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Monocrystalline MnZn ferrite dissolution in aqueous H_3PO_4–HCl solutions

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The dissolution of monocrystalline MnZn ferrite in H_3PO_4–HCl aqueous solutions has been studied at temperatures varying from 30 to 110° C. The dissolution rate determined for the two crystal orientations {1 0 0} and {1 1 1} is found to increase with higher H_3PO_4 concentration and higher temperatures with an activation energy of 62 to 77 kJ mol^{-1}. The dissolution is shown to be kinetically controlled, and the rate is determined by the absorption of H_3PO_4 molecules on the surface. At H_3PO_4 concentrations above 10 M, H^+ ions accelerate the dissolution. The dissolution rate of the {1 0 0} orientated surface is a factor of four larger than for the {1 1 1} orientated surface. Temperature and acid concentration do not have a significant influence on the anisotropy, which indicates a similar reaction mechanism for both orientations. When the ferrite surface is partly masked (e.g. by an SiO_2 film) the anisotropy in the dissolution rate yields etched regions which are bordered by planes with the lowest dissolution rates. By properly aligning the masks this results in three-dimensional structures such as V-grooves.

1. Introduction

The dissolution rate of a crystal in an etchant usually depends on the orientation of the surface of the substrate [1]. When a monocrystalline substrate, part of whose surface is masked with an inert film, is etched, crystal planes with the lowest dissolution rate are revealed at the edge of the masked surface region. Thus a well-defined geometric morphology is obtained in the window, an effect which can be used as a microfabrication technology. This technology can only be applied with good results when almost perfect monocrystalline materials are available, as is the case with silicon for example [2]. For this material the microfabrication technology is already widely used.

MnZn ferrite is a ferromagnetic material used in the magnetic cores of magnetic recording heads. In view of the decreasing dimensions of these devices (into the micrometre range), various microfabrication methods are currently being investigated. In this study the dissolution behaviour of monocrystalline MnZn ferrite in H_3PO_4–HCl–H_2O mixtures is investigated. This is carried out on crystal plates with surfaces having the {1 0 0} and {1 1 1} orientation. MnZn ferrite has a spinel crystal structure [3], in which the oxygen ions form a face-centred cubic lattice and the cations occupy part of the tetragonal and octahedral sites in this oxygen lattice. In the {1 1 1} plane the oxygens form a close-packed oxygen layer, while the other planes are occupied with both oxygen atoms and cations at different ratios. This is expected to affect the dissolution rate.

The dissolution rate of oxides in acids has been studied extensively. Although the reaction equation is simple, the mechanism of dissolution is complex and involves electrochemical processes, adsorption and desorption, diffusion, complexation and the formation of reaction product layers. Diggle's review [4] and studies by Sangwal and co-workers [5–7] on monocrystalline MgO dissolution present us with an overview of these processes. In this study we try to find the rate-determining step in the dissolution of monocrystalline ferrites.

2. Experimental procedure

The composition of the ferrite was $Mn_{0.62}Zn_{0.32}$-$Fe_{2.06}O_4$. Zinc and a fraction of the ferric ions occupy the tetrahedral sites while the manganese, ferrous and the remaining ferric ions occupy the octahedral sites. The material can thus be represented [3] as

$$(0.32Zn^{2+}0.68Fe^{3+})_{\text{tetr.}} \times (0.62Mn^{2+}0.06Fe^{2+}1.32Fe^{3+})_{\text{oct.}}O_4$$

Rectangular slabs (8 mm × 16 mm × 2 mm), with {1 0 0} and {1 1 1} surface orientation and having a misorientation of less than 0.3°, were used in this investigation. The slabs were mechanochemically polished with a colloidal SiO_2–NaOH solution to remove the surface layer and reduce the surface damage. The crystals were cleaned by rinsing with water, treatment for 5 min in an ultrasonic acetone bath, and dipping in concentrated HNO_3 for a few seconds. After washing in water and isopropanol the samples were dried.

In order to determine the dissolution rate, part of the crystal was covered with a layer of wax during the dissolution experiment. After removal of the wax the

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resulting step height was measured with a Talystep (Taylor-Hobson, Leicester, England).

On a number of crystals an SiO_2 film (thickness 150 nm) was deposited by chemical vapour deposition (CVD). Line-shaped regions were etched in this film using standard photolithography, the stripes being oriented parallel to a predetermined crystal orientation. Through these stripe windows the MnZn ferrite was dissolved, so as to form a groove. The edges of these grooves were formed out of slow-etching planes. After sawing the crystals perpendicular to the grooves the geometric effect of the anisotropy of dissolution could be observed by scanning electron microscopy (Philips SEM 500).

The dissolution rates were determined by immersing the samples vertically for 15 min in an unstirred solution (500 ml). In preliminary experiments we detected only small differences in dissolution rate in stirred and unstirred solutions. The solutions were prepared by mixing 85 wt% H_3PO_4, 37 wt% HCl (Merck analytical grade) and deionized water. The experiments were carried out in a temperature range of 32 to 108° C.

3. Results

3.1. Dependence on the composition of solution

Table I gives the dissolution rates $V_e\{1\,0\,0\}$ and $V_e\{1\,1\,1\}$ for the MnZn ferrite crystals in a series of aqueous H_3PO_4–HCl solutions at 76° C. Table I also gives the pH of the solution calculated from the equilibrium constant (0.0036 mol) for the $H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$ dissociation at 76° C [8]. The concentration of $H_2PO_4^-$ ions was also calculated and varied from 1 to 3% depending on the pH. In these experiments no influence of time on the dissolution rate was detected.

TABLE I Dissolution rates and anisotropy factor A of MnZn ferrite in aqueous H_3PO_4–HCl solutions at 76° C

Concentration (M)		pH	Dissolution rate (nm sec^{-1})		A
H_3PO_4	HCl		$V_e\{1\,0\,0\}$	$V_e\{1\,1\,1\}$	
5.49	0.00	0.86	2.33	0.72	3.24
14.83	0.00	0.64	4.32	1.92	2.25
6.73	0.048	0.75	3.05	0.75	4.06
12.67	0.048	0.63	4.17	1.07	3.90
3.63	0.060	0.94	1.95	–	–
0.00	0.121	0.92	0.00	0.00	–
2.82	0.121	0.75	0.62	0.47	3.45
5.79	0.121	0.67	2.62	0.72	3.65
7.28	0.121	0.64	2.73	–	–
8.76	0.121	0.61	3.68	0.85	4.33
8.81	0.121	0.61	3.70	0.95	3.89
9.43	0.121	0.60	3.72	0.95	3.92
11.72	0.121	0.56	4.68	1.05	4.46
14.69	0.121	0.45	6.75	2.37	2.85
7.27	0.169	0.58	2.98	0.73	4.08
9.94	0.169	0.54	4.58	1.05	4.36
4.03	0.242	0.54	2.05	0.62	3.31
11.87	0.242	0.45	5.95	1.38	4.31
14.42	0.242	0.41	14.5	–	–

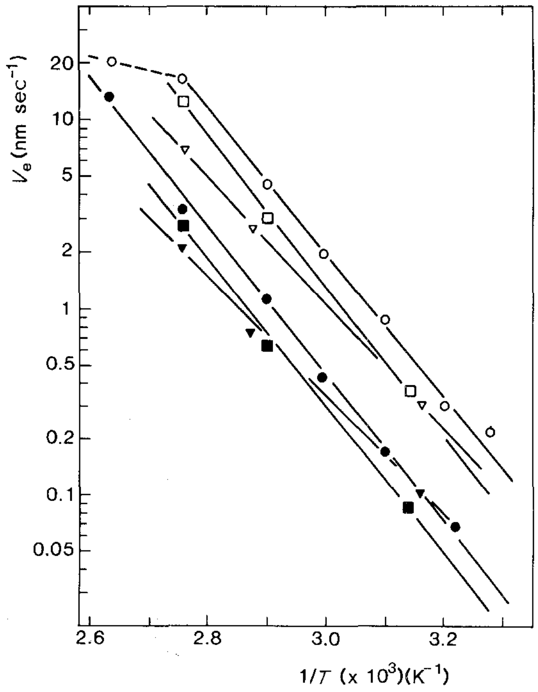

Figure 1 Temperature dependence of $V_e\{1\,0\,0\}$ (open symbols) and $V_e\{1\,1\,1\}$ (closed symbols): (○, ●) 0.60 M HCl–11.76 M H_3PO_4; (□, ■) 0.12 M HCl–10.23 M H_3PO_4; (▽, ▼) 0.12 M HCl–5.78 M H_3PO_4.

3.2. Temperature dependence

The activation energies E_a of the dissolution reaction for $\{1\,0\,0\}$ and $\{1\,1\,1\}$ oriented crystals are obtained for three aqueous H_3PO_4–HCl solutions from the temperature dependence of the dissolution rate (Fig. 1). Table II gives E_a, obtained by a best-fit procedure. The identical temperature dependences of $V_e\{1\,0\,0\}$ and $V_e\{1\,1\,1\}$ show that the degree of anisotropy of dissolution $A = V_e\{1\,0\,0\}/V_e\{1\,1\,1\}$ is not influenced by temperature.

4. Discussion of etching mechanism

The activation energies E_a obtained for the MnZn ferrite range from 62 to 77 kJ mol^{-1}. These values are comparable to the activation energies found for the dissolution of related oxidic materials in phosphoric acid aqueous solutions: 40.2 kJ mol^{-1} for sodium β''-alumina in concentrated phosphoric acid [9], 42 kJ mol^{-1} for MgAl spinel [10], 59.8 kJ mol^{-1} for MgO in 4 M H_3PO_4 [6] and 72.4 kJ mol^{-1} for gadolinium gallium garnet (GGG) in concentrated H_3PO_4 [11]. These E_a values and the anisotropic dissolution show that the dissolution rate is determined kinetically. For diffusion rate-controlled processes lower values of 20 to 25 kJ mol^{-1} are usually found.

TABLE II Activation energies

Etchant	Substrate	Activation energy (kJ mol^{-1})
10.2 M H_3PO_4–0.12 M HCl	$\{1\,0\,0\}$	76.9
	$\{1\,1\,1\}$	75.1
12.6 M H_3PO_4–0.60 M HCl	$\{1\,0\,0\}$	72.6
	$\{1\,1\,1\}$	76.9
5.78 M H_3PO_4–0.12 M HCl	$\{1\,0\,0\}$	64.6
	$\{1\,1\,1\}$	62.1

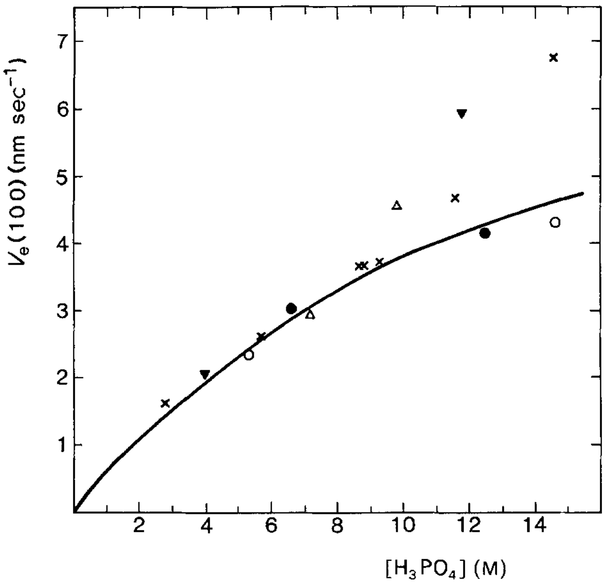

Figure 2 The dissolution rate $V_e\{1\,0\,0\}$ against the H_3PO_4 concentration: (○) 0 M HCl, (●) 0.05 M HCl, (×) 0.12 M HCl, (△) 0.17 M HCl, (▼) 0.24 M HCl.

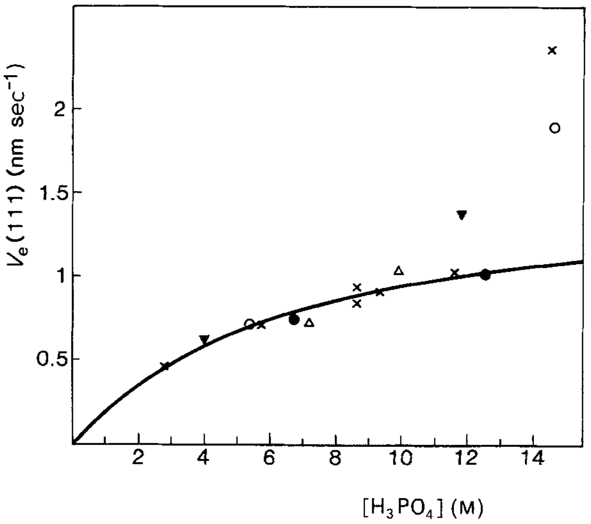

Figure 3 The dissolution rate $V_e\{1\,1\,1\}$ against the H_3PO_4 concentration: (○) 0 M HCl, (●) 0.05 M HCl, (×) 0.12 M HCl, (△) 0.17 M HCl, (▼) 0.24 M HCl.

For {1 0 0} plates at $T = 108°\,C$ the dissolution rate is a factor of two lower than expected (Fig. 1). This could indicate that at this temperature the reaction rate has become limited by the diffusion of reactants to the ferrite surface. The reaction rate at which the transition from a kinetically controlled to a diffusion-controlled dissolution occurs is about 20 nm sec^{-1}. The only study which reports the same transition has been on the dissolution of GGG in concentrated H_3PO_4 [11] which takes place at 200° C with $V_e = 80$ nm sec^{-1}. When the diffusion-controlled mechanism is extrapolated to 108° C, $V_e = 8$ nm sec^{-1} is obtained, which compares reasonably with the 20 nm sec^{-1} obtained for MnZn ferrite, even more so when the higher viscosity of concentrated H_3PO_4 is taken into account.

The dissolution process can be divided into a number of steps:

1. Adsorption of reactive agent(s).
2. Formation of an adsorbed complex, in a number of successive steps.
3. Desorption of the complex and diffusion into the solution.

The observation that the MnZn ferrite does not dissolve in HCl solutions indicates that H_3PO_4 molecules and $H_2PO_4^-$ ions are the reactive species. The data in Table I show that V_e primarily depends on the H_3PO_4 concentration. Figs 2 and 3 show plots of the H_3PO_4 concentration against V_e for {1 0 0} and {1 1 1} plates, respectively. The HCl concentration, which is also indicated, only influences V_e in more concentrated H_3PO_4 solutions.

Assuming a reaction rate determined by the adsorption of H_3PO_4 on the ferrite surface and using the Langmuir absorption isotherm equation, we find that V_e is given by

$$V_e = \frac{k\,a(H_3PO_4)}{1 + a(H_3PO_4)}$$

Fitting this curve to the data in Table I we obtain a good agreement with the proportionality constant $a = 0.058$ and the reaction rate constant $k = 10.1$ nm sec^{-1} for $V_e\{1\,0\,0\}$ and $a = 0.135$ and $k = 1.68$ nm sec^{-1} for $V_e\{1\,1\,1\}$, respectively. At low H_3PO_4 concentrations as well as at high H_3PO_4 concentrations with low HCl contents, the fitted curve corresponds very well with the experimental data (Figs 2 and 3). On the addition of HCl at higher H_3PO_4 concentrations the dissolution rate is substantially higher than predicted by the H_3PO_4 adsorption model. The cause of this effect could be the existence of other types of ionic species at the surface of the MnZn ferrite and in the solution at combined high HCl and H_3PO_4 concentrations.

Such an effect has been observed in a study of the complex chemistry of Fe^{3+} in phosphoric acid by Salmon and co-workers [12–15]. They concluded that pure phosphoric acid contains anionic complexes such as $Fe(HPO_4)_3^{3-}$ or $Fe(PO_4)_3^{6-}$. The addition of HCl leads to the formation of complexes containing fewer phosphate groups, such as $Fe(HPO_4)_2^-$ and $FeHPO_4^+$ with water molecules completing the coordination to six oxygens. For the formation of complexes containing fewer phosphate groups the same amount of absorbed H_3PO_4 can produce more desorbable complexes, thus increasing the dissolution rate of the material.

The difference between $V_e\{1\,0\,0\}$ and $V_e\{1\,1\,1\}$ is caused by the different packing of ions in the layers in these planes. In the {1 1 1} plane, layers are present that are built up of close-packed oxygen atoms. When these planes, two in each unit cell, are revealed the cations are shielded from the H_3PO_4 molecules; in other words, these planes contain no adsorption sites for H_3PO_4 molecules. The {1 0 0} plane, and all other planes, do not contain such a shielding layer, and have a much higher dissolution rate than the {1 1 1} plane.

The anisotropy factor $A = V_e\{1\,0\,0\}/V_e\{1\,1\,1\}$ has a tendency to increase as a function of the H_3PO_4 concentration (Fig. 4). Only at H_3PO_4 concentrations larger than 12 M is a significant decrease in A observed. Together with the constant activation energy in different etchants, this invariability of A indicates that the

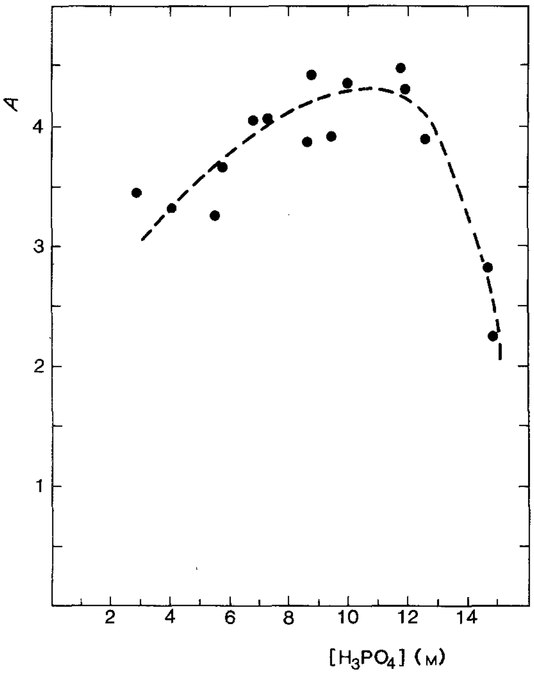

Figure 4 The anisotropy factor $A = V_e\{1\,0\,0\}/V_e\{1\,1\,1\}$ against the H_3PO_4 concentration.

same reaction mechanism controls the dissolution of the $\{1\,1\,1\}$ and $\{1\,0\,0\}$ planes.

5. Patterned etching

The anisotropy in the dissolution rate can be used to etch three-dimensional structures by masking part of the substrate and etching through the windows in the mask. When the mask is a stripe oriented along a predetermined crystal axis, grooves are obtained. Fig. 5 shows this effect schematically and Fig. 6 shows the result for a $\{1\,0\,0\}$ substrate with the stripe oriented parallel to the $\langle 0\,\bar{1}\,1\rangle$ direction. The groove is V-shaped and very similar to grooves obtained in $\{1\,0\,0\}$ silicon wafers etched in concentrated KOH solutions [2]. The planes make an angle of 42° with the surface. The theoretical angle between $\{1\,0\,0\}$ and $\{1\,1\,1\}$ planes is 54.7°. Although this is a significant deviation it is reasonable to assume that the slow-etching planes leading to the formation of the V-groove are of the $\{1\,1\,1\}$ type: $(1\,1\,1)$ and $(\bar{1}\,1\,1)$. The smaller angle can be caused by some undercutting of the mask which results in a higher etch-rate at the surface, or is due to the relatively small anisotropy factor. When the V-groove etch results on monocrystalline ferrite are compared with those obtained on monocrystalline silicon [2], it is evident that the shape of the V-groove in the former case is less constant over the stripe length. This can be caused by the fact that the MnZn ferrite crystals contain more dislocations than silicon, or it is also related to the much smaller anisotropy factor.

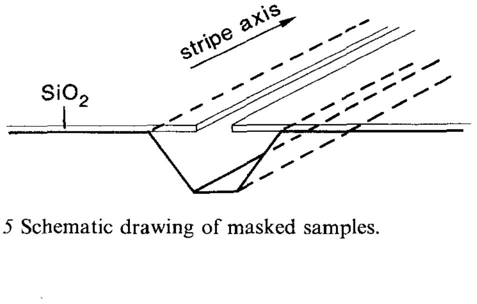

Figure 5 Schematic drawing of masked samples.

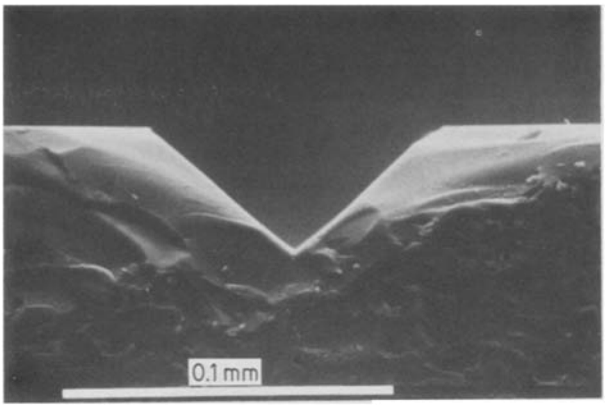

Figure 6 $(1\,0\,0)$ plates with $\langle 0\,\bar{1}\,1\rangle$ stripe direction. Etch time = 1800 sec, $T = 80°C$, etchant 0.60 M HCl–11.76 M H_3PO_4, stripe width 20 μm. Marker represents 100 μm.

6. Conclusions

The dissolution of MnZn ferrite in H_3PO_4–HCl aqueous solutions proceeds by reaction-rate-controlled mechanism. At low (< 10 M) HCl concentrations the reaction rate is proportional to the H_3PO_4 concentration, indicating that the quantity of adsorbed H_3PO_4 and $H_2PO_4^-$ determines the dissolution rate. When at large H_3PO_4 concentrations HCl is added a substantial increase in reaction rate is observed. This effect is probably due to the formation of other types of phosphate complex at the MnZn ferrite surface and in solution. The anisotropy in the dissolution rate $A = V_e\{1\,1\,0\}/V_e\{1\,1\,1\}$ is about 4. This anisotropy is related to the crystal structure. Only in the $\{1\,1\,1\}$ planes are densely packed oxygen layers present. Experiments on $\{1\,0\,0\}$ crystals show that in the $\langle 0\,\bar{1}\,1\rangle$ direction, V-grooves can be obtained with this anisotropic dissolution technique.

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