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Etch pit observations on the habit faces of gel grown nickel molybdate crystals

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Abstract. The results obtained from etching experiments on the habit faces of $NiMoO_4 \cdot xH_2O$ are described. Dilute solutions of chemical reagents such as HNO_3, CH_3COOH, NaOH, KOH are found to be the best etchants for revealing dislocation etch pits. The shape and nature of the etch pits are also described.

Keywords. Etch pits; dislocation; habit faces; gel grown; $NiMoO_4 \cdot xH_2O$ crystals

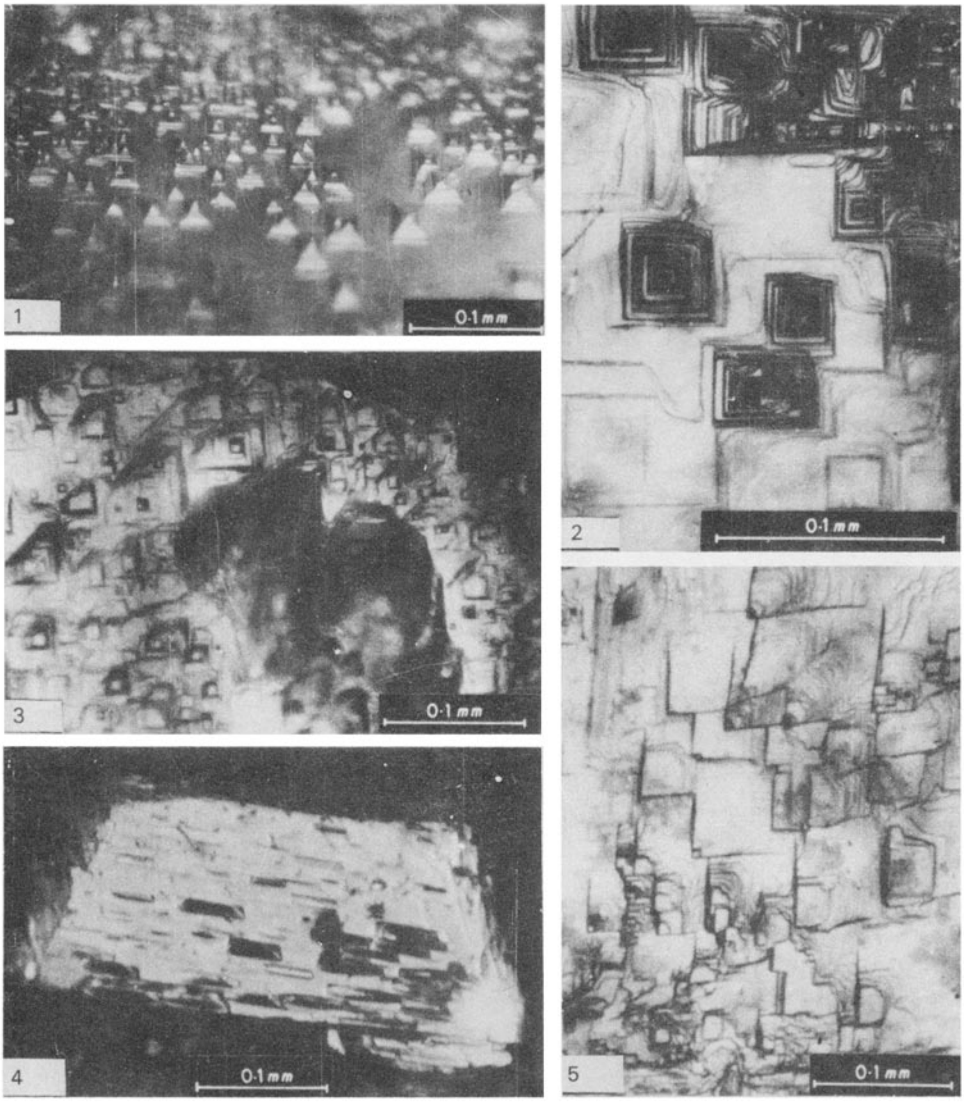
1. Introduction

Etching is a well-known technique for dislocation studies in crystals. It is the result of variation in surface reaction or dissolution rates influenced by crystallographic orientation effects, lattice imperfection and chemical combination. Etch patterns observed on crystal faces play an important role in obtaining information on the history of growth of crystals, as their etch patterns are intimately related to the growth phenomena. The first attempt to provide an explanation for the process of etching is due to Goldschmidt (1904). A satisfactory explanation regarding the origin of etch pits and their development has been given on the concept of lattice defect known as dislocation. A dislocation etch is an attractive means of studying the early stages of deformation in crystalline solids. This has led to the discovery of a number of etchants.

In the present work, an attempt has been made to investigate the nature and shape of etch pits by etching the (001) and (011) surfaces of gel-grown nickel molybdate crystals (Kurien and Ittyachen 1980). Well-shaped square and octagonal platelets (average size $3 \times 2 \times 0{\cdot}3$ mm^3) have been selected for this purpose.

2. Experimental and results

As there is no previous study of etching behaviour of these crystals, a number of prospective etchants were tried to reveal the dislocation sites and dislocation density. Water and quite a few acids were found to etch the cleavage faces of their flakes of nickel molybdate crystals. Nitric acid, acetic acid, sodium hydroxide, potassium hydroxide and a mixture of nitric acid and hydrochloric acid are suitable etchants for their action on the (001) face. Water has some polishing action on the surface. Sulphuric and hydroflouric acids were unsuitable for etching the faces of gel-grown nickel molybdate



Figures 1–5. **1.** Square type etch pits on the (001) face when etched in nitric acid. **2.** Well-defined square and rectangular etch pits with terrace when etched in acetic acid. **3.** Square-shaped pits with two sides well developed when etched in sodium hydroxide. **4.** Rectangular pits on the (001) face when etched in nitric acid. **5.** Square-shaped pits with two sides well-developed when etched in potassium hydroxide.

crystals. Increase in concentration or temperature resulted in the increase of surface dissolution without forming the visible pits tabulated in table 1. A large number of clusters of pits were formed first on the surfaces of thin flake-like crystals in the initial stages of etching. However, on repeated etching most of the pits became flat-bottomed, enlarged and eventually vanished. But some of the pits remained nearly constant during successive etching. A large number of pits were symmetrical pits, composed of closed rectangular and square terraces. Both nitric and acetic acids could yield identical etch

Table 1. Experimental conditions for etch pit formation on the (001) and (011) faces of gel grown nickel molybdate crystals

Etchant	Concentration	Time (min)	Observation
HCl	1:100 1:150	1	Rapid attack
	1:200	1	Few perfect pits were observed on the (001) and (011) faces
HF	1:150 1:200 1:400	1	Rapid attack
HNO_3	1:200 1:300 1:400	1–2	Well-defined square and rectangular pits were obtained on the (001) (figure 1) and (011) (figure 4) faces
CH_3COOH	1:200	1	Clustered etch pits of smaller size
	1:100 1:150	2	Well-defined square and rectangular pits with terrace (figure 2)
NaOH	0·05–0·1 N	2	Square-shaped pits with two sides well developed (figure 5)
$HF + HNO_3$	1:300	1	Destructive reaction: no etch pit formation

The experiment was conducted at room temperature.

pits. But in the case of sodium and potassium hydroxides only two sides of the square pits were well-developed. The sides of the square pits in all cases were parallel to the $\langle 100 \rangle$ direction. The average etch pit density was of the order of 10^4–$10^5\ cm^{-2}$. In isolated crystals, the dislocation density was between 10^2 and $10^3\ cm^{-2}$.

3. Discussion

Studies on different types of etch pits and their densities give useful information regarding the nature of the defects, impurity content and the history of growth of crystals. Etch pits may be produced due to several reasons. In the present case, initially a clustering of etch pits is formed. They are well-defined, very small point-bottomed, rectangular square pits. However, on repeated etching most of the pits became flat-bottomed and eventually vanished. The origin of flat-bottomed pits is due to the localised defects such as microprecipitates, vacancies etc. (Michael *et al* 1970). Evidently in this case etch pits are not being formed at the dislocation sites but at the impurity sites. The large flat-bottomed pits were assumed to be due to edge dislocations produced during the later stages of crystal growth (Johnston 1962). The edge and screw dislocations give rise to two distinct types of pits. The etch pits due to edge dislocations were generally small compared to those due to screw dislocation (Amelinckx 1976). The terrace nature of pits is a common phenomenon in the case of calcite, mica, etc. (Patel *et al* 1963). The terrace nature of pits obtained in this study can be explained by postulating the precipitation of some sort of impurities along the dislocation line which inhibits the action of the etchant depending on the nature, density and location of the impurities. The impurities might be evenly spaced along the dislocation line which result into pits having various types of terraces. The number of times the inhibition action is operated can be judged by the number of terraces—obtained when the inhibition action lasts longer, widely terraced pits are produced.

4. Conclusion

The high density etch pits obtained in the initial stages of etching suggests that the crystals have a high density of impurities adsorbed on the surfaces in the later stages of growth.

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