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Short Communication

A simple model for multicomponent etching

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ABSTRACT

We consider the situation where a multicomponent solid is etched using one or more acids. Of fundamental interest is the rate of surface etching but when this involves multicomponent surface reactions, it becomes unclear how the overall rate can be estimated. In this paper, we sketch a simple model designed to determine the effective etching rate by means of an atomic scale model of the etching process.

1. Introduction

This note deals with a model for *multicomponent* etching used in the production of lead crystal glassware. After cutting of the glass, polishing is required to restore its transparency [4]. This is attained by immersion of the glass in a mixture of hydrofluoric (HF) and sulphuric (H_2SO_4) acid, to dissolve all of the components of the glass, namely SiO_2, PbO and K_2O, followed by rinsing to remove insoluble lead sulphate particles from the interface. The etching and rinsing steps are repeated a number of times. Lead crystal consists largely of lead oxide PbO, potassium oxide K_2O, and silica SiO_2, and these react with the acids according to the reactions:

$$\begin{aligned} &PbO + H_2SO_4 \xrightarrow{r_1} PbSO_4 + H_2O, \\ &SiO_2 + 4HF \xrightarrow{r_2} SiF_4 + 2H_2O, \\ &K_2O + H_2SO_4 \xrightarrow{r_3} K_2SO_4 + H_2O, \\ &K_2O + 2HF \xrightarrow{r_4} 2KF + H_2O. \end{aligned} \tag{1.1}$$

We note that the lead sulphate ($PbSO_4$) is insoluble and is washed away in a rinsing bath.

The simplest models of macroscopic surface evolution have been well studied, for example, in etching using a mask [2] and the closely related process involving erosion via powder blasting [3]. If a surface is given by $F(\mathbf{x}, t) = 0$, then its velocity $\mathbf{v}$ satisfies $F_t + \mathbf{v}.\nabla F = 0$, whence also $F_t + v_p|\nabla F| = 0$, where $v_p = \mathbf{v}.\,\mathbf{n}$ denotes the normal velocity of the surface, and $\mathbf{n} = \frac{\nabla F}{|\nabla F|}$ is the unit normal. Our aim here is to show how to determine v_p for a multicomponent system.

There is a large literature concerning experimental studies of wet chemical etching of glass; see [4], who points out that the etching process has not been studied at molecular level. Nor has there been, to date, an experimental study of multicomponent glasses where different types of etchant are required. The emphasis in this note is on the *microscopic* model which captures the features of multicomponent etching, with the aim of determining the effective etching rate bearing in mind that the two components are etched at different rates.

2. The basic model

Consider first the situation where a (macroscopically) flat solid surface comprising three species, e.g., PbO, SiO_2 and K_2O is etched by an acid, e.g., H_2SO_4. We assume that the chemical reactions at the surface are the rate-determining step in the process, so that there is always an excess of acid available for reaction and that the reaction products are also quickly removed from the surface. We imagine the glass as being approximately a crystal lattice (this is not actually the case but the basic concept is still valid) where the different molecular species are distributed randomly. When the acid is introduced, it can etch away the PbO, and K_2O molecules and can progress downwards into the lattice until it reaches a SiO_2 molecule. Reaction at this horizontal location now ceases. Assuming that only vertical excavation occurs, eventually we will reach a situation where only SiO_2 molecules are exposed to the acid and no further reaction can occur. A simple cartoon of this process is provided in Fig. 1 where, for simplicity, the etching rates of the K and P molecules have untypically been assumed to be equal.

We now consider a slightly simpler system consisting of a solid comprising two species ($j = 1,2$), both of which are etched by an

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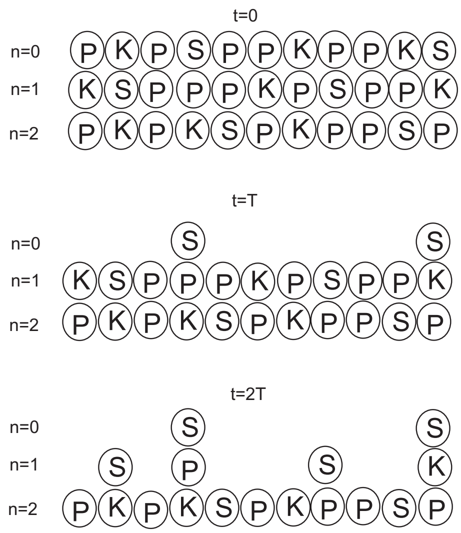

Fig. 1. Snapshots of a portion of a lattice consisting of three types of molecules at three different times. In the portion illustrated, $N = 2$, so there are three layers, $n = 0$, 1, 2, and $M = 11$ horizontal sites. It is assumed that it takes T seconds to etch a P and K molecule while S is not etched by this acid.

acid, but at different rates A_1 and A_2 which can in principle be related to the relevant chemical reaction rates [1].

We suppose that the molecules of the two species (indexed by $j = 1,2$) are arranged in an approximate lattice, with the horizontal layers denoted by an index n, with $n = 0$ indicating the initial surface, and n increasing with depth into the lattice. As etching proceeds, the surface will have exposed sites at different levels. We define ψ_n^j to be the fraction of exposed surface at level n of species j. In addition, the system is evolving in time so $\psi_n^j = \psi_n^j(t)$.

To clarify this, let us consider a small portion of the lattice in which there are M sites in the horizontal and $N + 1$ rows in the vertical (see Fig. 1) so that $n = 0, \ldots, N$. Then ψ_n^j, at any level or row, n, is the number of exposed sites of type j divided by M.

If the species j is present in a fraction of sites f_j in the crystal (i.e., f_j = number of j molecules divided by total number of sites), $M(N + 1)$, then

$$\sum_j f_j = 1. \tag{2.1}$$

Defining

$$\psi_n = \sum_j \psi_n^j \tag{2.2}$$

to be the fraction of etched or exposed sites at level n (i.e., the number of exposed sites at level n divided by the total number of sites M in any row), at any time t we must have

$$\sum_{n=0}^{N} \psi_n = 1. \tag{2.3}$$

For example, in the three species case of Fig. 1, at $t = T$ we have

$$\psi_0^K = \psi_0^P = 0, \quad \psi_0^S = 2/11, \quad \psi_1^K = 2/11, \quad \psi_1^P = 5/11, \quad \psi_1^S = 2/11 \tag{2.4}$$

with all other ψ_n^j being zero. We thus see that Eq. (2.3) is also verified. At this point, we will make a simplifying step by developing a continuous in time model. This introduces a small error when compared to the situation described in Fig. 1. The mathematical advantage is that the reaction equations are ordinary differential equations, describing the time evolution of exposed sites in the lattice. These are (no summation convention used):

$$\dot{\psi}_n^j = -A_j \psi_n^j + f_j \sum_k A_k \psi_{n-1}^k, \quad n \geqslant 1,$$
$$\dot{\psi}_0^j = -A_j \psi_0^j. \tag{2.5}$$

The negative term in (2.5) represents the reactive rate of removal of exposed j sites, while the positive term represents the creation of new exposed sites (a fraction f_j of which are j sites). The initial conditions are:

$$\psi_0^j = f_j; \quad \psi_n^j = 0, \quad n \geqslant 1. \tag{2.6}$$

Note that the above initial condition underlines the fact that the mathematical model is an averaged one in the sense that it depends on consideration of a large number of molecules in each horizontal layer. The cartoon in Fig. 1 is drawn to show just 11 of the molecules in each layer but this is only a portion of the whole layer (to illustrate the basic etching idea). In general such a small sample will not contain the same proportions as the complete layer.

2.1. Numerical solution

It is straightforward to solve the system Eq. (2.5) of ordinary differential equations numerically. Fig. 2 shows the solution for the fraction of exposed sites as a function of depth into the crystal at large times. It is apparent that the 'interface' (where ψ_n^j, the fraction of exposed sites at depth n into the crystal of type j, is positive) is diffuse (i.e., it spreads out as it moves down into the crystal). But it is also apparent that the interface is propagating downwards at an essentially constant rate. This is the key result of this note.

We define $n_w(t)$ to be the penetration depth of the wavefront into the crystal. If we neglect the spreading or diffusive aspect of the wavefront, it is possible to show that for large t and n_w we have the asymptotic relationship [1]:

$$n_w \sim v_p t \tag{2.7}$$

where

$$v_p = \left(\sum_j \frac{f_j}{A_j} \right)^{-1} \tag{2.8}$$

is effectively the speed of the wavefront into the solid. Here, f_j is the proportion of species j in the solid, while A_j is the reaction rate (rate

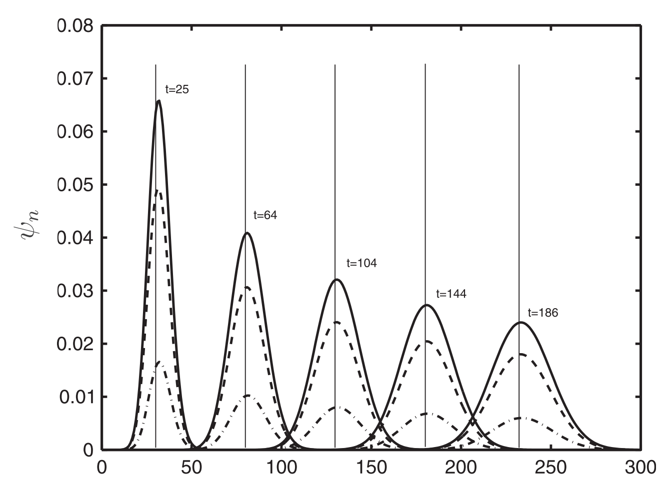

Fig. 2. Simulation results for the solution of Eqs. (2.5) and (2.6), using two species, with initial fractions $f_1 = 0.6$, $f_2 = 0.4$, and etching rates $A_1 = 1$, $A_2 = 2$. The vertical axis represents the fraction of exposed sites at a number of different times. The black curves represent the fraction of vacant sites at level n, i.e., ψ_n; dashed curves represent the fraction of vacant sites of species 1 at level n, i.e., ψ_n^1; dot-dash curves represent fraction of vacant sites of species 2 at level n, i.e., ψ_n^2. The vertical black lines are the approximate asymptotic solutions. The horizontal axis represents depth into the crystal ($n = 0$ is the top of the crystal).

of surface removal) of species j if present on its own. It is apparent that the effects of the different etching rates sum like electrical resistors in parallel ($1/R = 1/R_1 + 1/R_2$).

The vertical lines in Fig. 2 represent the asymptotic estimate Eq. (2.7). In terms of the numerical solutions presented in Fig. 2, this gives a basic etching rate of about $v_p \sim 1.25$, i.e., this predicts that the position of the wavefront is $n_w \sim 1.25t$ in Fig. 2, where n_w is located at the centre of each of the Gaussian-like curves. There is obvious good agreement. The solid behaves as if layered, with the layers running parallel to the surface, so that the overall rate is determined by the weighted sum of the inverse rates.

3. Summary

We summarise here a simple model for the etching of multicomponent lead crystal glass by an acid. The evolution of the surface is determined by the rate of the surface reaction which dissolves the solid surface. For a single solvent and a monomineralic surface, this rate is determined by the reaction rate kinetics. However, if more than one solvent is necessary to etch a surface with several different components, it is not clear what the effective surface dissolution rate should be.

In this note we demonstrate how to approach this problem when multiple reactions are necessary to remove the components of a surface. Our model shows that the interface nevertheless propogates downwards at a constant rate (which the model estimates), while simultaneously diffusing.

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