X-ray topographic analysis of dislocation line defects in calcium fluoride crystals

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Abstract. One-to-one correspondence of dislocation etch pits have been established on the matched cleavage faces and on the opposite sides of thin flakes of calcium fluoride crystals. By selecting $02\bar{2}$ and $02\bar{2}$ reflections and $\text{MoK}\alpha_1$ radiation, stereopair projection x-rays topographs were studied and critically compared with optical micrographs. The dislocation etch pits and dislocation out crop images show a close resemblance. The orientation of the Burgers vectors of the dislocation lines has been identified and these lines lie parallel to the $\langle 110 \rangle$ directions. The growth history of the stratigraphical pattern has been studied using x-ray topographic technique.

Keywords. Calcium fluoride crystals ; etch pits; x-ray topography ; stereopairs; dislocation contrast ; stratigraphical pattern.

1. Introduction

Crystalline materials have been studied using a variety of methods. The chemical etching and x-ray topographic techniques are commonly used to study the site, nature and orientation of dislocations in the crystals. Cockayne *et al* (1964) studied slip and polygonization during the crystal growth of calcium fluoride crystals using chemical etching method. Patel and Desai (1965 a) also used this method to study the nature of inclined dislocations in calcium fluoride crystals. Beswick and Lang (1972) and Tanner (1972) reported x-ray topographic observations on natural fluorite crystals. Desai (1979) reported surface structures of calcium fluoride crystals. The development of calcium fluoride lasers has encouraged studies on the properties of these crystals. The nature and orientations of dislocations in calcium fluoride crystals have been studied in this paper by comparing the correlation of dislocation etch pits and dislocation out crop images.

2. Experimental

Crystals of calcium fluoride were selected from stocks obtained from Durham mines in England. The crystals or their parts were selected after ensuring that

visible flaws, cracks and inclusions are absent as much as possible. These crystals have been cleaved along $\{111\}$ planes and freshly cleaved faces have been chemically etched (Desai 1966) in 2.6 N nitric acid solution and the etch patterns have been optically studied using Vickers projection microscope. X-ray projection topographs (Lang 1959a) and the stereopair projection topographs (Lang 1959b) of the same crystals have been obtained with suitable radiations and reflections by using a Lang camera and a standard microfocus x-ray unit.

3. Results

3.1 Etch pit studies

Figure 1a illustrates the etch patterns on (111) face, produced by etching for 13 hr in 2.6 N nitric acid solution. The following features may be noted: (a) All pits were of triangular shape and identical in size. The sides of the pits intersect the cleavage face along $\langle 110 \rangle$ directions and their edge lengths range from $20\text{--}25\mu$. (b) The pits were classified into two types: (i) point-bottomed and (ii) flat-bottomed. (c) The pits have rectilinear sides and sharp corners (d) All the point-bottomed pits are eccentric, *i. e.* the pits are not the geometrical centres of triangular pits but are displaced from them. (e) The corners of many of the pits make precise contact with the sides of the neighbouring pits. In some basal extensions are also produced. (f) Some pits occur in pairs. (g) The stratigraphical etch patterns (Patel and Desai 1965 b) are also observed. (h) The twin boundary is marked by a dark line (PQ) of cleavage steps, which separates the smaller area of very low dislocation pit density. The pits are oriented opposite each other on the two sides of a twin boundary which is seen at the bottom region of figure 1a.

To determine whether the individual point-bottomed pits reveal dislocation sites matched cleavage faces of the crystal were etched in the same etchant. One-to-one correspondence has been established with regard to the number and positioning of these individual isolated pits. To know how far the dislocation lines penetrate into the crystal the opposite side of the same crystal was carefully studied.

Figure 1 b shows the etch pattern on the opposite side ($\bar{1}\bar{1}\bar{1}$) on the face shown in figure 1 a. The etch patterns show considerable similarity, strongly suggesting that the etch pits are nucleated at the sites of dislocations in the crystal. When the etch patterns were viewed in transmitted light, there was a relative displacement in the etch patterns on the two sides of the same crystal. The displacement of the etch patterns was nearly uniform and was in the same sense for the different etch pits. The angle of inclination of the dislocation lines with the cleavage face was computed from the displacement (d) and thickness of crystal plate (t). These observations for four different flakes of calcium fluoride crystals are shown in table 1, and it is seen that dislocation lines have preferred orientation in the crystal.

3.2 X-ray topographic studies

To investigate the correlation of etch pits with dislocation out crop images, the x-ray topography of the same crystal was carried out by projection topography

Figure 1. ($\times 125$) a. Etch pattern produced by etching a (111) cleavage face in 2.6 N nitric acid solution for 13 hr. b. Etch pattern on opposite side $(\bar{1}\bar{1}\bar{1})$ of the crystal face shown in a.

Figure 2. ($\times 125$) Stereopair-projection topographs of the same crystal shown in figure 1. $\text{MoK}\alpha_1$ radiation. Edge length is 8mm. : a. $0\bar{2}2$ reflection and b. $02\bar{2}$ reflection.

The x-ray radiations used were $\text{MoK}\alpha_1$ ($\lambda = 0.709 \text{ \AA}$) and $\text{AgK}\alpha_1$ ($\lambda = 0.559 \text{ \AA}$). The latter was mainly used in view of its higher penetrating power. The micro-focus x-ray unit was operated at 50 kV and 2.5 mA current and giving exposure times from 30 to 40 hr *. The reflection $\bar{0}22$ and $0\bar{2}2$ were selected by using $\text{MoK}\alpha_1$ radiation. The location of dislocation out crop images was assisted by obtaining the stereopair-projection topographs. The topographs were recorded on Ilford (L-4) nuclear plates, with emulsion thickness of 50μ . Each topograph was subsequently enlarged by photographic techniques, after an intermediate contrast inversion step. Useful magnifications up to $\times 200$ were obtainable with $\text{AgK}\alpha$ and $\times 300$ with $\text{MoK}\alpha$ radiations. The resolution in the topographs is approximately 1μ . Samples of approximately 0.5 mm thickness and included platelets of main surfaces of $\{111\}$ type were chosen.

Figures 2 a and 2 b illustrate a part of $\bar{0}22$ and $0\bar{2}2$ stereopair-projection topographs obtained with $\text{MoK}\alpha_1$ radiation ($\mu t = 0.8$) of the same crystal as shown in figure 1. By critically comparing the optical micrographs (figure 1) and the x-ray projection topographs (figure 2) it is seen that (a) All dislocation out crop images have one-to-one correspondence with dislocation etch pits. (b) Due to the dislocation contrast, triangular pits and the associated dislocation out crop images are observed in the x-ray projection topographs. (c) The dislocation out crop images consist mainly of straight or slightly curved segments. (d) At the centre of the topographs the triangular shape inclusion is clearly revealed. (e) In some regions (e.g. left side of the topographs) there are no dislocation out crop images. (f) The inside traces of the stratigraphical patterns are clearly visible as heavy dark lines : oriented in $\langle 110 \rangle$ directions. (g) The twin boundary regions include some of the finely spaced Pendellosung fringes.

3.3 Determination of Burgers vectors of dislocations

The Burgers vector for the calcium fluoride crystals is $1/2 \langle 110 \rangle a$, where $a = 5.46 \text{ \AA}$ the lattice parameter, and the plastic deformation behaviour of this crystal agrees with this supposition. If all $\langle 110 \rangle$ oriented dislocations are equally probable, then a

Table 1. Displacement of etch patterns on the opposite sides of thin flakes.

Sample No.	Thickness of the crystal plate (t) in microns	Displacement of the etch patterns observed (d) in microns	Calculated angle of dislocation lines ($\theta = \tan^{-1} d/t$)
1.	17	3.0	$10^\circ - 01'$
2.	28	5.1	$10^\circ - 19'$
3.	31	5.8	$10^\circ - 36'$
4.	36	7.1	$10^\circ - 35'$

*A tube to sample distance of 50 cm was used

111-type reflection would show half of the dislocations and in a 220-type reflection five-sixths of them would appear. An understanding of the geometry of a regular tetrahedron enables identification of Burgers vectors of the dislocations. If the specimen slice is cut parallel to (111) plane, it may be identified with the base of the tetrahedron, and the other planes $(\bar{1}\bar{1}\bar{1})$, $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$ with the pyramidal sides of the tetrahedron. A dislocation invisible, say, in both reflections $\bar{1}\bar{1}\bar{1}$ and $\bar{1}1\bar{1}$ has its Burgers vectors parallel to the edge common to these tetrahedral faces, *i.e.* [110]. Thus important diagnostic reflections for identifying $1/2 \langle 110 \rangle$ Burgers vectors are of 111-type.

Hence topographs are taken with reflections from the three {111} planes inclined at 60° to the specimen surface. During the process of mounting the crystals, they were handled with tweezers tipped with very soft polyurethane foam. Despite this precaution, an appreciable amount of surface damage on the crystal was produced and hence the patches of intense blackening seen in figures 2 and 3. A set of projection topographs of the {111} face have been obtained with $\text{AgK}\alpha_1$ radiation by using $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}1$, $\bar{1}1\bar{1}$ reflections. The stereopair-projection topographs have been obtained with $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}1$ and $\bar{1}1\bar{1}$ reflections. In all cases, it could be so arranged that the diffracted beam left the {111} face nearly normal so as to form an undistorted topographic images. Thus figures 3a, 4a, 5a, and 3b, 4b, 5b represents $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}1$, $\bar{1}1\bar{1}$ and $\bar{1}\bar{1}1$, $\bar{1}\bar{1}\bar{1}$, $\bar{1}\bar{1}\bar{1}$ topographs respectively.* Key to dislocation regions marked by A to H in $\bar{1}\bar{1}\bar{1}$ topograph is illustrated in figure 5. Visibility of dislocation out crop images (figure 5) has been critically compared with figures 3 and 4. Under the contrast conditions, the images of dislocations are weak or absent when $g \cdot b = 0$ (where g is the reciprocal lattice vector of the Bragg reflection active and b is Burgers vectors of dislocations). Dislocation out crop images with $g \cdot b = 1$ should be clearly visible. The visibility of dislocation out crop images, in different regions marked by A to H in figure 6. The results given in table 2 show that dislocation out crop images are invisible in $\bar{1}\bar{1}\bar{1}$ and $\bar{1}\bar{1}1$ reflection topographs, suggesting that the Burgers vectors of the dislocation lines are parallel to [110] directions. Hence they are almost pure edge dislocations in character. The etchant 2.6 N nitric acid solution therefore produces etch pits at the emergence sites of dislocations on (111) faces of calcium fluoride crystals.

4. Discussion

One-to-one correspondence of etch pits observed on the matched faces and also on the opposite sides of thin flakes suggests that the pits nucleate at the sites of dislocations, which run into the body of the crystal. The close resemblance between etch pits and dislocation out-crop images strongly suggests that the etch pits are nucleated at the sites of dislocations.

* Due to twinning nature of the crystal, the bottom of the crystal has not been revealed.

Figure 3. a and b. Stereopair projection topographs using $11\bar{1}$ and $\bar{1}\bar{1}1$ reflection. $\text{AgK}\alpha_1$ radiation. ($\times 100$)

Figure 4. a and b. Stereopair projection topographs, using $1\bar{1}1$ and $\bar{1}1\bar{1}$ reflections $\text{AgK}\alpha_1$ radiation. ($\times 100$)

Figure 5. a and b. Stereopair projection topographs, using $\bar{1}\bar{1}1$ and $1\bar{1}\bar{1}$ reflections. $\text{AgK}\alpha_1$ radiation. ($\times 100$)

Figure 6. Key to dislocation numbering of the x-ray topograph shown in fig. 3 (a).

Table 2. Identification of Burgers vectors of dislocations.

Obs. No.	Regions in x-ray topograph	Number of dislocation crop images	Reflections			Orientation of Burgers vectors of dislocation line
			$\bar{1}1\bar{1}$	$\bar{1}\bar{1}1$	$\bar{1}11$	
1	A	1 to 11	0	x	x	[110]
2	B	1 to 2	0	x	x	[110]
3	C	1	0	x Faint	x	[110]
4	D	1 to 12	0	x	x	[110]
5	E	1 and 2	0	x	x Faint	[110]
6	F	1 to 7	0	x	x Faint	[110]
7	G	1 to 9	0	x	x	[110]
8	H	1 to 7	0	x	x	[110]

0 = Visible (clear); x : Invisible (not clear)

Invisibility of the dislocation out crop images in $\bar{1}1\bar{1}$, $\bar{1}\bar{1}1$, $\bar{1}11$ and $11\bar{1}$ stereo-pair projection topographs confirmed that the Burgers vectors of the dislocation lines have been parallel to $\langle 110 \rangle$ directions and they are almost pure edge dislocations in calcium fluoride crystals. Inside traces of the stratigraphical patterns have been clearly revealed in $02\bar{2}$ and 111 topographs. The linear patterns are strictly crystallographically oriented in $\langle 110 \rangle$ directions. It is conjectured that the stratigraphical patterns might have been formed along the edges of the imperfect layers deposited during growth of the crystal.

5. Conclusions

- (i) Etchant 2.6 N nitric acid solution produces pits at the emergence sites of dislocations on (111) faces of the crystal.
- (ii) X-ray topographs of the same crystal show that the dislocation etch pits are usually associated with the dislocation out crop images.
- (iii) One-to-one correspondence between dislocation etch pits and dislocation out-crop images has been established.
- (iv) The Burgers vectors of the dislocation lines are parallel to $\langle 110 \rangle$ directions. They are pure edge dislocations in character.
- (v) The average dislocation density is $10^2/\text{cm}^2$. The dislocation free regions are clearly seen in the optical and x-ray topographs.
- (vi) The twin boundary regions show some of the finely spaced Pendellosung fringes.
- (vii) Inside traces of the stratigraphical patterns clearly reveal the growth history of the crystals.

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