CHAPTER 13

MICROSTRUCTURES AND KINETICS OF ETCHING

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13.1 Introduction

The microtopographical study of crystal faces gives the information regarding their growth history. Because growth features are exhibited on the habit faces in their final forms. Since the growth and dissolution pattern affected by imperfections, one can also obtain information regarding these. Attempts are made to unfold the growth mechanism of different crystals by studying their growth patterns[1-4].

Studies of materials by etching is dependent upon the painstaking discovery of etchants by trial and error which reveal dislocations. The etchants are often complex in composition[5-7] and their exists little possibility of determining the detailed mechanism of etching. The formation of visible etch pits depends on the nucleation rate for unit pit at dislocation (V_d) and the rate of motion of steps across the crystal surface (V_s). Pits of good visibility is obtained when $V_d/V_s \geqslant 1.0$[8]. The ratio V_d/V_s is increased by : (i) increasing V_d as in the case of most etchants for metals, which uses a segregated impurity for this purpose, (ii) decreasing V_s by addition of an inhibitor and (iii) varying the temperature to take advantage of decrease in activation energy of V_d and V_s.

The present chapter deals with a detailed investigation carried out on surface micro-structures with the specific aim of understanding the mechanism of growth. A detailed study of the time and temperature dependent and hence kinetics of etching of dissolution are also presented in this chapter.

13.2 Experimental

13.2.1 Study of Microstructures

For surface microstructure studied, gel grown RHT crystals cleaned with acetone and are coated with silver to enhance the contrast. These faces are then examined under a metallurgical and electron microscopes.

12.2.2 Study of Kinetic of Etching

For etching kinetics study, the

cleaved (010) faces of RHT crystals are etched in formic acid solutions at different temperature. The pit dimensions (length (l) and breadth (b)) of rectangular pits are measured using a filar micrometer eyepiece at a constant magnification. Measurements are made only on isolated symmetric etch pits to avoid the overlapping of neighbouring pits and those due to the different inclinations of the dislocation lines to the cleavage face. The depths of the pits are measured by using an interference microscope. An average dimension of thirty pits are taken.

13.3 Observations, Results and Discussion

13.3.1 Microstructure Study

During the microstructure studies, the dissolution lines are observed on the (010) surfaces of the crystals. This may be because of the increase in the solubility of the crystal at higher temperature, such dissolution lines are illustrated in Figure 13.1. Sometimes growth striations are also observed, these are believed to be due to self exciting variations in growth rate, that arose from the temperature oscillations.

It is observed that the edges of (010) surfaces work as centers for initiation of growth layers. Figure 13.2 illustrates a typical example wherein the starting of growth layers from several points is clearly seen. This figure shows a build up of material on the crystal edges with a filling towards the centre indicating that edge nucleation is the predominant growth mechanism.

13.3.2 Kinetics Study

Figure 13.3 illustrates typical etch pattern produced on cleaved (010) faces of RHT crystals by etching.

The time dependence of pits dimensions length (l), breadth (b) and depth (d) are found to be linear i.e. the rate of growth of pit dimension is independent of etching time as shown in Figures 13.4 (a, b, c). According to the kinetic theory of Burton et al[9] the rate of selective etching either in the presence of inhibiting ions or in their absence should be independent of time. The time independence is in accordance with above theory and is similar to the one reported by Popkova[10].

The logarithm of the dissolution rate (V) plotted against the reciprocal of temperature of the etchant in temperature range 30 to 50^{o}C are observed to follow the well known Arhenius equation[11,12].

$$V_{l,b,d} = A_{l,b,d} \exp\left[-\frac{E_{l,b,d}}{kT}\right] \qquad (13.1)$$

where l, b, d stands for length, breadth and depth of the pit respectively, V is the growth rate of pit, A the pre-exponential factor and E is the activation energy of the dissolution process. This is shown in Figure 13.5. From the slope of these plots the values of activation energy of dissolution are calculated. The determined values of E and A are given in Table 13.1. It is clearly seen from the Table 13.1 that the values of E_l is greater than that of E_b, due to the anisotropic nature of the crystal. E_l/E_b is always greater than one, which implies that the temperature variation of the dissolution along [001] direction is greater than

Table 13.1

Activation energies and Arhenius factors for RHT

Crystal	Activation energy (eV)			Arhenius factor		
	E_l	E_b	E_d	A_l	A_b	A_d
RHT	0.79	0.67	0.53	6.1	5.2	4.7

that along [100] direction, i.e. the ratio 1/b is increasing with increase in temperature. The high values of activation energies indicate that the dissolution in formic acid solution is reaction-rate controlled.

13.4 Conclusions

1. At allconcentrations of feed solutions layer growth mechanism is predominant. It is observed that the growth layers initiate from the edges, steps and inclusions on the crystal surfaces.

2. The laterla as well as normal rate of dissolution at dislocations are found to be independent of etching time indicating a weak absorption to the dissolution ledges of the parent crystal.

3. The temperature dependence of the dissolution rates are of activation character.

4. The activation energies of dissolution along different directions are different.

5. The ratio of E_l/E_b is always greater than one.

6. The dissolution of these crystals in formic acid is reaction-rate controlled.

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Captions of the figures

Figure 13.1 (X 250)	Typical etch pattern produced on (010) cleavage faces of RHT crystals.
Figure 13.2 (X 75)	Crystallographic oriented dissolution lines on (010) surface.
Figure 13.3 (X 75)	Growth layer initiating from the edge of a crystal
Figure 13.4(a)	Plot of the length (l) of etch pits against etching time.
Figure 13.4(b)	Plot of the breadth (b) of etch pits against etching time.
Figure 13.4(c)	Plot of the depth (d) of etch pits against etching time.
Figure 13.5	Plot of log of the rate of dissolution of the etch pits against the reciprocal of the temperature.

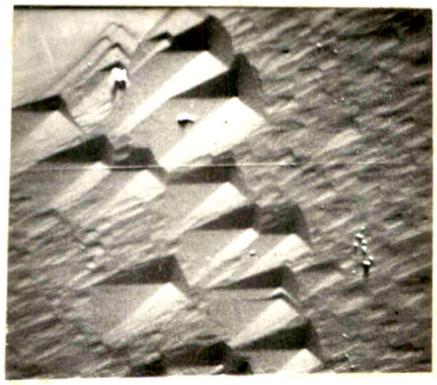


Fig. 13.1

Fig. 13.2

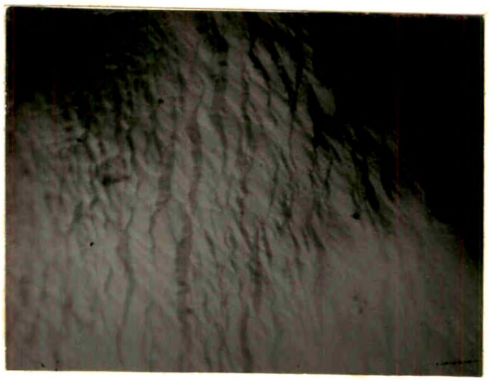


Fig. 13.3

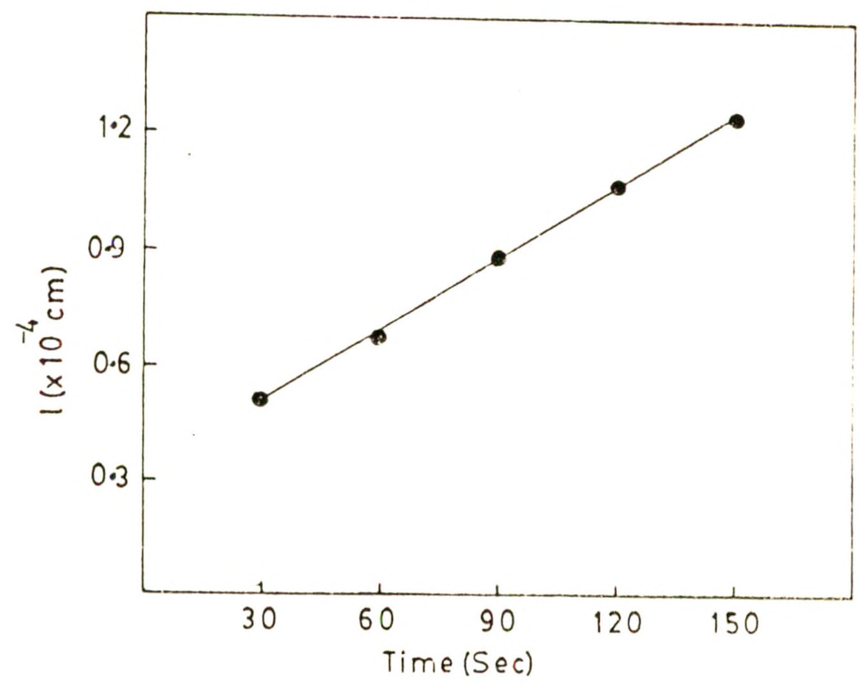
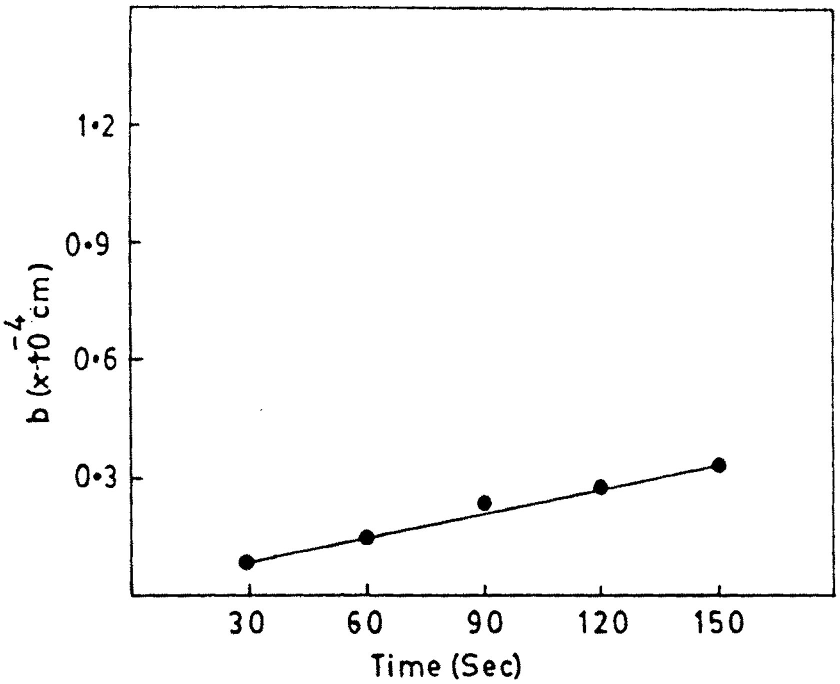


Fig. 13.4(a)



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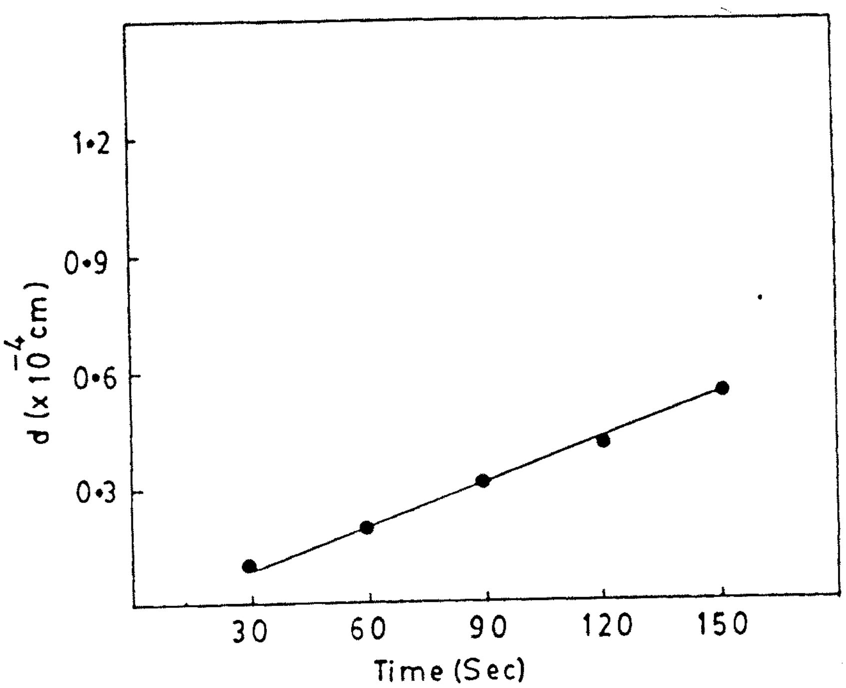
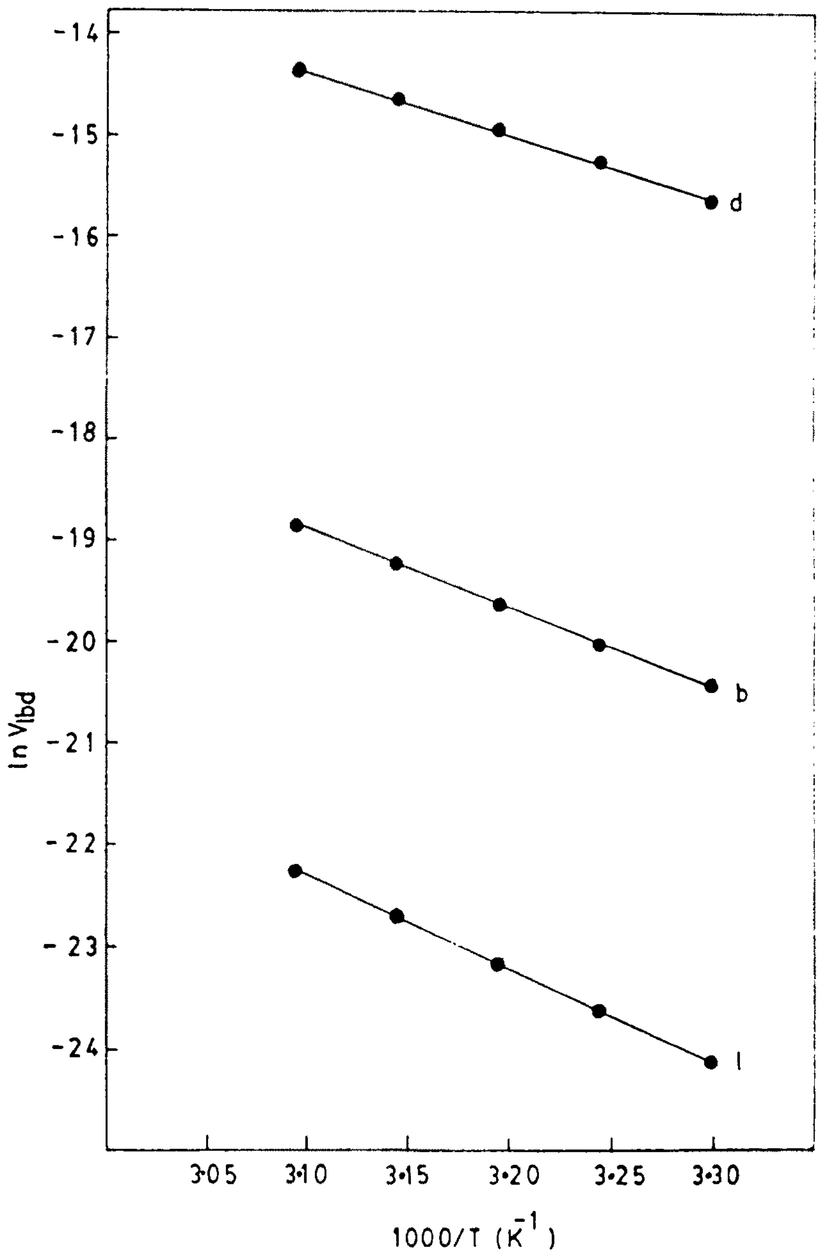


Fig. 13.4(c)



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-24
ln V_lbd
d
b
l
3·05
3·10
3·15
3·20
3·25
3·30
1000/T (K⁻¹)

Fig. 13.5