Acta Cryst. (1949). **2**, 383

Fractographic Study of an Ammonium Dihydrogen Phosphate Single Crystal*

By C. A. Zapffe and C. O. Worden
6410 *Murray Hill Road, Baltimore* 12, *Md., U.S.A.*

(*Received* 28 *March* 1949)

The technique of fractography is applied to the cleavage surfaces of an ammonium dihydrogen phosphate synthetic single crystal, using both dark-field and oblique illumination. Excellent hackle patterns are observed; and other markings are also found which relate to crystallographic deformation mechanisms and to crystal imperfection. These latter are: (*a*) lamellar and blocklike markings suggesting fine-scale crystallographic weakness of a micellar type, (*b*) dendritic formations of unknown origin, (*c*) inclusions of foreign phases, and (*d*) thin textural effects on the cleavage surface. Fractography is accordingly proposed as a tool for studying the perfection of such crystals, also the manner in which they respond to deformation and cleavage.

Introduction

In the preceding communication (Zapffe & Worden, 1949), the microscope technique 'fractography' is extended into the general field of non-metallic crystal chemistry from the field of metallurgy, where it has had its principal development. It is shown that the cleavage facets of non-metallic crystals, as well as metallic crystals, contain detail by which both the material and its history can often be readily identified. More importantly, it is demonstrated that on these facets there is displayed direct visual evidence of the imperfection architecture of the crystal—a matter of much interest to all students of the solid state to-day.

Particularly in the preparation of certain synthetic crystals (Walker, 1947) whose perfection is a requisite for the purposes for which they are intended, the ability to detect and to study their imperfection has real usefulness. Such is the case for ammonium dihydrogen phosphate ($NH_4H_2PO_4$). The preparation of synthetic single crystals from this material has been carefully studied by Egli, Smith, and Zerfoss in the Crystal Section of the Naval Research Laboratory, to a point where, as Egli states: 'It is useless to attempt further to improve texture until we can measure it' (Egli, private correspondence).

Because textural aberrations deflect the cleavage traverse and therefore tend strongly to express themselves on cleavage facets, the present study of an ammonium dihydrogen phosphate synthetic single crystal was undertaken, using the technique of fractography. Previous work would indicate that fractography might serve as a tool in single-crystal studies, both from the practical standpoint of detecting imperfection textures, and from the theoretical standpoint of opening new fields for fundamental studies of both crystal texture and deformation mechanisms. The principal purpose of this manuscript, therefore, is not to explore the identity of any particular cleavage phenomenon, but to call attention to a number of phenomena which are revealed on the cleavage facet and which invite further investigation.

* From research conducted in the laboratory of the senior author under contract with the Office of Naval Research.

Observations

Macrophotograph

In Fig. 1 a macrophotograph shows the gross fracture of a large 'ADP' crystal, as it shall hereafter be designated, which was prepared at the Naval Research Laboratory and submitted to the authors' laboratory by P. H. Egli. The fracture is clearly 'hackle' and glass-like on this gross scale. Nucleation of the cleavage traverse is plainly visible at the flat top edge of the crystal; and the surface undulations of the facet give no indication of either the rectilinear symmetry of this tetragonal crystal, nor of any important imposition of structural deformity upon the typically hackle progress of the fracture. Much unlike some metallic crystals, where cleavage so strongly follows directional weaknesses characteristic of and intrinsic to the crystal, the gross pattern here plainly relates to the nature of the deforming stress, rather than to the nature of the deformed matrix or crystal. If crystal imperfections exist, they are on a fine scale, requiring higher magnification.

Fractographs comparing dark-field with oblique illumination

In the preceding communication (Zapffe & Worden, 1949) the technique of fractography is described briefly by illustration, and by reference to articles containing further details. Slight obliquing of the illumination, one will recall, is most commonly used with metals to give definition and depth to the field, although other techniques of illumination may also be used.

'Dark-field' illumination is one of these; and it is illustrated in Fig. 2. The light strikes the field at a low angle from outside the lens, brightening slopes and edges. A vast amount of detail is evident in this figure, even at a magnification of only 40 diameters.

Nevertheless, slight obliquing of the vertical beam within the lens provides at least as fine a picture. In Fig. 3 a field similar to that in Fig. 2 is shown, but at higher magnification. The textural detail here is excellent, allowing the closest study. There are in this single fractograph (1) fanlike markings which may be hackle, but are suggestive of subtle lineage effects, (2) heavy diagonal fault-like markings bounding the major fanlike formations, (3) light diagonal markings bounding lesser fanlike areas, (4) strong indications of lamellar structure both in profile and throughout the surface texture, (5) thin and straight striae which are closely parallel across the entire field, and (6) some evidence of minor deformities.

In the earlier communication (Zapffe & Worden, 1949) two fundamental pattern types are defined: (I) patterns determined by factors within the crystal, and (II) patterns determined by the nature of the stress. The latter are the so-called 'hackle' structures, and are principally significant to the extent that they reveal the conformation of the fracturing force as it traversed the matrix. The former, however, represent deflections impressed upon the cleavage traverse by structural factors within the crystal and are therefore of paramount importance in studying crystal imperfection. Some of the pattern in Fig. 3 can be ascribed to hackle effects, but there are certainly markings indicating the presence of substructural details within the crystal which are exposed on the cleavage surfaces and which can therefore be usefully studied with the fractographic technique.

Hackle structure

To aid in distinguishing between Type I and Type II patterns, which is a principal preliminary problem, the fractograph in Fig. 4 is presented. This is a splendid example of pure Type II hackle structure on a microscopic scale. It would be difficult to claim that any of these markings were importantly related to the structure of the crystal. They are instead typical displays of the stress pattern produced by the rupturing force as it traversed the crystal. No pronounced directional weaknesses within the crystal have played a role in determining the cleavage path, although some slight textural flaws may possibly be indicated as a surfacial roughness in the lower central portion of the field.

In Fig. 5 an especially fine display of hackle detail at higher magnification shows how elaborate a Type II pattern may become. Here are major radial separations probably indicating the direction of propagation of the fracture; and between them in fine array, and at almost perfect perpendicularity, are markings probably relating to the pulsating fracture front, although there is the possibility that these finer traces have a relationship to a lamellar crystal texture, so frequently observed in fractographs of metallic and certain non-metallic crystals (Zapffe & Worden, 1949).

Crystallographic markings

In Fig. 6 an individual hackle contour is brought to higher magnification; and details now become visible which are almost certainly the result of crystal characteristics, rather than stress characteristics, at least in this particular locus. A marked angularity is evident, and so is a lamellar texture. Fracture would not have proceeded along such facets unless they presented a path of minimum strength. While the angularity can be ascribed to the atomic regularity of the crystal, the equi-spaced lamellar traces raise again the issue of a fine-scale substructure and are in keeping with the concept of a micellar constitution, as discussed previously.

In Fig. 7 two fractographs display patterns which more strongly present this lamellar texture. A broad hackle background can be observed in both patterns, particularly in Fig. 7 (*b*); but on a fine scale the cleavage has followed a traverse which is much more readily explained on the basis of a subtle lamellar texture than on a concept of stress acting on a physically homogeneous lattice. The micellar theory amply accounts for these observations (Zapffe & Worden, 1949; Zapffe, 1949).

Specific crystallographic markings appear in Fig. 8. The rectangularity of the heavy markings suggests that these are all cleavages, both basal and prismatic, and that the similar heavy markings in the previous Fig. 3 are therefore also crystallographic, rather than hackle. Striae are also observed in markedly parallel array across the whole field, as in the previous Fig. 3. The role of these latter markings in the deformation of ADP would be interesting to know. They suggest slip or twin activity, on the basis of similar observations with metals.

Dendritic structures

In Fig. 9 a structure appears which clearly has no relationship to stress conformations. This is the pronounced dendritic form occurring in the clear area between the two rows of hackle markings, and the lesser similar forms that can be observed imbedded within the hackle structure itself.

Such structures might express growth imperfection. They might also express a deliquescent etch activity, which may or may not be related to crystal imperfection. Several fractures were studied as rapidly after formation as convenient without further special apparatus, in an attempt to find such patterns in the act of developing. So far as could be determined, the dendrites are either present within the crystal, or they form extremely rapidly after fracturing.

In Fig. 10 a great number of minute surfacial dendritic markings appear which are particularly interesting because of their apparently irregular interrelationships and orientations. Note that they overlie a hackle pattern and virtually obscure it.

As for the possibility that these markings are only thin surface effects, Fig. 11 presents a cleavage which

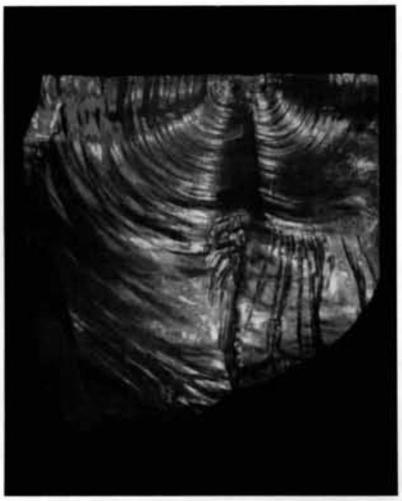


Fig. 1. Macrophotograph of the fracture surface on a synthetic single crystal of ammonium dihydrogen phosphate. $\frac{4}{5}\times$.

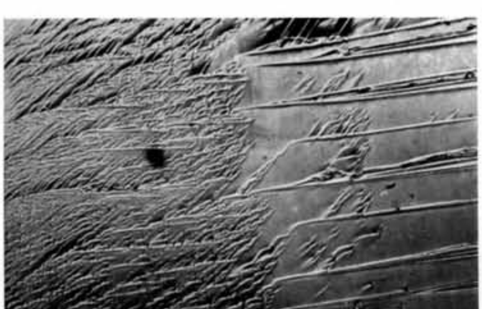
Fig. 2. Fractograph of ADP crystal in preceding figure, taken with dark-field illumination. 40×.

Fig. 3. Fractograph of field similar to that in preceding figure, but taken with oblique illumination and at higher magnification. 140×.

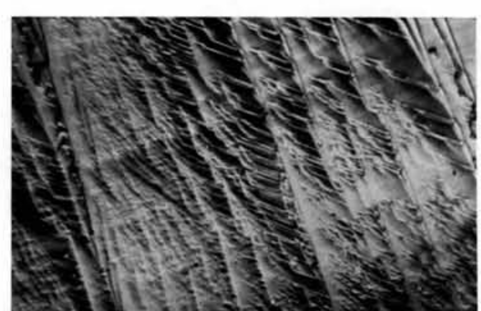
Fig. 4. Fractograph showing typical hackle structure. 96×.

Fig. 5. Fractograph showing an elaborate hackle detail. 160×.

Fig. 6. Hackle surface at higher magnification, showing an indication of crystallographic and lamellar effects. 310×.



(a)



(b)

Fig. 7. Cleavage surfaces displaying lamellar constitution. 180×.

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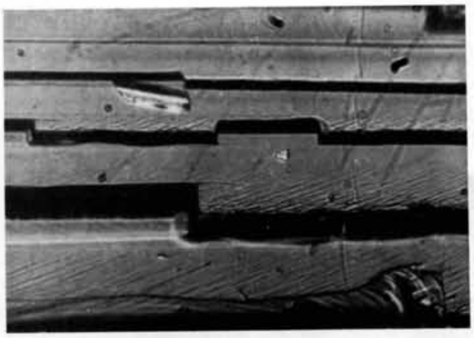

Fig. 8. Fractograph showing an instance of rectilinear cleavage, and possibly of slip or twin phenomena. 240 ×.

Fig. 9. Fractograph revealing an elaborate dendritic structure on the cleavage facet. 56 ×.

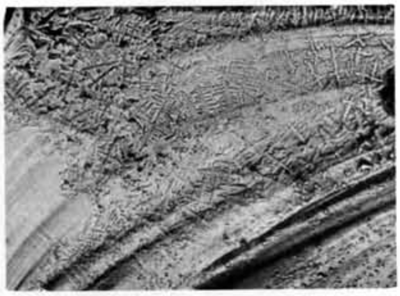

Fig. 10. Small dendritic structures superimposed on a hackle fracture. 160 ×.

Fig. 11. Deep pitlike markings on a hackle surface, possibly representing cross-sections of the dendrite-type defects shown in the two preceding figures. 180 ×.

Fig. 12. Cleavage facet lightly etched with water vapor. 180 ×.

Fig. 13. Cleavage surface deeply etched with water vapor. 330 ×.

seems to have caught similar markings in cross-section. At least in this case, the defect has marked depth, showing as outright tunnelling.

To examine further the suggestion that the dendrites represent an action of deliquescence, or atmospheric etching, fresh fractures were carefully examined to assure an absence of dendrites and were then given brief and progressive treatments in the mist from a warm water bath.

Fig. 12 shows an early stage of the attack on the crystal by a thin film of water. The action is primarily pitting. The two areas of advanced solution show no dendritic conformations.

In Fig. 13 an astonishing change in the cleavage surface is shown for advanced water-etching. Indeed, this is an elaborate structure for which no explanation can be offered at this time.

However, the pattern still has no suggestion of dendritism; and the explanation of the dendritic structures in Figs. 9, 10 and 11 must be left for further work.

Conclusion

It has been the principal purpose of this investigation to demonstrate the applicability of the fractographic technique to the study of the texture and imperfection structure of single crystals, specifically synthetic crystals of ammonium dihydrogen phosphate, and the mechanisms by which they deform and cleave. From this preliminary study, the following conclusions can be tentatively drawn:

(1) ADP crystals, even though transparent, can be studied fractographically with either dark-field or oblique illumination with excellent resolution of cleavage detail.

(2) Cleavage facets of these crystals, as of all crystals in general, show patterns of two fundamental types: (I) patterns which express factors intrinsic to the crystal, and (II) patterns which express factors intrinsic to the rupturing stress.

(3) Type II patterns, the so-called 'hackle' structures, occasionally display elaborate forms and provide interesting disclosures regarding the propagation and progression of the rupturing stress, but they contain little or no information regarding characteristics of the crystal.

(4) Type I patterns depict special crystal weaknesses following from preferred crystallographic directions and from textural irregularities, and are therefore by far the most important from the standpoint of the present study.

(5) Type I textural patterns disclose: (1) cleavage markings on (001) and (110), (2) crystallographic striae, perhaps relating to slip or twin activity, (3) pronounced indications of lamellar substructure of a micellar nature, (4) fanlike markings which may relate to a subtle lineage structure, (5) inclusions of foreign phases, (6) slight surfacial roughnesses of unknown origin, and (7) occasional dendritic structures of remarkable form and unknown origin.

(6) An attempt to reproduce the dendritic structures by etching a fresh cleavage facet in moist air failed to do so, but developed instead a most unusual pattern which is unlike any previously observed.

(7) Since at least the last five categories under (5) concern crystal imperfection, and since several of these concern features possibly never before observed or studied, fractography warrants immediate further study both as a control tool for the growing of single crystals and as a research technique for disclosing new fields for fundamental studies.

Acknowledgment is due to the Office of Naval Research for its sponsorship of the basic research program from which the present manuscript stems as a special study; and to Messrs P. Egli, P. Smith and S. Zerfoss of the Naval Research Laboratory for their contribution of samples, and for their encouraging interest in the study.

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