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A note on the dissolution mechanism of MgO crystals in acids

According to the recent treatment of the dissolution of MgO crystals [1], the rates of surface dissolution, v_s, and selected etching, v_d, are given by

$$v_s = 1.1 \times 10^7 \alpha^{-0.9} c^{0.2} \mu^{-0.5} r_m^{-0.25} \exp\left[-E_s/kT\right] \tag{1}$$

and

$$v_d = 6.0 \times 10^8 \alpha^{-0.9} c^{0.2} \mu^{-0.5} r_m^{-0.25} \exp\left[-E_d/kT\right], \tag{2}$$

where μ is the reduced mass of an activated complex, E_s and E_d are the activation energy of dissolution at a surface and the activation energy of dissolution at a dislocation site, respectively, α is the degree of dissociation of an acid, c its concentration and r_m the ratio of the mass of an anion to that of an H^+ ion. It was, however, noted that in various acids containing light and heavy anions, $\mu^{0.5}$ and $r_m^{0.25}$ have values ranging from 8.7 to 15.2 and from 2.45 to 6.63, respectively. When explaining the concentration dependence of dissolution rates, it was assumed [1] that $\mu^{0.5} = 10$ and $r_m^{0.25} = 3$. In this article the hydration of acid

TABLE I Estimated radii of hydrated ions, number of water molecules and $r_{mh}^{0.25}$

Ion	Crystallographic radius R_c (Å)	Hydrated ion radius R (Å)	Number of associated water molecules n_h	Mass of hydrated ion m_h	$r_{mh}^{0.25}$
F^-	1.36	3.3	4.7	104	0.96
Cl^-	1.81	2.6	1.7	66	0.85
Br^-	1.95	2.6	1.3	103	0.95
I^-	2.16	2.6	1.0	145	1.03
NO_3^-	(2.5)*	2.7	0.7	74	0.86
HSO_4^-	(2.5)	2.6	0.3	103	0.96
HCO_2^-	(2.0)	3.3	4.0	121	1.00
$CH_3CO_2^-$	(2.5)	3.6	4.3	137	1.01
SO_4^{2-}	(2.5)	3.6	4.3	174	1.08
$C_2H_5CO_2^-$	(2.7)	3.8	4.0	145	1.03
$C_3H_7CO_2^-$	(3.0)	3.8	4.0	157	1.05
$(CO_2)_2^{2-}$	(2.5)	3.8	5.0	148	1.03
$H(CO_2)_2^-$	2.0	2.6	1.3	119	0.99
H^+	–	3.7	7.0	127	1.00

*Values in parenthesis are uncertain.

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TABLE II Mass, m_h, reduced, μ_h, and $\mu^{0.5}$ of some hydrated complexes

Hydrated complex	m_h	$\mu_h = m_h/2$	$\mu_h^{0.5}$
$2MgO\ HCl.8.7H_2O$	465.6	232.8	15.3
$2MgO\ HBr.8.3H_2O$	541.2	270.6	16.4
$2MgO\ HNO_3.8.3H_2O$	506.6	253.3	15.9
$2MgO\ H_2SO_4.7.3H_2O$	540.6	270.3	16.4
$2MgO\ HCO_2H.11H_2O$	568.6	284.3	16.9
$2MgO\ CH_3CO_2H.11.3H_2O$	608.6	304.3	17.5
$2MgO\ C_2H_5CO_2H.11H_2O$	624.6	312.3	17.7
$2MgO\ C_3H_7CO_2H.11H_2O$	648.6	323.3	18.0
$2MgO\ (CO_2H)_2.8.3H_2O$	544.6	272.3	16.5

ions in aqueous solutions is considered and it is shown that the values of $\mu^{0.5}$ and $r_m^{0.25}$ are constant for the dissolution of MgO crystals in acids.

Electrical conductivity of an electrolyte depends on the mobility of its ions in solution. The mobility is determined by the size and charge of an ion in solution. The effective radius, R, of an ion in solution is different from the crystallographic radius, R_c, and is determined by the number, n_h, of water molecules surrounding it [2]. The effective radius of an ion is estimated from corrected Stokes' law radius. From the value of R and the volume, $V = (4\pi/3)(R^3 - R_c^3)$, the number of the water molecules involved in hydration, $n_h = V/30$, is computed. A detailed description of the procedure of estimating n_h from the mobility of ions is given in [2].

Hydrated Li^+ and H^+ ions are of nearly the same size and involve about the same number of water molecules [2]. Thus, using the number of water molecules attached with a bare ion and the mass of the hydrated entity, m_h, the ratio of the mass of a hydrated anion to that of a hydrated H^+ ion, r_{mh}, may be calculated. The values of R_c, R, n_h, m_h and $r_{mh}^{0.25}$ for some anions are given in Table I. Using the number of water molecules, the estimated values of the reduced mass, μ_h, and $\mu_h^{0.5}$ for different hydrated activated complexes formed by different acids containing light and heavy anions can be calculated, and these values are given in Table II. It may be seen that for acids involving light and heavy anions the values of $r_{mh}^{0.25}$ and $\mu_h^{0.5}$ are practically constant at 1 and 16, respectively. Substitution of these values for $r_m^{0.25}$ and $\mu^{0.5}$ in Equations 1 and 2 gives

$$v_s = 7.0 \times 10^5 \alpha^{-0.9} c^{0.2} \exp\left[-E_s/kT\right] \quad (3)$$

and

$$v_d = 3.8 \times 10^7 \alpha^{-0.9} c^{0.2} \exp\left[-E_d/kT\right]. \quad (4)$$

These equations show that, in different acids giving similar values of the activation energy of dissolution, for a constant value of the degree of dissociation, the dissolution rate should increase with the concentration of different acids.

It was reported [3] that the value of activation energy of dissolution in HNO_3, HCl and H_2SO_4 is approximately the same. Therefore we invesigated the lateral etch rates at fresh screw dislocations emerging on the {1 0 0} face of MgO crystals due to each of these acids at $\alpha = 0.4$. The concentrations of the acids for $\alpha = 0.4$ and the corresponding etch rates are given in Table III. It may be noted that the etch rates and acid concentrations change in the order: $H_2SO_4 < HCl < HNO_3$.

To verify that the above order is the only one that gives the dependence of etch rate on acid concentration, the orders of the variation of the values of $c^{0.2}$, $c^{0.2} r_m^{-0.25}$ and $c^{0.2} r_m^{-0.25} \mu^{-0.5}$, as required by Equations 1 and 2, were determined. From the values of $c^{0.2}$, $c^{0.2} r_m^{-0.25}$ and $c^{0.2} r_m^{-0.25} \mu^{-0.5}$, also included in Table III, it may be observed that in the latter two cases the order is: $H_2SO_4 < HNO_3 < HCl$.

From the foregoing it may be concluded that

TABLE III Concentration of acids, selective etch rate, $r_m^{0.25}$, $\mu^{0.5}$ and possible trends of the change of selective etch rate from a consideration of unhydrated ions and complexes*

Acid	c(M)	v_d(μm h^{-1})	$r_m^{0.25}$	$\mu^{0.5}$	$c^{0.2}$	$c^{0.2} r_m^{-0.25}$	$c^{0.2} r_m^{-0.25} \mu^{-0.5}$
HCl	0.214	25.8	2.45	8.76	0.735	0.290	0.0332
HNO_3	0.278	35.2	2.80	10.16	0.774	0.276	0.0272
H_2SO_4	0.075	17.0	3.12	11.76	0.596	0.192	0.01635

*Values of $r_m^{0.25}$ and $\mu^{0.5}$ are taken from Reference [1].

within the framework of the formalism of dissolution of MgO crystals, as proposed earlier [1], the concept of the participation of hydrated etching species offers a better explanation of the dependence of etch rate on acid concentration. A detailed discussion, dealing with the nature of the species involved in the dissolution of MgO crystals, will be reported later.

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