Etching of MgO crystals in acids: kinetics and mechanism of dissolution

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Kinetics of etching of MgO crystals have been studied in H_2SO_4, HNO_3 and HCl. The effects of etching time, acid concentration and temperature on the growth of hillocks, on the selective etch rate and on the rate of overall dissolution are demonstrated. It is observed that etch rates are independent of time, but are determined by the temperature and concentration of the acid. The etch rate–concentration curves show maxima which are characteristic of an acid. The values of activation energy for the processes of dissolution, selective etching and hillock growth and the corresponding frequency factors are computed. It is established that the process of dissolution in concentrated H_2SO_4 is diffusion controlled, while in H_2SO_4 with concentrations below 18 N and in HNO_3 and HCl it is reaction rate controlled. The pre-exponential factor is found to be a function of acid concentration. The results are discussed from the standpoint of chemistry. A comment on the data published on MgO by previous workers is made.

1. Introduction

Composition and temperature of an etching solution have profound influence on, *inter alia*, the shape of etch features and on the dissolution-rate of crystals [1–11]. A study of the effect of etching parameters, especially those which can be controlled, e.g. temperature, composition and time, can serve as a source of valuable information about our scanty knowledge of the mechanism of dissolution of crystals. In metals and semiconductors the process of dissolution is fairly well understood [1, 2], but in alkali halides it remains unclear [3, 5]. The mechanism of dissolution of crystals of sparingly soluble salts, e.g., CaF_2, MgO, $BaSO_4$, etc., which are easily etched in dilute or concentrated acid solutions, is little studied [7, 9–11].

Ghosh and Clarke [10] studied the influence of temperature on the dissolution rates of saturated solutions of $NH_4Cl + H_2SO_4$ (1:1 ratio by volume) and 88% H_3PO_4 on {1 0 0} faces of MgO crystals and calculated the parameters of etching. Sangwal and Sutaria [11] investigated the influence of concentration and temperature of different acid solutions on the formation of various surface features on {1 0 0} faces of MgO.

However, both the hypothesis proposed for the mechanisms of the formation of various surface features [11], and the role of viscosity of the etching solution in the dissolution mechanism, require additional experimental investigations. The present article describes the effect of etching time, of etchant concentration and temperature on the overall dissolution rate and lateral etch rate at dislocations and hillocks formed on {1 0 0} faces of MgO crystals. The mechanism of dissolution is discussed in the light of the chemistry of the processes.

2. Experimental procedure

The specimens were prepared in the form of parallelopipeds weighing between 0.3 and 0.8 g with surface areas between 1.2 and 2.8 cm^2, from a large single crystal obtained from Norton Research Corporation, Canada. The samples were first polished in 33.08 N H_3PO_4 at 100 to 110°C [11], then weighed to an accuracy of 10^{-4} g. Thereafter their dimensions were measured employing a micrometer screw gauge with an accuracy of 10^{-3} cm. They were then subjected to etching by placing them in 100 ml beakers con-

TABLE I Weight loss, pit size and hillock size in 27 N H_2SO_4 at 21°C after 2 h

Etching characteristics	Experiment I	Experiment II
Weight loss ($\times 10^{-3}$ g cm^{-2})	1.769	1.770
Pit size (μm)	40	41
Hillock size (μm)	92–115	104–120

taining 30 to 35 ml of etching solutions at constant temperatures, with the long dimension either in a slanting position or vertical. Etching temperature was controlled within ± 0.5° C by using a constant temperature water bath whose temperature was regulated by a toluene temperature regulator operated by a magnetic relay system [12]. After specific durations, the samples were extracted
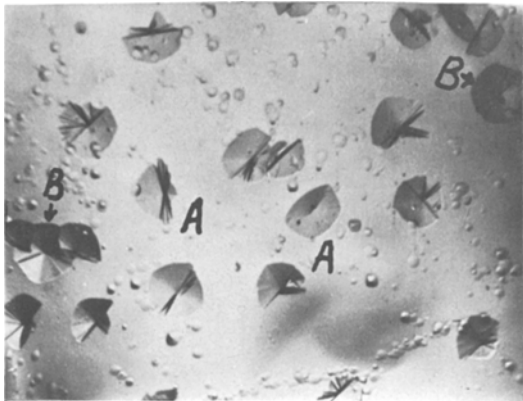

Figure 1 Growth of hillocks in 27 N H_2SO_4 at 21° C for 1 h etching period. Some of the half-filled hillocks are marked as A, while the completely filled ones as B ($\times$ 130).

Figure 2 An example of single (marked S) and multiple (marked M) nucleation centres for growth of hillocks. Etching time 4 h, temperature 21° C ($\times$ 126).

from the beakers, rinsed under running water and dried with filter paper. They were then examined under an optical microscope and measurements of the size of etch pits (along $\langle 1\,0\,0 \rangle$) developed at the sites of fresh dislocations, and that of hillocks were taken at a magnification of $\times$ 100. After measurements and photography, the samples were re-weighed and the loss of weight by etching was calculated. The results are shown in Table I.

From 5 to 10 measurements of etch pit and hillock sizes, and from the loss in weight divided by the surface area of the sample, the lateral etch rate V_t, the rate of hillock growth V_h and the rate of overall dissolution V_d were calculated.

3. Results
3.1. Effect of etching time
The size of the hillocks was found to increase with the etching period. For shorter durations a good number of hillocks (Fig. 1) are underdeveloped and lack a morphology; but for longer durations they become completely filled and acquire a spherulite-like morphology (Fig. 2). On some of them even etch pits are developed, the size of which is always smaller than the size of the pits produced on the surface. A hillock can develop around one or more nucleation centres as seen in Fig. 2. Since multi-nucleation hillocks are larger than mono-nucleation hillocks, hillock size measurements were made only on mono-nucleation hillocks.

The curves of the time dependence of V_d, V_t and V_h by etching $\{1\,0\,0\}$ surfaces in 27 N H_2SO_4 at 21° C are shown in Fig. 3. Apart from a short initial period, the rates are independent of time.
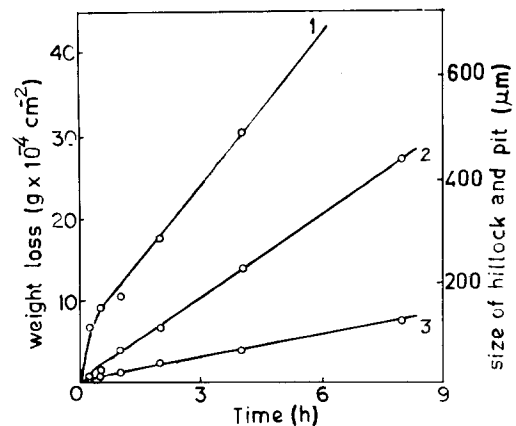

Figure 3 Plots of (1) weight loss, (2) hillock size and (3) pit size versus etching time in 27 N H_2SO_4 at 21° C.
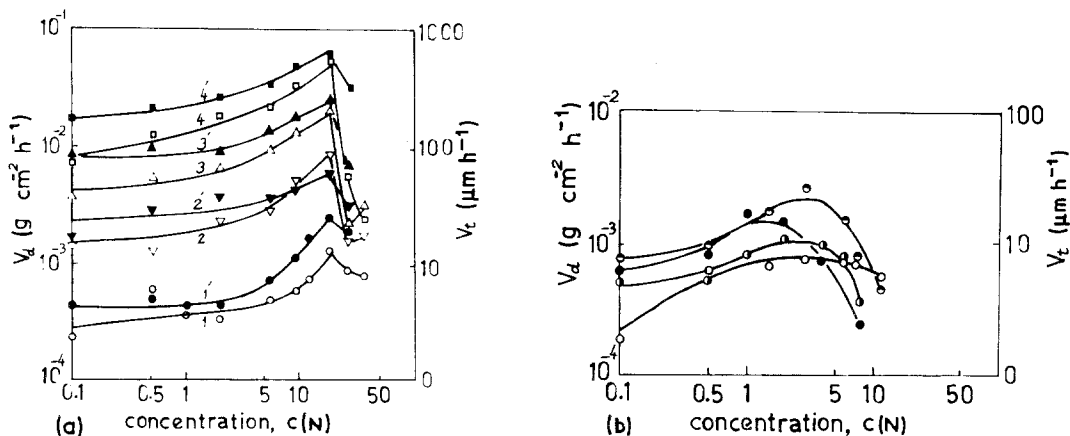
Figure 4 (a) Plots of overall dissolution rate V_d and selective etch rate V_t versus H_2SO_4 acid concentration c. Temperature of etching for curves 1 and 1′, 21° C, 2 and 2′, 45° C; 3 and 3′, 60° C and 4 and 4′, 77° C. Curves 1, 2, 3 and 4, and 1′, 2′, 3′ and 4′ are for dissolution and selective etch rates, respectively. (b) Graph of overall dissolution rate V_d and selective etch rate V_t versus HNO_3 and HCl concentration c. Points marked ○ and ● represent V_d and V_t respectively, for HCl acid at 24° C, while ◐ and ● stand for V_d and V_t respectively, for HNO_3 at 26° C.

3.2. Effect of etchant concentration

The plots of V_d and V_t versus concentrations of H_2SO_4, HNO_3 and HCl are presented in Fig. 4. For a particular acid, the nature of the V_d–c and V_t–c curves is similar. The curves also show well-defined maxima, which are characteristic of a particular acid. In the case of HNO_3 and HCl (Fig. 4b), a well-defined peak is obtained at that acid concentration where circular etch pits are formed [11]. In H_2SO_4 (Fig. 4a), a well-defined peak is

observed at 18 N concentration when in addition to ⟨1 0 0⟩ etch pits, ⟨1 0 0⟩ pyramids at decorated dislocations are produced [11]. At low concentration a peak corresponding to circular etch pit formation in H_2SO_4 is also found.

3.3. Influence of temperature
3.3.1. H_2SO_4

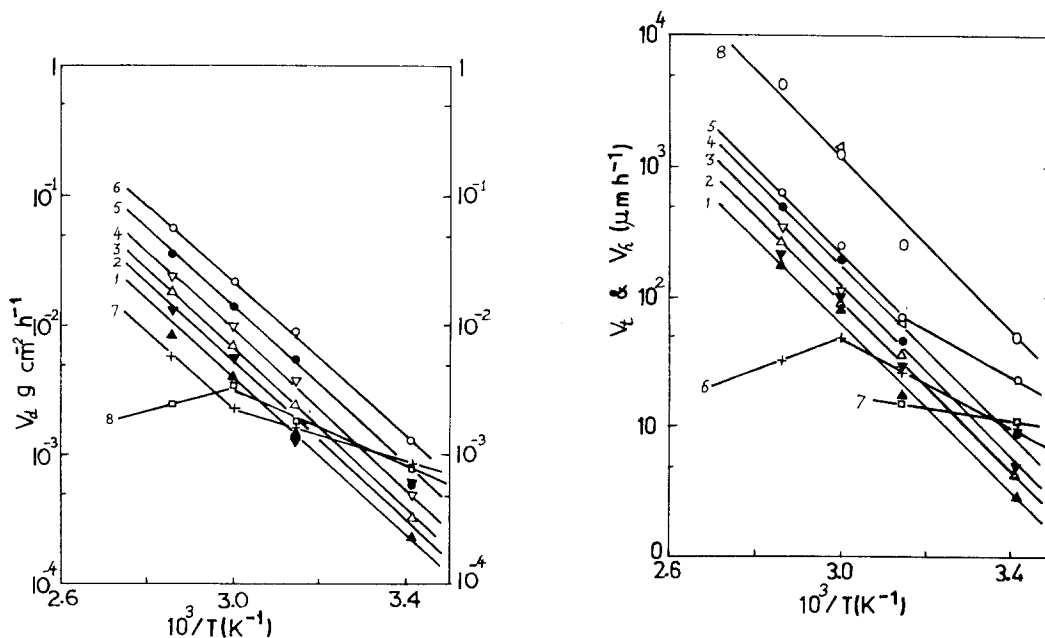The plots of $\log V_d$, $\log V_t$ and $\log V_h$ versus $1/T$ (where T is temperature on the Kelvin scale)

Figure 5 Plots of $\log V_d$ versus $1/T$ for different H_2SO_4 solutions: 1 – 0.1 N, 2 – 0.5 N, 3 – 2 N, 4 – 5.5 N, 5 – 9 N, 6 – 18 N, 7 – 27 N, 8 – 36 N.
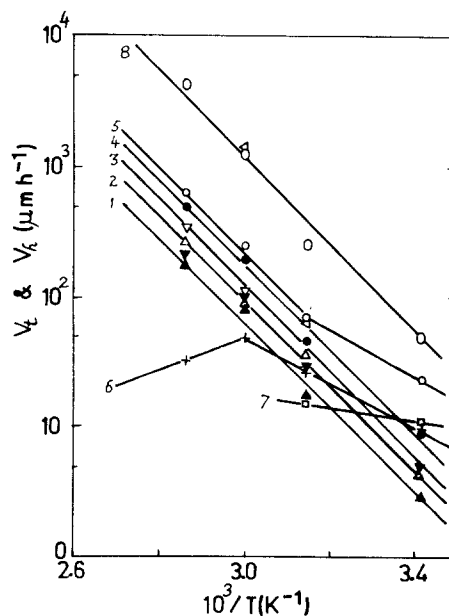

Figure 6 Plots of $\log V_t$ versus $1/T$ for various H_2SO_4 solutions: 1 – 0.1 N, 2 – 0.5 N and 2 N, 3 – 5.5 N, 4 – 9 N, 5 – 18 N, 6 – 27 N and 7 – 36 N. Plot 8 represents $\log V_h$ versus $1/T$.
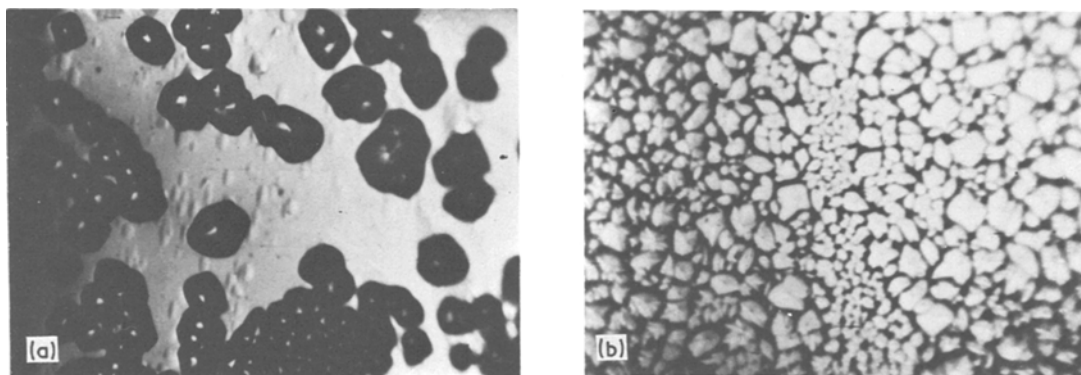
Figure 7 Formation of hillocks by 36 N H_2SO_4 at (a) 21° C and (b) 77° C. Time of etching (a) 1 h and (b) 11 min (× 120).

in the interval 20 to 80° C are shown in Figs. 5 and 6. Except at 27 N and 36 N H_2SO_4, the dependence of $\log V_d$ on $1/T$ can be approximated to parallel straight lines in the whole temperature interval for all the acid concentrations. This suggests that the value of the activation energy for overall dissolution, E_d, is constant but that of the pre-exponential factor, A_d, is dependent on the concentration of the etchant. In the temperature interval between 20 and 60° C, E_d for 27 N H_2SO_4 is less than that for lower H_2SO_4 concentrations. In the same interval the value of E_d for 36 N H_2SO_4 is higher than that of 27 N H_2SO_4. Above 60° C, the behaviour of 27 N and 36 N H_2SO_4 solutions is quite different; for the former E_d increases, whereas in the latter it becomes negative.

The trend of the $\log V_t$ versus $1/T$ curves for H_2SO_4 concentrations lower than 18 N is similar to that for the overall dissolution process. For 18 N, 27 N and 36 N H_2SO_4, the curves show a difference in the temperature interval 20 to 60° C.

The curve of $\log V_h$ versus $1/T$ for 27 N H_2SO_4 solutions (plotted in the upper part of Fig. 6) shows that the process is activation controlled. For 36 N solution, this dependence is irregular as is shown by the points. A comparison of the photographs of the surface features formed by 36 N H_2SO_4 solutions at different temperatures, illustrated in Fig. 7, shows that at higher temperature the density of hillocks has considerably increased.

The values of E_d, E_t, E_h, and the corresponding A's are given in Table II.

TABLE II Activation energy and pre-exponential factor for various solutions

Acid	Normality N	E_d (eV)	E_t (eV)	E_h (eV)	A_d (g cm^{-2} h^{-1})	A_t (μm h^{-1})	A_h (μm h^{-1})
H_2SO_4	0.1	0.59	0.65	—	2.61×10^6	3.69×10^{11}	—
	0.5	0.59	0.65	—	3.98×10^6	5.01×10^{11}	—
	2.0	0.59	0.65	—	4.82×10^6	5.01×10^{11}	—
	5.5	0.59	0.65	—	6.43×10^6	6.59×10^{11}	—
	9.0	0.59	0.65	—	9.44×10^6	1.04×10^{12}	—
	18.0	0.59	0.35	—	1.57×10^7	1.26×10^{12}	—
			(0.65)*			(2.19×10^7)	
	27.0	0.20	0.35	0.65	1.53×10^6	8.25×10^6	7.22×10^{12}
		(0.59)	(−0.23)		(2.15×10^6)	(16.5)	
	36.0	0.31	0.06		1.47×10^2	24.2	—
		(−0.19)			(4.64×10^{-6})		
HNO_3	0.5	0.59	0.68	—	3.83×10^6	1.75×10^{12}	—
	6.0	0.59	0.68	—	3.83×10^6	6.52×10^{10}	—
HCl	0.5	0.59	0.68	—	3.83×10^6	1.75×10^{12}	—
	6.0	0.59	0.56	—	3.83×10^6	3.40×10^{10}	—

*The values of E_d, E_t, A_d and A_t given in brackets correspond to the higher temperature region.
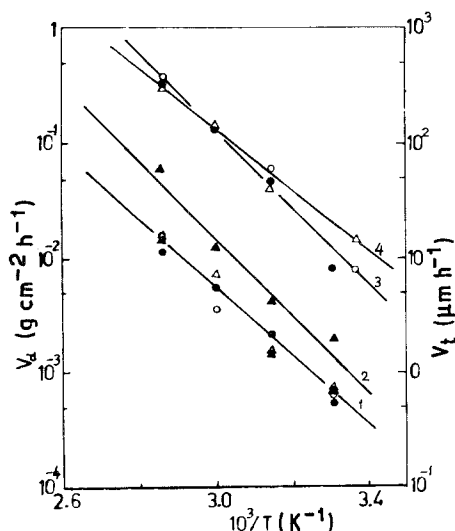
Figure 8 Log V_d and log V_t versus $1/T$ plots for $\bullet$ – 0.5 N HNO$_3$, $\blacktriangle$ – 6 N HNO$_3$, $\circ$ – 0.5 N HCl and $\triangle$ – 6 N HCl. Curve 1 is for overall dissolution while curves 2, 3 and 4 are for selective etching.

3.3.2. HNO₃ and HCl

The dependence of log V_d and log V_t versus $1/T$ for 0.5 N and 6 N solutions of HNO$_3$ and HCl in the same temperature interval is shown in Fig. 8. If the scatter in the points is ignored, the value of E_d is 0.59 eV. The values of activation energy and pre-exponential factor for different solutions of HNO$_3$ and HCl are also included in Table II.

4. Discussion

Dissolution of a surface may be considered to involve five consecutive steps [13]:

(1) Diffusion of the reacting molecules to the surface.

(2) Adsorption of the reacting molecules on the surface.

(3) Reaction on the surface.

(4) Desorption of the reaction products.

(5) Diffusion of the desorbed products into the solution.

Steps 1 and 5 of the transport of the reacting and reacted species are determined by diffusion kinetics, whereas 2, 3 and 4, which are usually regarded as a single step, are limited by the reaction rate between the acid and the solid. Since the dissolution rate is determined by the slowest step, the process of dissolution may be diffusion controlled or reaction rate controlled, depending on the conditions of the experiment.

Let us first analyse the temperature dependence of dissolution rates. Examination of log V_d and log V_t versus $1/T$ curves shows that the processes of dissolution exhibit similar dependence although the etching parameters are different in the two cases (Table II). In particular, the values of E_d vary markedly at 27 N and 36 N H$_2$SO$_4$ concentrations, and there are instances when, at a particular concentration (e.g. at 27 N above 60° C), E_d is positive and E_t is negative. The lower values of E_d and E_t at 27 N and 36 N H$_2$SO$_4$ concentrations in comparison with those < 18 N suggest that at higher concentrations the process may be diffusion limited.

With an increase in the concentration of an acid, its degree of dissociation is appreciably reduced, but it remains constant with temperature [14]. Consequently, at a particular acid concentration, it can easily be found out whether or not the dissolution process is diffusion controlled by plotting log σ (where σ is viscosity of the solution) versus $1/T$ in the temperature interval of interest. For liquids which have a low viscosity at room temperature, the value of activation energy for the viscosity decrease, E_σ, is usually 0.14 eV (see Table III). On the other hand for denser solutions, the curves of log σ versus $1/T$ (Fig. 9) always have two slopes, each corresponding to relatively high values of activation energy. It should be noted that the value of E_σ is not connected with the degree of dissociation of the solution. In general, the acti-

TABLE III Activation energy for the rate of viscosity decrease with temperature for various solutions

Liquid	Viscosity at 20° C σ	Activation energy E (eV)	Degree of dissociation at 18° C
CH$_3$OH	0.597 cP	0.11[a]	–
C$_2$H$_5$OH	1.200 cP	0.15[a]	–
HCOOH	1.804 cP	0.15[a]	–
CH$_3$COOH	1.26 cP	0.14[a]	0.004
36 N H$_2$SO$_4$	25.4 cP	0.19, 0.27[ac]	0.57
H$_2$O	1.0 cS	0.14[b]	–
2.21 – 13.23 N H$_3$PO$_4$	1.0–2.2 cS	0.14[b]	–
22.05 N H$_3$PO$_4$	4.3 cS	0.14, 0.21[b]	–
33.08 N H$_3$PO$_4$	15.0 cS	0.19, 0.26[b]	–
37.50 N H$_3$PO$_4$	28.0 cS	0.21, 0.29[b]	–
44.10 N H$_3$PO$_4$	140.0 cS	0.22, 0.39[b]	0.17

[a] calculated from the data of [15].
[b] calculated from the data of [16].
c the two values correspond to temperature interval above and below 45° C.
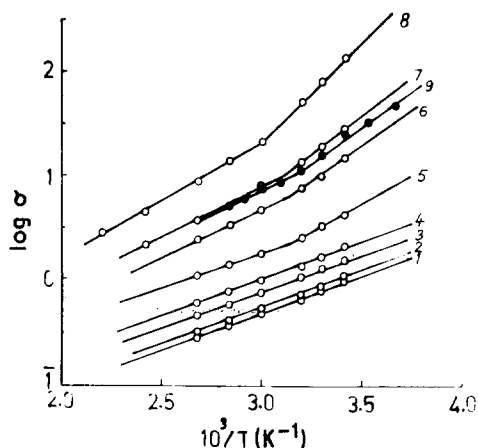
Figure 9 Dependence of viscosity σ of H_3PO_4 and H_2SO_4 on temperature T: $1 - H_2O$, $2 - 2.21\,N\,H_3PO_4$, $3 - 8.82\,N\,H_3PO_4$, $4 - 13.23\,N\,H_3PO_4$, $5 - 22.05\,N\,H_3PO_4$, $6 - 33.08\,N\,H_3PO_4$, $7 - 37.50\,N\,H_3PO_4$, $8 - 44.10\,N\,H_3PO_4$ and $9 - 36\,N\,H_2SO_4$.

vation energy increases with the concentration of the acid. The E_d values of $0.31\,eV$ and $0.20\,eV$ for $36\,N$ and $27\,N$ H_2SO_4 at temperatures below $60°C$ may thus be attributed to the diffusion limited dissolution kinetics. Similar behaviour has also been reported for Ge and Si crystals [17].

The high values of E_d in dilute solutions of H_2SO_4 and different solutions of HNO_3 and HCl is obviously connected with chemically controlled dissolution kinetics.
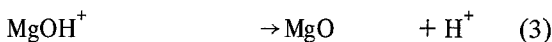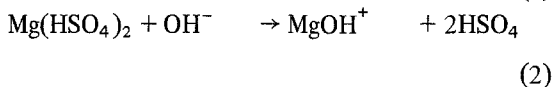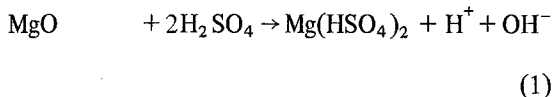
In the lower temperature interval for $18\,N$, $27\,N$ and $36\,N$ H_2SO_4, E_t has values of $0.35, 0.35, 0.06\,eV$, respectively. This indicates that the process of dislocation etching could well be diffusion controlled or, in particular for $18\,N$ and $27\,N$ H_2SO_4 it could be controlled by both diffusion as well as reaction rate processes. At lower H_2SO_4 concentrations and at different HNO_3 and HCl concentrations, the kinetics of selective etching are limited by reaction rate. However, in some cases, as for example during selective etching in $18\,N$ H_2SO_4 and during overall dissolution in $27\,N$ H_2SO_4, the kinetics appear to have switched over from diffusion controlled to chemically controlled ones. The negative values of E_d in $36\,N\,H_2SO_4$ and of E_t in $27\,N\,H_2SO_4$ above $60°C$ seem to be connected with the instability of the reaction products. Indeed, the photograph of Fig. 7b points to this possibility.

For concentrations lower than $18\,N$ H_2SO_4, $E_d < E_t$. This difference, though small, may be attributed to the localization of energy around dislocations. Whenever the condition $E_d \geqslant E_t$ prevails, and if etch pits are formed at some stage with the increase of temperature, the pits disappear (compare the curve for $36\,N$ H_2SO_4 of Figs. 5 and 6).

The curves of $\log V_d$ and $\log V_t$ versus $1/T$ for $0.5\,N$ and $6\,N$ HNO_3 and HCl acids show a behaviour similar to that of $0.5\,N$ and $5.5\,N$ H_2SO_4 acid. The value of E_d in the case of HNO_3 and HCl is equal to E_d in $5.5\,N$ H_2SO_4. The value of E_t for $0.5\,N$ HCl, $0.5\,N$ HNO_3 and $6\,N$ HNO_3 is equal to $0.68\,eV$, but that for $6\,N$ HCl is $0.56\,eV$. These values differ from the values of E_t corresponding to $0.5\,N$ and $5.5\,N\,H_2SO_4$ solutions. In $0.5\,N\,HCl$, $0.5\,N$ HNO_3 and $6\,N$ HNO_3 where $E_d < E_t$, pits retain their contrast but where $E_d > E_t$ they become invisible. When various solutions have the same values of E_d and E_t, the dissolution rates are determined by the values of the frequency factor A (Table II, Figs. 5, 6 and 8).

We now attempt to explain the mechanism of dissolution from the standpoint of chemical kinetics. The system under consideration is one in which the processes of diffusion, adsorption—desorption and chemical reaction all take part. Let us write down the chemical reactions [11]:

$$MgO + 2H_2SO_4 \rightarrow Mg(HSO_4)_2 + H^+ + OH^-$$

$$\tag{1}$$

$$Mg(HSO_4)_2 + OH^- \rightarrow MgOH^+ + 2HSO_4$$

$$\tag{2}$$

$$MgOH^+ \rightarrow MgO + H^+ \tag{3}$$

The first equation represents the formation of the reaction products, while the latter two represent the formation of hillocks in concentrated H_2SO_4 and $HCOOH$ and weak H_3PO_4. If the reactions proceed as represented above, it may be possible to observe the formation of some insoluble reaction products under certain conditions. This may happen especially at high concentrations of the solution when the sulphate and hydrosulphate are soluble only in alkalis, glycerol and ether [15]. Actually in concentrated H_2SO_4, after sufficiently long durations of etching, it is observed that the appearance of the liquid surrounding the crystal becomes milky. If the behaviour of $Mg(HSO_4)_2$ and $Mg(OH)_2$ (formed by the union of OH^- ions present in the solution with $MgOH^+$ of Reaction 2) is taken into consideration from the viewpoint of their solubility in water,

the likely compound is $Mg(OH)_2$. Indeed, this product remains to be identified chemically. However, from the observations that the hillocks grow with time, and that the size of etch pits on the surfaces of hillocks is always smaller than that on the surface, it is certain that back reaction leading to the formation of MgO from $Mg(HSO_4)_2$ takes place.

In the state of equilibrium, Equation 1 may be written as

$$MgO + 2H_2SO_4 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} Mg(HSO_4)_2 + H_2O \quad (4)$$
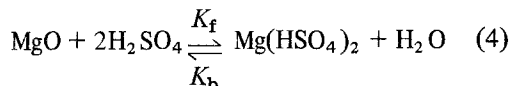
where K_f and K_b are the rate constants in the forward and the backward directions, respectively. Then the dissolution rate V may be expressed as

$$V = K_f [HSO_4]^2 - K_b [Mg(HSO_4)_2]$$

or $\quad V = [K_f - K_b K_1] [H_2SO_4]^2 \quad (5)$

taking $\quad [Mg(HSO_4)_2] = K_1 [H_2SO_4]$.

For dilute solutions, $K_b = 0$, and hence

$$V = K_f [H_2SO_4]^2, \quad (6)$$

which implies that if K_f is independent of concentration, $V \propto [H_2SO_4]^2$, and that at a particular concentration when K_f or $(K_f - K_b K_1)$ is constant, the weight loss, growth of pit or hillock size should increase linearly. The curves shown in Fig. 3 support the above conclusion. A rapid initial increase in the curves is associated with the establishment of an equilibrium at the crystal surface [18].

An examination of V versus c curves for various acids shows that in H_2SO_4 the concentration dependence of etch rates is initially quite weak, but later is is quite marked. In HNO_3 and HCl somewhat different behaviour is observed. The value of n, defined as the order of the reaction by an expression $V = Kc^n$, where c is the concentration of the acid, is about 1 in the range of 9 to 18 N H_2SO_4, 0.5 to 1.5 N HCl and 0.5 to 1.5 N HNO_3. From a consideration of the circular morphology of etch pits, it may, however, be inferred that the reasons for the developments of these peaks are different. The modification of the morphology of $\langle 100 \rangle$ orientation etch pits by increasing the dilution of the acids may be the reason for the development of peaks in HCl and HNO_3 acids. Weakly-defined maxima in dilute H_2SO_4 may also be due to such effects. Their nature may be better understood by considering the adsorption and desorption processes.

We assume that both the acid and the reaction product adsorb on the dissolution steps. The dissolution rate for bimolecular reactions in cases when two molecules adsorb is expressed by [13]

$$V = \tfrac{1}{2} S K c_a c_p L \quad (7)$$

$$V = \tfrac{1}{2} S K L \frac{c_a c_p}{(1 + K_{eq} c_a)^2} \quad (8)$$

and $\quad V = \tfrac{1}{2} S K L \frac{c_a c_p}{(1 + K_{eq} c_p)^2} \quad (9)$

for cases when the surface is sparsely adsorbed, the acid is more strongly adsorbed than the product, and when the product is more strongly absorbed than the acid. Here S and L have the same significance as in [13] with $K = $ constant, $K_{eq} = $ equilibrium constant, $c_a = $ acid concentration, and $c_p = $ product concentration.

It follows from Equations 8 and 9 that the formation of a peak in every acid is, as explained above, a natural consequence of adsorption and desorption of acid and reaction product. The second peak observed in H_2SO_4 is associated with the concentration and viscosity effects. A relatively low value of the order of the reaction, n, may be attributed to the decreased degree of dissociation with increasing acid concentrations.

Finally some remarks should be made on the activation energy of hillock formation, dependence of the pre-exponential factor on acid concentration, and on the reported data on MgO crystals. The activation energy, E_h, of hillock formation in 27 N H_2SO_4, equal to 0.65 eV, is quite high as compared with the value 0.20 eV of the activation energy, E_d, of overall dissolution. However it is equal to the value of E_t. This means that the process of hillock formation is reaction controlled, and may be related to the reversible reaction of MgO and H_2SO_4 into MgO again. At 36 N H_2SO_4, this reversible reaction does not show a systematic behaviour, as may be seen from the points given in Fig. 6.

It was remarked earlier that below 18 N H_2SO_4, while the values of E_d and E_t remain constant, the values of A_d and A_t increase with increasing acid concentration, which means that A_d and A_t are functions of concentrations. The graph of $\log A_d$ and $\log A_t$ versus $\log c$, illustrated in Fig. 10, shows
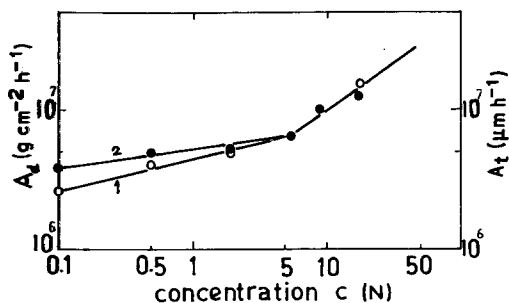
Figure 10 Dependence of frequency factors A_d (curve 1) and A_t (curve 2) on H_2SO_4 concentration c.

however that below and above $5.5\,N\,H_2SO_4$, they can be represented by the empirical relations,

$$A_d = 4.5 \times 10^6\ c^{1/5}$$

$$A_t = 5.1 \times 10^{11}\ c^{1/7.5}$$

and

$$A_d = 2.2 \times 10^6\ c$$

$$A_t = 2.2 \times 10^{11}\ c$$

(10)

respectively. This enables us to re-write the Arrhenius equation,

$$K = A \exp\left[-E/kT\right]$$ (7a)

into the form

$$K = A_0 c^m \exp\left[-E/kT\right]$$ (7b)

where A_0 is the temperature independent part of A and the exponent, m, describing the concentration dependence has values characteristic of whether we talk of selective etching or overall dissolution, and of the concentration interval.

In order to determine dissolution rate, v, at an arbitrary point on the surface, Cabrera [19] introduced the expression

$$v = a\,\gamma_s \exp\left[-E_s/kT\right]$$ (8)

where γ_s is the frequency factor characterizing the frequency of nucleation, a is the height of a step ($\sim 10^{-8}$ cm) and E_s is the activation energy of the formation of a nucleus. The frequency factor should, in principle, be a function of acid concentration and the value of E_s should depend on the nature of the acid used. In general, E_s should have different values for dissolution in H_2SO_4, HCl and HNO_3. The values obtained of the pre-exponential factor, A, shown in Table II and Equation 6, support the concentration dependence of fre-

quency factor, but the values of E_d and E_t (Table II) merely indicate the possibility of their dependence on the acid employed, but do not prove it unequivocally.

The values of E_d using solutions of saturated NH_4Cl and concentrated H_2SO_4 in equal parts and 88% H_3PO_4, reported by Ghosh and Clarke [10], are 0.65 eV and 0.45 eV, respectively. Their value of E_d for H_2SO_4 etchant is somewhat higher than that found in the present investigation but still suggests that the dissolution kinetics are reaction rate controlled in this etchant. The activation energy of dissolution E_d in the case of H_3PO_4 is higher than the activation energy of the viscosity decrease E_σ (Table III). This indicates that the dissolution process in H_3PO_4 solution is likely to be partly diffusion controlled.

5. Conclusions

(1) Spherulitic as well as dendritic patterns can be obtained by etching.

(2) The observation of peaks in etch rate versus concentration curves indicates (i) a transition from a chemically controlled mechanism to a diffusion controlled one and (ii) adsorption of the reacting and reacted species at the crystal surface. Viscosity of a solution is responsible for the diffusion limited mechanism.

(3) In H_2SO_4 of concentrations less than 18 N, the dissolution process is chemically controlled with a constant value of activation energy. The dissolution rates below $18\,N\,H_2SO_4$ are determined by the values of the frequency factor. At higher concentrations when the process is diffusion controlled, activation energy decides the dissolution rates. The negative and sometimes very low values of activation energy are possibly associated with the instability of reaction products.

(4) In H_2SO_4 solutions with concentrations $< 18\,N$, the frequency factor is concentration dependent, but the dependence of the value of activation energy of dissolution on the nature of the acid, as demanded by the theory [19], has not been proved. This, however, requires more experimentation.

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