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The dissolution of Na_2O–MgO–CaO–SiO_2 glass in aqueous HF solutions

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The dissolution (or etching) of a multicomponent (Na_2O–MgO–CaO–SiO_2) silicate glass in aqueous HF solutions is studied. The solutions were chosen in the systems HF–HNO_3–H_2O, HF–HCl–H_2O and HF–H_2SO_4–H_2O, and the temperatures varied from 25 to 60° C. SEM micrographs of the glass surface after etching show an "orange peel" surface structure which develops during etching and which originates from surface flaws. The dissolution rate of the glass was found to increase with higher HF concentration, higher strong-acid concentrations and higher temperatures. The dissolution rate is determined by the reaction of HF molecules and HF_2^- ions with the Si–O–Si grouping surrounding the SiO_4 tetrahedron. In the multicomponent glass some of these bonds are non-bridging due to the presence of Na_2O, CaO and MgO, increasing the dissolution rate significantly. H^+ ions introduced by adding strong acids to the etch solution adsorb on the surface and catalyse the dissolution reaction. Several models used to describe the relation between the dissolution rate and the H^+ concentration are discussed.

1. Introduction

The etching of silicate glasses with HF-containing solutions to change the surface morphology of a glass object, e.g. for frosting and chemical polishing, is well known. Etching can also be applied in pattern etching by dissolving material from selected parts of the surface. Examples of the latter application of etching, using masking techniques to obtain partial dissolution of the glass substrate, are:

1. fabrication of depressions in a large flat glass sheet which can be filled with liquid crystals;
2. etching of cylindrical grooves to act as channels through which liquids are transported, e.g. in ink jets, or to be filled with material of higher refractive index to make passive optical devices, e.g. splitters;
3. etching half-spheres which can be filled with material of higher refractive index to make a Luneburg lens;
4. etching of an optical fibre cladding to expose its core for the fabrication of passive optical components.

The dissolution of vitreous SiO_2 in an HF–acid aqueous solution has been well studied [1–6] and models for the reaction mechanism have been put forward [1, 2]. Considerably less information is available [3, 7] on multicomponent silicate glass etching.

In this study the dissolution of a multicomponent silicate glass is examined in more detail. In particular the effect of the composition of the HF-strong acid solution and temperature on the dissolution rate are studied. Some results of an SEM examination of the morphology of the etched glass surface are reported.

2. Experimental details

A commercial Na_2O–MgO–CaO–SiO_2 glass available in sheets with a controlled surface quality was used in this study. (LOB sheet glass, Glaverbel, Belgium. The composition of the glass is given in Table I.) The sheets (54 mm × 54 mm × 0.6 mm) were cleaned by dipping in a H_2SO_4–$K_2Cr_2O_7$ solution for 10 min, rinsing in isopropanol, and drying. A 600 nm chromium layer was sputtered onto the cleaned glass substrates and a photoresist layer was applied by spinning. The photoresist was exposed to UV radiation through a mask with lines of 100 μm width and the exposed part of the photoresist was developed and removed. The chromium was etched away in a cerium (IV) ammoniumnitrate solution.

With the chromium pattern as a mask the glass was etched for 10 min in HF–HNO_3, HF–HCl and HF–H_2SO_4 aqueous solutions at 25, 40 and 60° C. (Acid mixtures were prepared from pro analysis grade chemicals, E. Merck, Darmstadt, West Germany.) This resulted in 100 μm wide flat etched regions with cylindrically shaped edges, due to the undercutting of the chromium mask. This is shown schematically in Fig. 1. The dissolution depth was measured microscopically after breaking the sheets.

SEM micrographs of the etched region were made from the samples etched in HF–HNO_3 mixtures at 25° C, using an SEM 500 apparatus (N.V. Philips I and E. Division, Eindhoven, The Netherlands).

TABLE I The composition of the LOB glass

	wt %	mol %
SiO_2	72.2	71.2
Al_2O_3	1.6	0.9
K_2O	0.6	13.5
MgO	4.5	6.6
CaO	7.0	7.4

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TABLE II The ionic compositions of the etchant and the etch rate r for HF–HNO_3 mixtures

	HNO_3 (M)	$[H^+]$ (mol l^{-1})	$[HF_2^-]$ (mol l^{-1})	$[HF]$ (mol l^{-1})	r (nm sec^{-1})
1.45 M HF	0	0.14	0.127	1.18	6.3
(T = 25° C)	0.36	0.42	0.054	1.34	6.8
	0.72	0.76	0.032	1.38	7.2
	1.45	1.46	0.017	1.41	8.3
	2.90	2.90	0.009	1.43	11.2
2.90 M HF	0	0.27	0.259	2.37	15.0
(T = 25° C)	0.18	0.39	0.200	2.49	16.3
	0.36	0.53	0.158	2.58	17.3
	0.72	0.83	0.108	2.68	18.5
	1.45	1.51	0.064	2.77	21.3
	2.90	2.92	0.034	2.83	28.8
	5.80	5.80	0.018	2.86	47.3
T = 40° C	0	0.29	0.280	2.33	33.3
	0.36	0.54	0.176	2.54	34.7
	0.72	0.85	0.122	2.65	35.5
	1.45	1.52	0.073	2.75	40.0
	2.90	2.93	0.040	2.82	58.8
T = 55° C	0	0.30	0.298	2.30	57.5
T = 60° C	0	0.31	0.304	2.29	68.3
	0.36	0.56	0.199	2.50	71.7
	0.72	0.87	0.142	2.61	78.8
	1.45	1.53	0.087	2.72	81.3
	2.90	2.94	0.048	2.80	107.5
5.80 M HF	0	0.54	0.524	4.74	35.0
(T = 25° C)	0.36	0.72	0.424	4.94	38.8
	0.72	1.05	0.318	5.16	43.3
	1.45	1.67	0.216	5.36	52.2
	2.90	3.02	0.127	5.54	69.7

3. Results

Tables II and III present the results of the etching experiments. The concentrations of the reactive species in the etching (H^+, HF and HF_2^-) were calculated from the equilibrium constants for the equilibria in the HF etch solutions (Table IV).

3.1. Dependence on temperature

From the dissolution rate data in Table II the activation energy E_a is calculated for dissolution of the Na_2O–MgO–CaO–SiO_2 glass in HF–HNO_3 aqueous solutions (Table V). E_a is found to be in the 30 to 35 kJ mol^{-1} range and shows a tendency to decrease on the addition of HNO_3. This corresponds very well with the E_a values reported for the dissolution of vitreous SiO_2 in HF-containing aqueous solutions [1–3, 6, 8]. This value for the activation energy indicates a reaction-rate-controlled dissolution process. Typical values for diffusion-rate-controlled reaction processes in aqueous solutions are about 20 kJ mol^{-1} (see [9]).

TABLE III The dissolution rate r for HF–HCl and HF–H_2SO_4 mixtures

T (° C)	HCl (M)	r (nm sec^{-1})	H_2SO_4 (M)	r (nm sec^{-1})
25° C	0	15.0	0	15.0
	0.36	17.0	0.45	18.2
	0.72	18.8	0.90	21.3
	1.46	22.0	1.35	24.5
	2.93	30.5	2.70	39.7
40° C	0	33.3	0	33.3
	0.36	33.8	0.45	36.6
	0.72	35.5	0.90	40.3
	1.46	44.5	1.35	46.7
	2.93	62.2	2.70	75.0

3.2. Dependence on HF concentration

The relationship between the dissolution rate and the total HF concentration $[HF]_t$ is determined by fitting the dissolution rate data for the HF–HNO_3 solutions to the curve $r = a[HF]_t^b$. This yields values for the parameters a and b shown in Table V. For the dissolution of crystalline potassium feldspar ($KAlSi_3O_8$) in HF–HCl mixtures a similar value of $b = 1.2$ has been reported [10] while for vitreous SiO_2 a comparable behaviour is observed [2, 10].

3.3. Dependence on the strong acid concentration

A substantial enhancement in dissolution rate is obtained when strong acids are added to the HF solution. By normalizing r with respect to the extrapolated value of r at pH = 0, and by plotting this

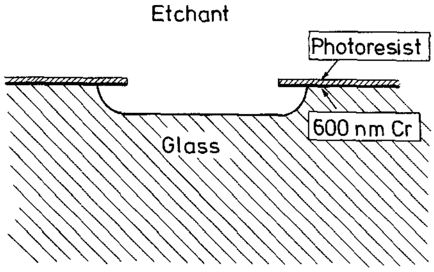

Figure 1 Schematic representation of the samples obtained after the etch experiments.

TABLE IV The equilibrium constants used in this paper

	25° C	40° C	60° C	Reference
$HF \rightarrow H^+ + F^-$	1.30×10^{-3}	9.32×10^{-4}	6.57×10^{-4}	[12]
$HF_2^- \rightarrow HF + F^-$	0.104	0.064	0.0366	[12]

normalized value (in HNO_3–HF mixtures at 25° C) against the pH (Fig. 2) it is shown that the relative increases in r are, to a first approximation, independent of the HF concentration. An analogous effect of H^+ ions on this dissolution rate is observed for vitreous silica [1, 2] and for feldspars [10].

3.4. Dependence on the type of acid

In general the effect of adding strong acids to the etchant is identical for HNO_3, HCl and H_2SO_4. This again indicates that H^+ ions play a major role in the dissolution reaction (Tables II and III). In HF–H_2SO_4 solutions a somewhat higher dissolution rate is observed, particularly at higher H_2SO_4 concentrations. This is observed at both 25 and 40° C. The reason for the higher dissolution rate in HF–H_2SO_4 mixtures is not clear, but it could be related to the formation of fluorosulphuric acid (HSO_3F).

3.5. SEM micrographs

SEM micrographs of the 100 μm-wide flat etched area show the "orange peel" morphology typical of an etched silicate glass surface. Figs 3 and 4 show this surface after etching for 10 min in 1.45 M HF + 0.72 M HNO_3 and 5.8 M HF + 0.72 M HNO_3, respectively. Cups with typical dimensions of 0.5 to 1.5 μm are present. At 1.45 M HF the micrographs show a porous surface, while at 5.8 M HF very small particles are also observed. These may be undissolved fluorides, e.g. MgF_2 or CaF_2. On the addition of HNO_3 no significant change in cup size or surface morphology was observed.

Two hypotheses have been put forward to explain this "orange peel" structure. One suggests that the cups are formed by heterogeneities in the glass and the other suggests that they are due to surface flaws which are either intrinsic or are formed during sample preparation, e.g. polishing. Recently, it was shown that surface flaws can indeed give rise to an "orange peel" morphology after prolonged etch times and large etch depths [11]. At such a surface flaw the etch rate is enhanced and a cup is formed which, due to the reaction controlled dissolution, do not disappear during etching.

At the boundary of the etched region undercutting of the chromium layer occurs (Fig. 1). In the wall formed at this boundary well-defined grooves are observed, with a typical width of 0.2 to 1 μm. From Fig. 5 it is clear that these grooves are a continuation of the cups in the planar etch region, and consequently have the same origin. These grooves are formed from the flaws which are present in the glass surface exactly below the edge of the chromium layer (Fig. 1). As the glass dissolves and the cylindrical etch wall is formed, the irregularities started at the mask edge, grow into grooves. In fact, the existence of such a grooved wall proves that the "orange peel" etch structure originates from surface flaws. The height of the irregularities (cup and grooves) is estimated to be smaller than 0.1 μm. The surface quality obtained by etching the Na_2O–MgO–SiO_2 glass is satisfactory for most of the applications mentioned in the introduction.

TABLE V Activation energy and curve fit results for $r = a[HF]_t^b$

HNO_3 (M)	Activation energy (kJ mol^{-1})	a	b
0	35.4	3.98	1.23
0.36	33.4	4.35	1.26
0.72	34.1	4.50	1.30
1.45	31.5	5.17	1.32
2.90	30.8	6.83	1.32

4. Discussion

Most of the systematic studies of the dissolution of glasses have been performed on vitreous SiO_2 [1–3, 5, 6]. Doped vitreous SiO_2 [4] and some glasses in the CaO–Al_2O_3–SiO_2 system have also been examined [3], and extensive studies of the dissolution of quartz [13] and other crystalline silicates such as feldspars have been published [10, 14–16].

Usually the reaction of HF-containing solutions with silicate materials is considered to be reaction rate controlled [2, 8]. This can be concluded from the value of the activation energy (see section 3.1) and from the insensitivity of the dissolution rate to agitation of the etching solution [6]. Furthermore the large differences in dissolution rate found for glasses with various compositions also indicate such a mechanism [17].

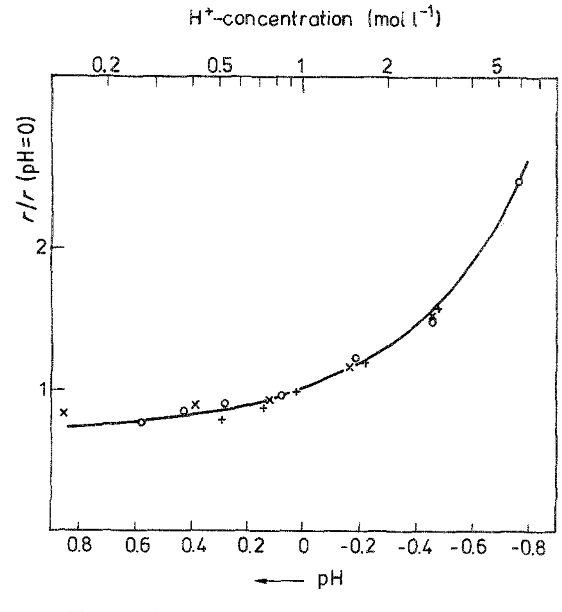

Figure 2 The dissolution rate r as a function of pH. The values for r are normalized as r/r (*pH* = *0*) for etching in HF–HNO_3 mixtures at 25° C; for r (*pH* = *0*) an extrapolated value is used. (×) 1.45 M HF, (o) 2.9 M HF, (+) 5.8 M HF.

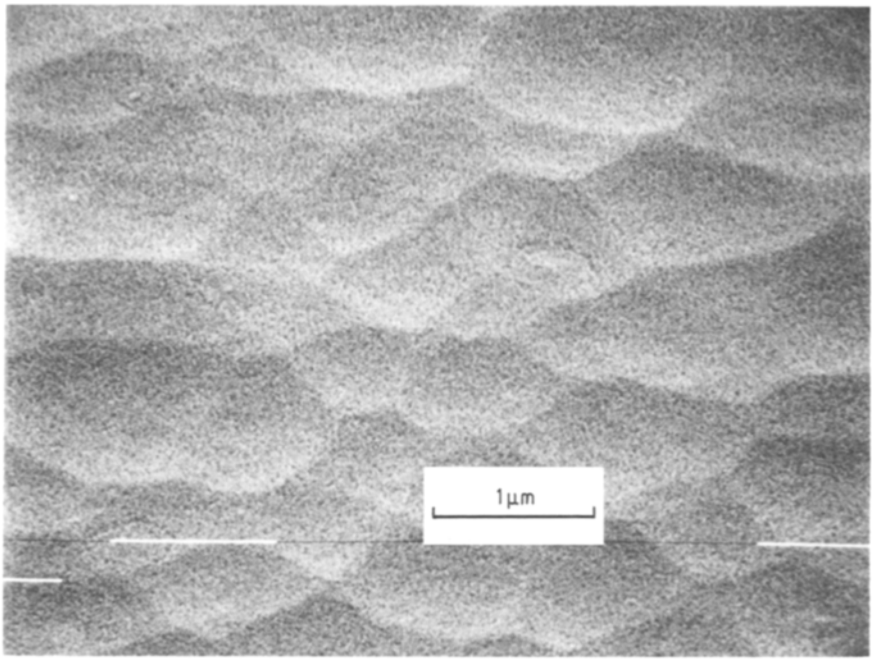

Figure 3 SEM micrograph of the surface of the etched region after 10 min etching in 1.45 M HF + 0.72 M HNO_3 at 25° C.

Dissolution of silicate glasses in HF-containing solutions proceeds by the reaction of a fluorine species with the silicate network to form SiF_4 or H_2SiF_6. The other glass components are also transformed into fluorides or hexafluorosilicates which dissolve in the etchant. The reactive species is either the HF_2^- ion or the HF molecule. It has been observed that the fluoride ion does not show any reactivity towards silicates [18].

Judge [1] concluded from a study of the dissolution of vitreous SiO_2 films on silicon in HF–NH_4Cl aqueous solutions that the HF_2^- ion has a reactivity towards vitreous SiO_2 which is about 4 to 5 times higher than that of the HF molecule. However, it has been shown [16] that the dissolution rate is also influenced by the presence of NH_4^+ ions, an effect which was not taken into account by Judge [1], and which may affect the conclusions.

Born and Prigogine [2] proposed a model for vitreous SiO_2 dissolution, in which the reaction of HF with the Si–O–Si groupings only takes place after H^+ adsorption. This adsorption can occur at any Si–O–Si site but strong adsorption sites are created after nucleophilic replacement of OH-groups with F^- ions after reaction with HF_2^- ions. The rate equation obtained in this case is:

$$r = k[H^+][HF_2^-] + m[H^+] \qquad (1)$$

This equation is tested by plotting $r/[H^+]$ against the HF_2^- ion concentration for the 25° C data shown in Table II (Fig. 6). Although a linear relation is obtained for a set of data with a fixed $[HF]_t$ concentration, there is no overlap for different concentrations. This indicates that adsorption of HF_2^- ions does not control the dissolution reaction.

Fogler and co-authors [10, 14–16] have systematically

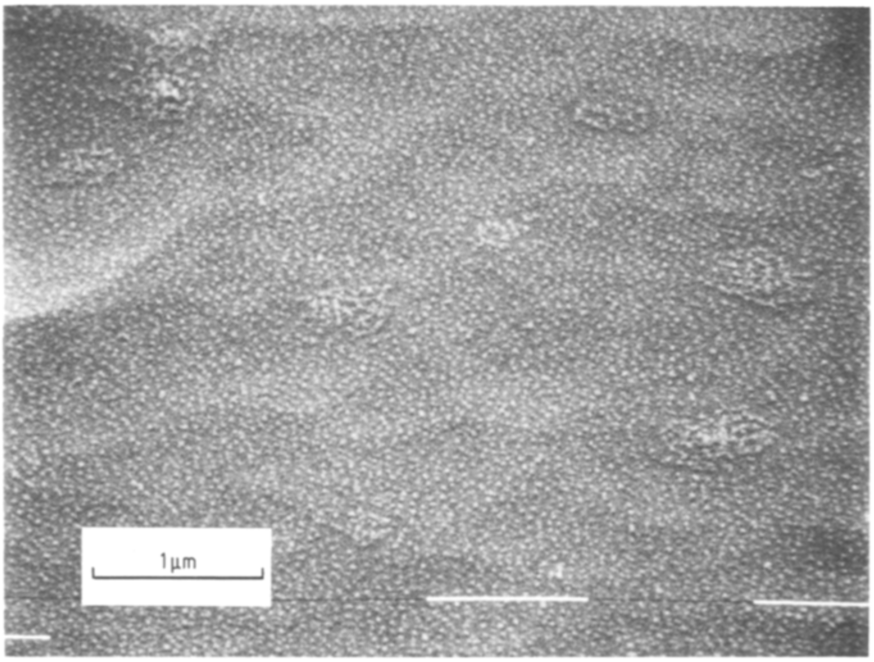

Figure 4 SEM micrograph of the surface of the etched region after 10 min etching in 5.8 M HF + 0.72 M HNO_3 at 25° C.

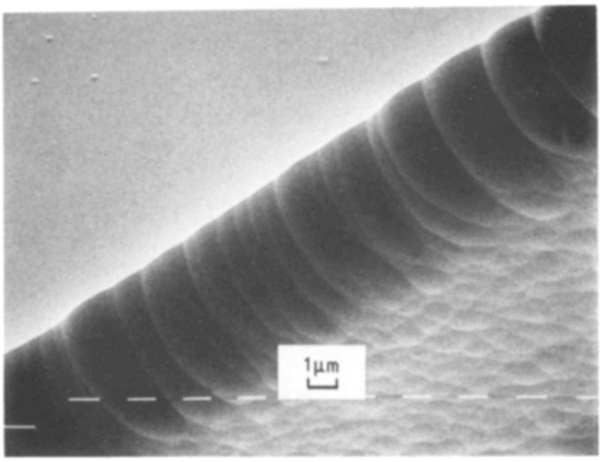

Figure 5 SEM micrograph showing the grooves in the wall at the edge of the etched region (etchant 1.45 M HF + 0.72 M HNO_3, etch time 10 min, $T = 25°C$).

investigated the dissolution of crystalline silicates in strong acid–HF solutions. They concluded that the breaking of the SiO bond in a Si–O–Si grouping limits the dissolution rate. Adsorption of H^+ ions decreases the Si–O bond strength and catalyses the reaction with the fluorine-containing species, which was shown to be the HF molecule. Thus, both the non-catalysed and the catalysed reaction occur simultaneously. Assuming that both the H^+ and HF adsorption follow the Langmuir adsorption isotherm, rate Equation 2 is obtained:

$$r = k_1 \left(\frac{m_1\, a(HF)}{1 + m_1 a(HF)}\right)\left(1 + k_2 \frac{m_2 a(H^+)}{1 + m_2 a(H^+)}\right) \tag{2}$$

Taking $m_1 a[\text{HF}] \ll 1$ and $m_2 a[H^+] \ll 1$, Equation 2 reduces to:

$$r = k_1 m_1 a\,(HF)\,(1 + k_2 m_2 a(H^+)) \tag{3}$$

In the $[H^+]$ range from about 0.1 to about 1 the mean activity constant of HCl is to a first approximation constant [19]. This allows the replacement of $a(H^+)$ by the H^+ concentration $[H^+]$ in Equation 3. In Fig. 7 the value of $r/[H^+]$ is plotted against $[H^+]$ for $0.14 \leqslant [H^+] \leqslant 1.05$, using the 25° C data from Table II. A relatively large scatter of experimental data about the best fit line is obtained. This means that the theory developed by Kline and Fogler does not satisfactorily describe the dissolution rate of the glass studied in this paper.

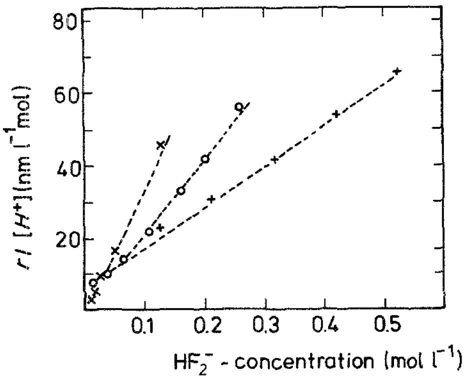

Figure 6 Plot of $r/[H^+]$ against the HF_2^- concentration for the etch data in HF–HNO_3 mixtures at 25° C. (×) 1.45 M HF, (o) 2.9 M HF, (+) 5.8 M HF.

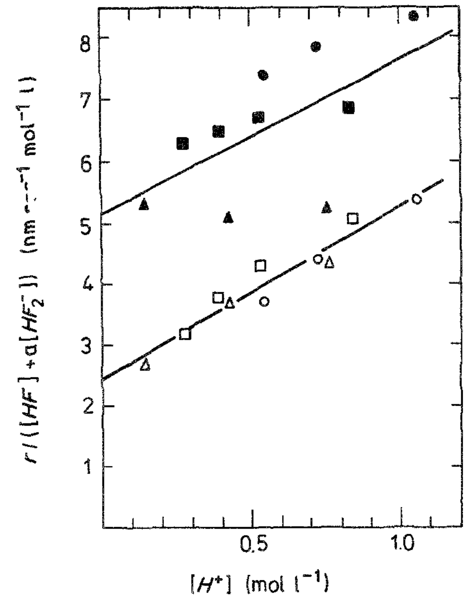

Figure 7 Plot of $r/([HF] + a[HF_2^-])$ against the H^+ concentration for the etch data in HF–HNO_3 mixtures at 25° C. Open symbols: $a = 0$, closed symbols: $a = 9$. (△, ▲) 1.45 M HF, (□, ■) 2.90 M HF, (○, ●) 5.80 M HF.

When it is assumed, as suggested by Judge [1], that the HF_2^- ions are also reactive towards the silicate material, and that the H^+ ions have the same catalytic action, in that case Equation 3 can be rewritten as:

$$r = k_1 m_1([HF] + a[HF_2^-])\,(1 + k_2 m_2[H^+]) \tag{4}$$

where a is the relative reactivity of the HF_2^- ion compared with the HF molecule. By again taking this dissolution rate value for $0.14 \leqslant [H^+] \leqslant 1.05$ at 25° C from Table II, a best fit calculation yields $a = 9$. The plot $r/([HF] + 9[HF_2^-]$ against $[H^+]$ is also shown in Fig. 7. For $a = 9$ a much better correlation is obtained than for $a = 0$. This indicates that HF_2^- ions are reactive, in any case towards the multicomponent silicate glass studied here. But in view of the earlier mentioned similarities, this conclusion is probably valid for other silicate materials as well, although Kline and Fogler [14] present some evidence that indicates no reactivity of HF_2^- ions. It can therefore be concluded that reaction rate Equation 3 satisfactorily describes the dissolution rate–H^+ concentration dependence in HF–strong acid aqueous solutions.

Nevertheless, for glasses with different compositions large differences in the dissolution rates are observed [17]. For examples: the dissolution rates for the Na_2O–MgO–CaO–SiO_2 glass and for vitreous SiO_2 are 15 and 0.3 nm sec^{-1} [3], respectively, in 2.9 M HF at 25° C. Vitreous SiO_2 and feldspars contain SiO_4 tetrahedra which are surrounded by four Si–O–Si groupings. According to Fogler *et al.* [9] the first order behaviour suggests that the dissolution rate is determined by the breaking of one Si–O bond and is independent of the breaking of the three other Si–O bonds. In the multicomponent glass studied here with the composition given in Table I, all of the first Si–O bonds are already broken by the presence of Na_2O, CaO and MgO to form non-bridging SiO-groupings. The dissolution rate of the multicomponent glass is then determined by the breaking of the next Si–O bond in the SiO_4 tetrahedron. This leads to the substantially larger dissolution rate of the multicomponent glass, but essentially by the same mechanism.

5. Conclusions

The following effects are observed upon the dissolution of a Na_2O–MgO–CaO–SiO_2 glass in HF–acid aqueous solutions.

1. The reaction rate r increases with temperature with an activation energy of 30 to35 kJ mol^{-1}, indicating a kinetically controlled dissolution rate.

2. The addition of acids to the etchant results in an increase in r due to the higher rate of rupture of Si–O–Si bonds. This is caused by the catalytic action of adsorbed H^+ ions.

3. The dissolution mechanism of Na_2O–MgO–CaO–SiO_2 glass is similar to that of vitreous SiO_2 or crystalline feldspars. In this investigation it is shown that both HF molecules and HF_2^- ions are reactive towards the silicate material. The reaction rate–H^+ concentration relationship can be described by the model proposed by Kline and Fogler [14–16], but with taking the reactivity of HF_2^- ions into account.

4. The reaction order with respect to the total HF concentration is 1.25.

5. No significant differences in dissolution rates for HCl, HNO_3 or H_2SO_4-based etchants were observed.

6. The dissolution rate of the multicomponent glass studied here is more than one order of magnitude larger than that of vitreous SiO_2. This is due to the fact that in the multicomponent glass part of the Si–O bonds is already broken by the alkali and alkaline earth oxides.

7. The "orange peel" structure of the etched glass surface originates from surface flaws.

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