JOURNAL OF MATERIALS SCIENCE 11 (1976) 1501–1508

Dislocation etch pits in gold

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Newly developed etch-pitting technique for gold is reported. A one-to-one correspondence is obtained between etch pits and dislocations, with etchants of 1 : 3 aqua regia and aqua regia plus suitable modifiers. The usefulness of these etchants has been established by several experimental results, such as the appearance of etch pit rosette patterns produced by indentation, correspondence between slip line and pit arrays in deformed crystals and climb polygonization arrays after annealing. It is also confirmed that the etchants are capable of differentiating positive and negative edge dislocations.

1. Introduction

The dislocation etch pit technique for producing etch pits at the points of intersection of undecorated dislocations has provided an effective way of studying the dislocation densities and distributions arising from the deformation of both non-metallic and metallic crystals, since the early work of Gilman and Johnston [1] in Lif, Stein and Low [2] in Fe–Si alloys, and Lovell and Wernick [3] in Cu. Detailed studies of etch pitting in copper were subsequently carried out by Livingston [4–6], Young [7–10] and Hordon [11] to establish many features of the plastic deformation in copper crystals. Basinski and Basinski [12], and Basinski *et al.* [13] were the first to realise the advantage of using etch pit methods to supplement observations made by transmission electron microscopy in working out the mechanisms of plastic deformation and also fatigue deformation in single crystals of copper.

A dislocation etch pit technique for silver crystals was first introduced by Levinstein and Robinson [14]. The technique has been applied to studies of dislocation arrangements in deformed silver crystals by Robinson and his colleagues [15–17]. Recently, in order to provide a one-to-one correspondence between etch pits and dislocations, a modification of the etchant used by Levinstein and Robinson was proposed by Chen and Hendrickson [18, 19].

These techniques have the advantage of being of a non-destructive nature and producing a large observable area. This enables us to directly observe the response of dislocation behaviour in the same specimen

Although in f c c pure metals, several reliable etchants for revealing dislocations were established for copper and silver, until the present time there has been no etch-pit technique for gold reported in the literature. A research programme has been undertaken to establish a reliable etch pitting technique for gold, which can contribute to a study of the fundamentals of plastic deformation or of mechanisms on corrosion concerned in dislocations in f c c metal crystals. The purpose of this paper is to report a detailed investigation of the etching characteristics of new dislocation etchants which yield etch pits at both grown-in and fresh dislocations on the {1 1 1} planes of gold. The reliability of the etchants were confirmed by several experimental results, such as the appearance of an etch-pit rosette pattern produced by indentation, and correspondence between slip lines and pit arrays in a deformed crystal, or climb polygonization arrays after annealing. Based on the size and appearance of etch pits, the correlation between types of pits and types of dislocations is also discussed.

2. Experimental procedures

2.1. Crystal growth and cutting

The starting material used in this experiment was

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in the form of sheet, purity 99.99%. A gold single crystal about 30 mm in length and $8 \times 10\,mm^2$ in rectangular cross-section was grown by the Bridgman method in a dynamic vacuum of 5×10^{-5} Torr at a growth rate of $3\,cm\,h^{-1}$. A split high purity graphite mould was employed. The bulk single crystal was cemented to a goniometer and Läue-reflection photographs were taken to determine the positions of the $\{1\,1\,1\}$ plane. The crystal was sectioned parallel to the $\{1\,1\,1\}$ plane within $\pm 2°$ and then cut into parallel pipeds measuring $4 \times 4 \times 25\,mm^3$, using a spark-cutter attachment with tungsten wire. With this orientation, one pair of crystal faces were parallel to the $(1\,\bar{1}\,\bar{1})$ plane and the long axis was parallel to the $[6\,5\,1]$ direction.

2.2. Surface preparations

The damage due to sparking could be entirely removed by mechanical polishing, and chemically polishing off a layer of 0.7 mm from the sectioned surfaces. The mecahnical polishing was performed using 400, 600, 800 and 1200 grit papers, followed by rubbing with aluminium oxide grinding powders. The crystals were then dipped for several minutes into aqua regia.

Since the surface obtained by this chemical polishing was rough, the crystals were then electropolished. The electrolyte was of the following composition: potassium syanide, 5 g; anhydrous potassism carbonate, 10 g; silver cyanide, 2 g; and distilled water, 250 ml [20]. A stainless steel cathode was used. The solution was maintained at a temperature of about 25° C and stirred thoroughly during polishing. The voltage of the polishing cell and the current density ranged from 10 to 14 V and $0.01\,A\,mm^{-2}$ respectively. The polishing rate was of the order of $1.5\,\mu m\,min^{-1}$.

2.3. Annealing

After studying the as-grown dislocation structure, the crystals were given a cyclic annealing treatment to lower the dislocation densities. The crystals were sealed in a quartz tube in a dynamic vacuum of 1×10^{-4} Torr and annealed in a furnace at 850 to 1030° C for 110 h. After annealing, the crystals were carefully electropolished again to remove rough layers caused by any evaporation during the annealing.

2.4. Etch pitting

The basic solution employed to produce etch pits at dislocations on the $\{1\,1\,1\}$ surface of gold single crystals consisted of one part of conc. nitric acid and three parts of conc. hydrochloric acid, which will be referred to as the A.R. The quality of an etchant can be improved by adding impurities to the solvent, which poison the kink sites in the surface steps and make the pits deepen [21]. Various cations of A^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, and Cu^{2+}, and Br_2 were added to the basic solution of 1:3 aqua regia to find which impurities act as the active poison in order to produce good etch pits. The various etchants for gold employed in this experiment are summarized in Table I.

TABLE I Various dislocation etchants for gold

Etchant	HNO_3 (ml)	HCl (ml)	Impurity
A.R.	15	45	–
A.R.Br	15	45	Br_2, 0.6 ml
A.R.Cr	15	45	CrO_3, 0.24 g; H_2O, 1.2 ml
A.R.Fe	15	45	$FeCl_3 \cdot 6H_2O$, 0.6 g
A.R.Al	15	45	$AlCl_3$, 0.6 g
A.R.Zn	15	45	$ZnCl_2$, 0.6 g
A.R.Cu	15	45	$CuCl_2$, 0.6 g

Etching times and temperatures in these solutions ranged from 1 to 2 min and from 15 to 20° C respectively, except for etchant A.R.Br, which required at about 2° C. The as-etched surfaces were rinsed thoroughly in running water and dried with a cool air drier.

2.5. Indentation testing

Sewing needles were used for the production of dislocation arrays around indentations. The indentation loads were altered by shortening the upper part of the needle. A standard load of 0.15 or 0.03 g was applied for several seconds whilst letting the needle descend slowly, by using a thread.

2.6. Mechanical testing

Specimen was stressed by applying a pure bending moment using a four-point bending jig at room temperature. Etch pitting was performed using the A.R.Cu etchant. Before bending to just beyond the yield stress, etch pits were produced on the surface of the specimen. After unloading, the specimen was double etched, and in order to compare the distribution of etch pits before and after bending, ithe sample was single etched after electropolishing the surface.

3. Observation and discussion
3.1. Realiability of the etchants
3.1.1. Annealing effects
3.1.1.1. As-grown and annealed structures. As a preliminary experiment, two types of etchants referred to as A.R. and A.R.Br were employed for revealing dislocations. First, etch pits in an as-grown crystal were observed as shown in Fig. 1a. The etch pit densities in the as-grown condition were in the range 1 to 4×10^6 cm^{-2}. No sub-boundaries were observed. The dislocation densities in as-grown crystals of copper and silver grown from the melt by the Bridman method are generally of the order of 10^6 cm^{-2} [2, 4, 18]. The densities of etch pits in the as-grown crystal of gold are thus considered to be reasonable compared with other etch pit observations in as-grown crystals of copper and silver.

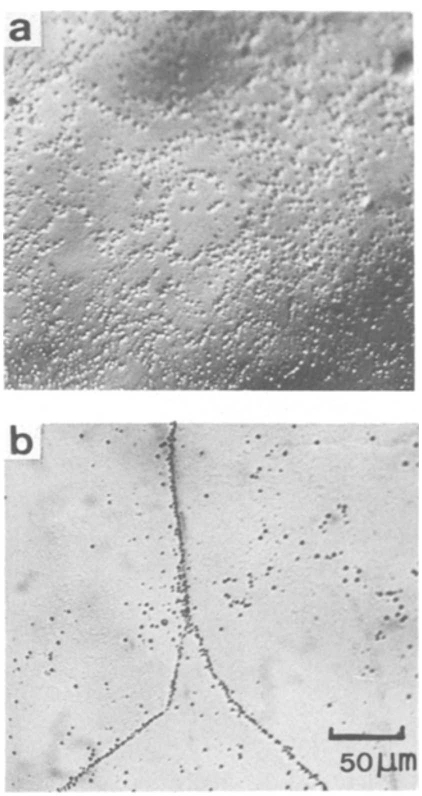

Figure 1 (a) Etch pit distribution in an as-grown crystal etched with A.R. etchant. (b) Different regions of the same crystal after annealing (A.R.Br etchant).

Subsequent annealing lowered the total density markedly, as shown in Fig. 1b. As annealed, the etch pit density within sub-grain averages about 5×10^5 cm^{-2}. A relatively higher density region is shown in Fig. 2. Conical etch pits were produced with the A.R.Br etchant, Two types of etch pits, one large and dark, and the other small and light were found. and the densities of both type of pits were approximately equal, as can be seen in the figure. This suggests that these different types of pits correspond to dislocations of opposite sign.

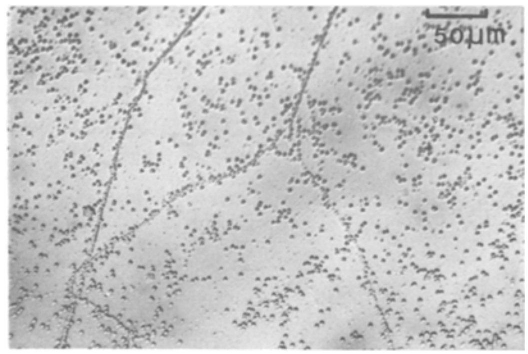

Figure 2 Sub-boundaries after annealing (A.R. etchant). Large and dark, small and light pits are revealed in approximately equal densities.

3.1.1.2. Climb polygonization. Well-defined climb polygonization was observed in the as-annealed crystal, as shown in Fig. 3, probably because the crystal was deformed locally by mishandling in the course of etching prior to the annealing. Similar etch-pit arrays of climb polygonization have been reported in bent or lightly deformed crystals of copper [4] and silver [18] after annealing at temperatures near the melting point. Polygonization boundaries are usually formed by the row of edge dislocations of the same sign perpendicular

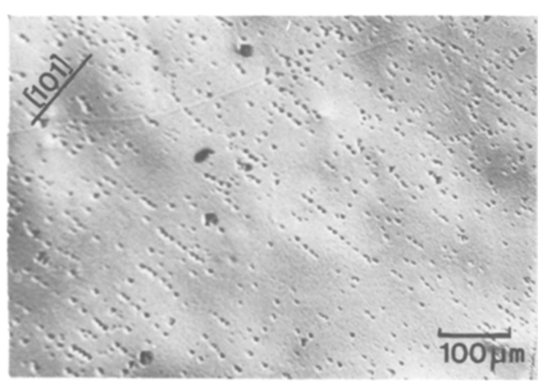

Figure 3 Climb polygonization after annealing (A.R. etchant).

to the slip direction ⟨1 1 0⟩. It appears clear that the boundaries were formed by the dark pits perpendicularly to the slip direction [1 0 1]. The evidence strongly suggests that the etchant is a reliable solution for revealing dislocations on {1 1 1} surfaces and the distinction between positive and negative edge dislocations.

3.1.2. Indentation testing

Indentation of a crystal surface which produces etch pit patterns when the surface is etched is an effective and convenient means of establishing the realibility of an etchant in revealing fresh dislocations. Moreover, it is known that dislocation patterns around indentations consist of dislocation half-loops, whose ends emerge on the crystal surface as pairs of pits which correspond to edge dislocations of opposite sign [18, 22–26].

Fig. 4 shows an etch-pit pattern in the vicinity of an indentation with the A.R.Br etchant. Here an indentation load of 0.15 g was applied for 5 sec. Rather short rosette arms were observed to lie along close packed directions of ⟨1 1 0⟩. Both large and small etch pits were found to be approximately equal in density around the indentation.

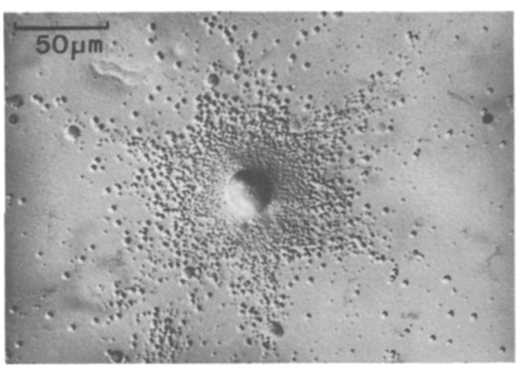

Figure 4 Rosette pattern due to indentation (0.15 g for 5 sec, A.R.Br. etchant).

Because the indentation load was considered to be too high to produce more sharply defined rosette patterns, the following indentations were made with a load of 0.03 g applied for 1 sec. Modified etchants referred to as the A.R.A and A.R.A.Cu, were then used to produce etch-pit patterns, since it was found that these were capable of producing more sharply defined triangular pits. A comparison between the various etchants will be shown in a later section. Fig. 5 shows typical rosette patterns around an indentation. made with the A.R.A and A.R.Cu etchants.

First, the crystal was etched with in A.R.Al, as shown in Fig. 5a, and then a layer of several microns was removed by electropolsihing before etching again in A.R.Cu, as shown in Fig. 5b. The area shown in the figure is identical. It may be seen from these figures that each rosette arm consists mainly of two rows of etch pits, one large and one small, and there is one-to-one pairing of large and small pits.

The feature of the rosette patterns and the appearance of large and small pits in each arm is similar to the observation of Chen and Hendrickson [18] in silver. They confirmed that large and small pits in silver correspond to the situation in which the compression side (extra-half plane side) of the near-edge dislocation lies in the acute and obtuse angle, respectively, between the slip plane of the dislocation and the surface. Thus the etchants of these types for silver corre-

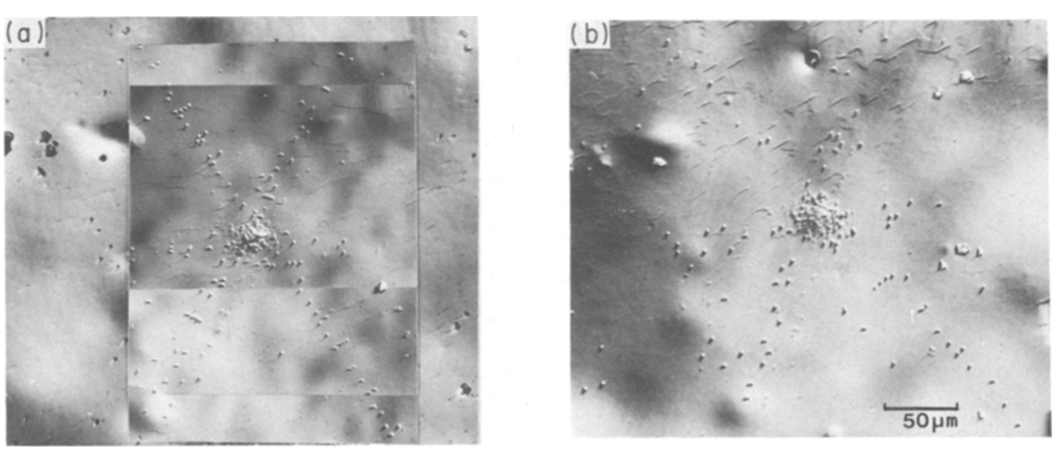

Figure 5 Rosette pattern showing a one-to-one pairing of large and small etch pits after indentation of 0.03 g for 1 sec. (a) Etched with A.R.Al etchant. (b) The same area fter removing several microns from the surface (A.R.Cu etchants).

spond to the Livingston etchant [5] for copper where dark and light pits occur if the compression side of the edge dislocation lies in the acute and obtuse angle, respectively, between the slip line and the surface. From the present results and a comparison with the earlier work [18], it, therefore, appears conclusive that the present etchants for gold enable the positive and negative edge dislocations to be distinguished.

3.1.3. Light deformation

An as-annealed crystal was lightly deformed by handling. In a certain area, many slip markings in the form of bands along the [1 0 1] direction were observed, as shown in Fig. 6a. After these surface observations, the crystal was etched with the etchant A.R. The results of etching in almost the same region are shown in Fig. 6b, the width of the band of pit arrays and in mean spacing between bands were coincident with those of slip markings Fig. 7a shows an annealed structure and the significant increase in dislocation density due to the multiplication of dislocations by the deformation (Fig. 7b) with the etchant A.R. Photographs of each were taken from the identical area.

Dislocation distributions were rather irregular, probably because a non-uniform stress was applied in the region. These results suggest conclusive evidence that the aqua regia etch is a reliable reagent for revealing dislocations in gold.

3.1.4. Etch pits in the specimen deformed by four-point bending

The specimen whose long axis was parallel to the [6 5 1] direction and deformed by single glide in bending, was stressed using a four-point bending jig until just above the yield stress on the stress–strain curve at a strain-rate of $4.7 \times 10^{-5}\ sec^{-1}$.

The yield point was clearly observed at a shear stress of $22\ g\ mm^{-2}$ and with the shear strain of 2.8×10^{-4}. Considering that the crystal used in this experiment had a dislocation density of $1 \times 10^{5}\ cm^{-2}$ the value of the yield stress is similar to that of copper single crystals measured by Young [8, 9], Argon *et al.* [27] and silver single crystals by Sabol and Robinson [17]. Fig. 8 shows that its etch pits were formed regularly along [1 0 1] slip direction from the centre

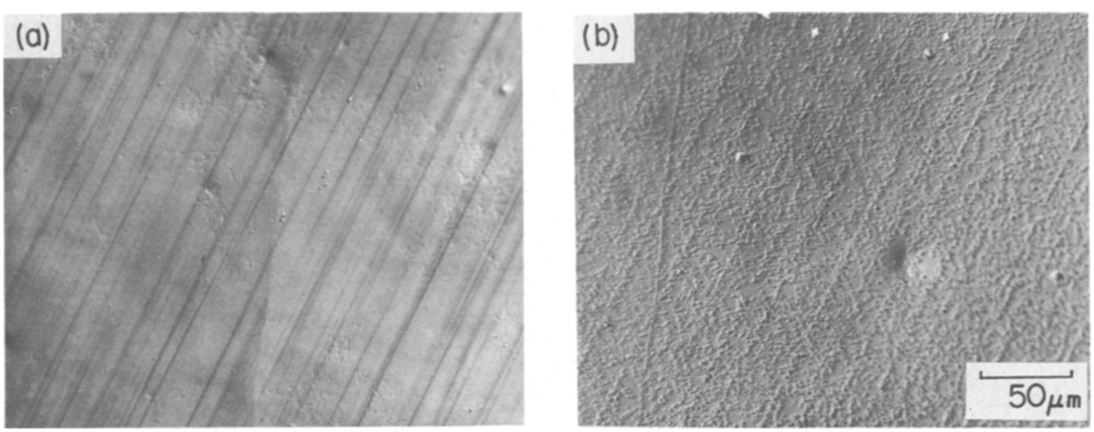

Figure 6 Correspondence between slip markings and etch-pit arrays after a light deformation. (a) Slip markings. (b) Etch-pit arrays near the same area (A.R. etchant).

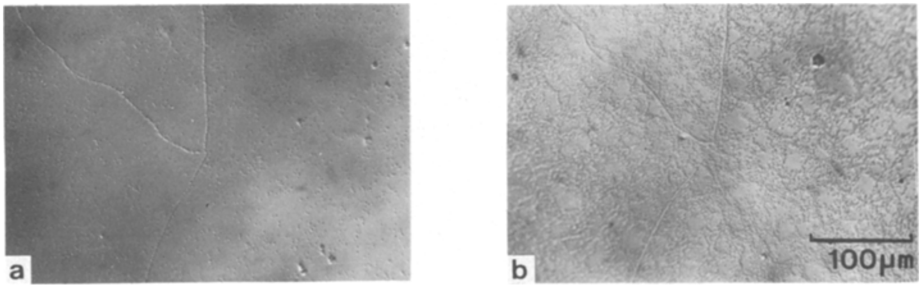

Figure 7 Dislocation multiplication due to deformation (A.R. etchant). (a) Etch pit distribution in an as-annealed crystal. (b) The same area after a deformation.

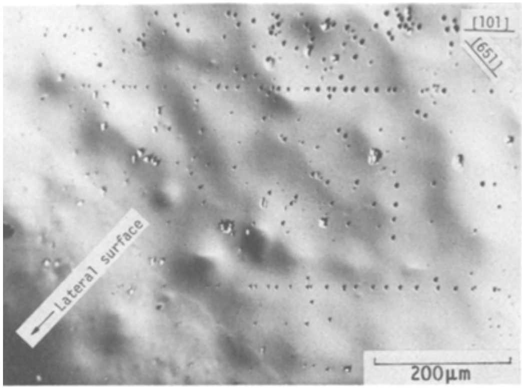

Figure 8 Arrays of etch pits in the specimen deformed by four-point bending.

to the edge of specimen. It is considered that the etch pits were formed at the position of dislocations which were formed at the yield point.

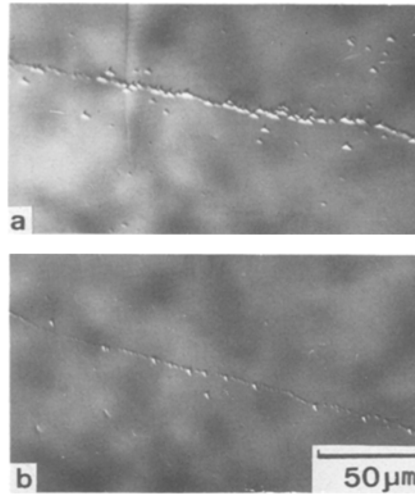

Figure 10 Large and small pits at sub-boundaries (A.R.Zn etchant). (a) Sub-boundary consisting of large pits. (b) Sub-boundary consisting of small pits.

3.2. Large and small etch pits

In Section 3.1.2 it was shown that the etchants are capable of producing two types of etch pits corresponding to edge dislocations of opposite sign. Further evidence to support this is now suggested. Pairs of large and small pits were observed in an as-annealed crystal, as shown in Fig. 9, and it is believed that the marked pairs of pits in the figure correspond to dislocation half-loops which may be parts of the dislocation networks. The dislocations in each pair of pits, therefore, belong to the same Burgers vector, so that the terminal on the surface has a character of the opposite sign to the other.

It is well known that, in general, sub-boundaries consist of dislocations of like sign. Thus, the sub-boundaries should produce etch-pit arrays of the same shape. Fig. 10 shows etch pitting examples for such a sub-boundary with the etchant A.R.Zn. In some cases only large pits were observed, whilst in others small pits were observed (Fig. 10 a and b).

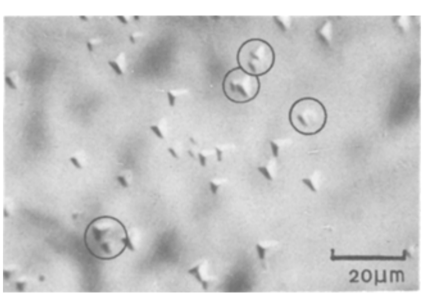

Figure 9 Pairs of etch pits consisting of a large and small pit (A.R.Cu Etchant).

It was also observed that approximately equal amounts of large and small etch pits were formed on the surface of specimen which was lightly deformed.

From the features of the etch pits observations discussed above, it is evident that the present etchants for gold are reliable solutions which differentiate positive and negative edge dislocations on {1 1 1} surfaces.

3.3. The effect of impurities in the etchant

The cross-section of a pit is essentially determined by the ratio V_s/V_n, where V_s is the lateral displacement velocity of surface steps and V_n the normal dissolution rate. Well defined pits result only if the ratio V_s/V_n is sufficiently small. The quality of an etchant can be improved by changing either V_n or V_s. The usual method of decreasing V_s is to add impurities to the solution which poison the kink sites in the surface steps. For LiF, Gilman *et al.* [21] have reported that V_s depends very much on the concentration of ferric ions of a dilute solution of iron fluoride. According to Sears [28] and Vermilyea [29], the role of the impurities is simply to slow down the dissolution rate so that a high undersaturation can be maintained. But as no adequate theory to produce suitable etchants has been established, one is compelled to use trial and error to produce good etch pits.

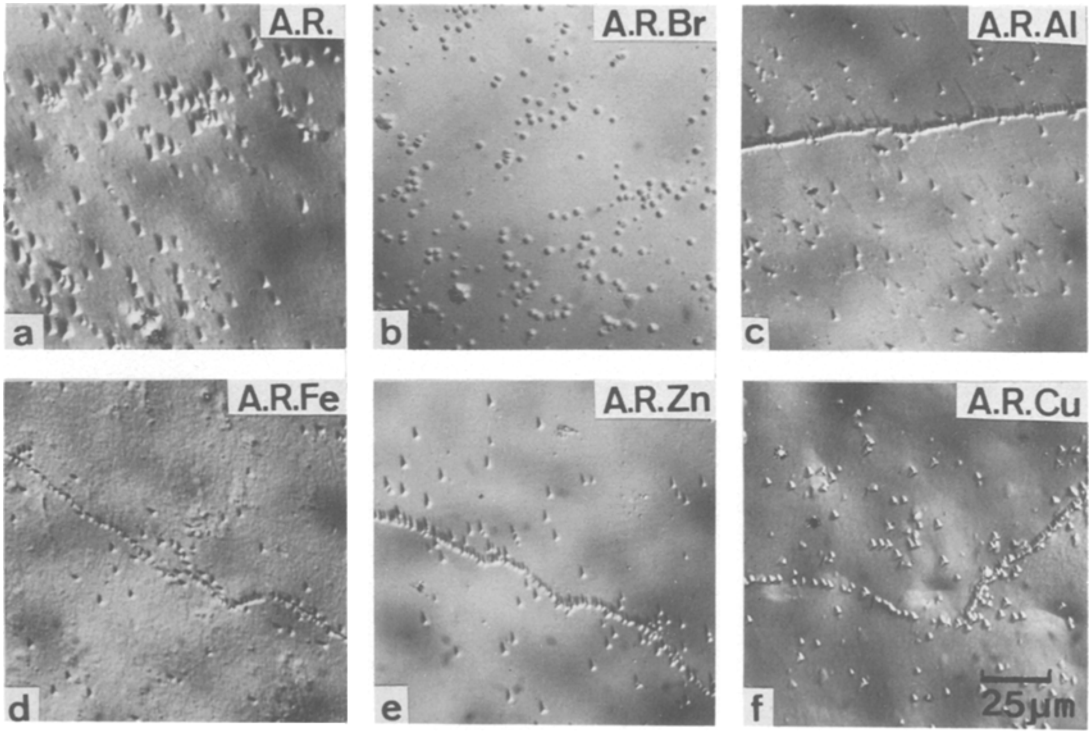

Figure 11 The effect of additional impurities into a base etchant of 1:3 aqua regia, (a), in an as-annealed crystal. Compositions of the etchants for (b) to (f) are given in Table I.

The results of such an attempt are summarized in Fig. 11. The result of the etchant A.R.Cr is not represented because of its inferior quality. A good etchant must fulfill the requirement that there is no contamination of matrix as well as producing sharply defined pits. Among the etchants employed in the present investigation, A.R.Zn and A.R.Cu are selected as the best ones, since these etchants produced the most sharply defined triangular etch pits and did not form any surface contamination layer.

4. Conclusions

To establish an etch pitting technique for revealing dislocations in gold, etch pit distributions in as-grown, annealed and deformed gold single crystals were investigated with a solution of 1:3 aqua regia and its modified solutions. The main results can be summarized as follows:

(1) there is considerable evidence to suggest that the etch pitting technique described is a reliable means for revealing both grown-in and fresh dislocations on {1 1 1} surfaces in gold;

(2) large and small etch pits were revealed with the etchants in as-annealed and deformed crystals, whose appearance is similar to those produced in silver by Chen and Hendrickson [24];

(3) from the various observations made, it is concluded that these different types of pits correspond to the edge dislocations of opposite sign;

(4) the crystals employed had dislocation densities of 1 to 4×10^6 cm^{-2} as-grown, but high-temperature annealing treatment reduced te density of dislocations within sub-boundaries by an order of magnitude;

(5) well-defined climb polygonization in a slightly deformed crystal was observed after annealing;

(6) gold single crystals of 99.99% purity having a dislocation density of 1×10^5 cm^{-2} was found to yield at a stress of 22 g mm^{-2}. Etch pit observations indicate that the multiplication of dislocations occurred at that stess and the arrays of fresh dislocations were formed regularly along the [1 0 1] slip direction.

Acknowledgements

The authors wish to acknowledge the financial support of Matsunaga Science Foundation (1973) and Hattori Hoko Fund (1975). Also the authors thank Mr I. Iida for helpful suggestions on the experimental techniques.

References

1. J. J. GILMAN and W. G. JOHNSTON, *J. Appl. Phys.* **30** (1959) 129.
2. D. F. STEIN and J. R. LOW, *ibid* **31** (1960) 362.
3. L. C. LOVELL and J. H. WERNICK, *ibid* **30** (1959) 590.
4. J. D. LIVINGSTON, *ibid* **31** (1960) 1071.
5. J. D. LIVINGSTON, "Direct Observations of Imperfections in Crystals" (Interscience, New York, 1962) p. 116.
6. *Idem, Acta Met.* **10** (1962) 229.
7. F. W. YOUNG, *J. Appl. Phys.* **32** (1961) 192.
8. *Idem, ibid* **33** (1962) 1815.
9. *Idem, ibid* **33** (1962) 963.
10. *Idem, ibid* **33** (1962) 3553.
11. M. J. HORDON, *Acta Met.* **10** (1962) 999.
12. Z. S. BASINSKI and S. J. BASINSKI, *Phil. Mag.* **9** (1964) 51.
13. S. J. BASINSKI, Z. S. BASINSKI and A. HOWIE, *ibid* **19** (1969) 899.
14. H. J. LEVINSTEIN and W. H. ROBINSON, *J. Appl. Phys.* **33** (1962) 3149.
15. F. J. WORZALA and W. H. ROBINSON, *Phil. Mag.* **15** (1967) 939.
16. G. P. SABOL and W. H. ROBINSON, *ibid* **16** (1967) 419.
17. G. P. SABOL and W. H. ROBINSON, "Work Hardening" (Gordon and Breach, New York, 1968) p. 195.
18. C. C. CHEN and A. A. HENDRICKSON, *J. Appl. Phys.* **42** (1971) 2208.
19. *Idem, J. Inst. Met.* **100** (1972) 255.
20. F. RAMSTEINER, *Mater. Sci. Eng.* **1** (1966) 206.
21. J. J. GILMAN, W. G. JOHNSTON and G. W. SEARS *J. Appl. Phys.* **29** (1958) 747.
22. F. SEITZ, *Phys. Rev.* **79** (1952) 723.
23. R. J. STOKES, T. L. JOHNSTON and C. H. LI, *Phil. Mag.* **3** (1958) 718.
24. C. C. CHEN and A. A. HENDRICKSON, *J. Appl. Phys.* **42** (1971) 5375.
25. *Idem,* "The Science of Hardness Testing and Its Research Applications" (American Society for Metals, Cleveland, Ohio, 1972) p. 274.
26. Y. MIURA, *J. Appl. Phys.* **43** (1972) 2917.
27. A. S. ARGON and W. T. BRYDGES, *Phil. Mag.* **18** (1968) 817.
28. G. W. SEARS, *J. Chem. Phys.* **32** (1960) 1317.
29. D. A. VERMILYEA, *Acta Met.* **6** (1958) 381.

Received 31 December 1975 and accepted 26 January 1976.