁵⁾. Therefore,

Photo. 2 Etch pits appearing around a hollow. Shaded area in the figure shows the region where the development of etch pits is favoring. The X and Y axes indicate the surface angles deviated from the $\{100\}$ plane.

dislocations will move as superlattice dislocations composed of two unit dislocations connected with the antiphase domain boundary. The calculated separation between the two unit dislocations is 8.8 nm for edge dislocations and 5.6 nm for screw ones⁽⁶⁾. Therefore, a superlattice dislocation will be observed as a single etch pit.

When crystals are deformed, slip traces are formed and dislocation arrays may be developed along them. Therefore, if etch pit arrays are revealed along slip traces, the correspondence between etch pits and multiplied fresh dislocations is established, although the correspondence is not individual but in a group. Photograph 3(a) and (b) were taken in the same area. Photograph 3(a) was taken after the specimen was etched and deformed 0.5% in plastic strain. Subboundaries and grown-in dislocations were observed together with slip lines. After the above treatment, the specimen was polished and etched again. Then Photo. 3(b) was taken. The correspondence between strong slip lines and arrays of etch pits is evident. In addition, there can be observed many etch pits along faint slip lines and between them. The results imply that the dislocation multiplication has taken place between slip lines as well as in slip lines, and that the multiplied dislocations, i.e. fresh dislocations have been revealed as etch pits.

The change in the distribution of etch pits on the $\{100\}$ plane by annealing is shown in Photo. 4. The crystals with the long axis

Photo. 3 Correspondence between slip traces and etch pits in the same area. (a) Etched and deformed. (b) Polished and etched after the treatment (a).

Photo. 4 Distributions of etch pits in the same slip band. (a) As deformed, (b) After annealing at 673 K for 100 s, (c) After annealing at 673 K for 200 s, (d) After annealing at 673 K for 300 s.

parallel to [015] was deformed to 0.2% in plastic strain at room temperature. In Photo. 4(a) a slip band along the trace of the $(\bar{1}01)$ plane, containing etch pits of high density ($8 \times 10^{10} \text{ m}^{-2}$), is observed. A transmission electron micrograph taken by Yamagata *et al.*⁽⁷⁾ shows the existence of closely spaced long superlattice dislocation dipoles. Therefore, each etch pit may correspond to a superlattice dislocation dipole. Photograph 4(b)~(d) show the distribution of etch pits in the same slip band, taken after annealing at 673 K for 100, 200 and 300 s, respectively. The etch pit density decreases to $1.8 \times 10^{10} \text{ m}^{-2}$ by annealing only for 300 s. Also, the difference in the distribution of etch pits between the slip bands and the non-slipped regions becomes obscure as the annealing proceeds.

The transmission electron microscopy on etched thin foils provides the most powerful evidence to show the correspondence of etch pits one to one to dislocations emerging at the surface. In spite of many trials of this method, the results have not always been successful⁽⁸⁾⁽⁹⁾. In the present study thin foils with the top surface parallel to the (100) plane were prepared from a [015] crystal deformed 2% in plastic strain. They were electrolytically polished to the thickness transmittable in the electron microscope and then etched in the solution.

Photo. 5 Transmission electron micrograph of an etched foil. Schematic representation of dislocations and their contrasts at emerging points are also shown.

Photograph 5 was taken from such a foil. There can be observed isolated dislocations and a few dislocation dipoles inclined from the

surface. If the emerging point of dislocations at the surface are preferentially etched, bright contrasts are expected there, as observed in copper⁽⁸⁾, Fe-Si alloy⁽⁹⁾ and tungsten⁽¹⁰⁾. In the present case peculiar contrasts are observed at almost all the emerging points of dislocations. The bright or dark contrasts are observed there, elongated parallel to the [001] direction, which corresponds to the major axis of etch pits observed in the optical microscope. These contrasts may result from the strain field of dislocations emerging at the surface where an etch pit is developed. These contrasts are not observed in unetched foils. Compared to the case of copper, the etching rate perpendicular to the surface is smaller than that parallel to the surface. Therefore, etch pits in the present case are not very clear in the electron microscope.

The above results show that there is good correspondence between etch pits and dislocations. Therefore, the present etchant revealing etch pits on the {001} plane of β -CuZn is applicable to the study of the arrangement and distribution of dislocations at a relatively early stage of deformation (the dislocation density lower than $5 \times 10^{11} \text{ m}^{-2}$), especially to the study of the micro-yield region where slip traces cannot be observed.

IV. Conclusion

The new etchant for dislocations was found on the {001} surface of β -CuZn. The typical composition of the etchant is 20 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.8 cm³ of HCl and 100 cm³ of distilled water. By using several methods, it was concluded that the etch pits corresponded well to the dislocations and this etchant could be used to study the early stage of plastic deformation.

REFERENCES

- (1) G. Bassi and J. P. Hugo: *J. Inst. Metals*, **87** (1958-59), 155.
- (2) L. C. Lovell and J. H. Wernick: *J. Appl. Phys.*, **30** (1959), 590.
- (3) J. D. Livingston: *J. Appl. Phys.*, **31** (1960), 1071.
- (4) F. W. Young, Jr.: *J. Appl. Phys.*, **32** (1961), 192.
- (5) D. Chipman and B. E. Warren: *J. Appl. Phys.*, **21** (1950), 696.
- (6) M. J. Marcinkowski: *Electron Microscopy and Strength of Crystals*, Interscience Pub., (N.Y.), (1963), p. 333.
- (7) T. Yamagata, H. Yoshida and Y. Fukuzawa: *Trans. JIM*, **17** (1976), 393.
- (8) A. W. Ruff, Jr.: *J. Appl. Phys.*, **33** (1962), 3392.
- (9) H. W. Pickering: *Acta Met.*, **13** (1965), 437.
- (10) Y. Nakayama, S. Weissmann and T. Imura: *Direct Observation of Imperfections in Crystals*, Gordon and Breach, (N.Y.), (1962), p. 573.