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DISSOLUTION OF Al_2O_3 IN $Na_2O \cdot 2SiO_2$ GLASS

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The dissolution process consists of two steps, the entry of atoms from the solute into the solvent and a subsequent diffusion of these atoms through the solvent. Either of the two steps can be the slow step, and therefore the dissolution process can be either interface-controlled or diffusion-controlled. If the rates of the two steps are approximately equal then neither could be considered as the only step influencing the rate of dissolution.

In the case where the entry step is rate controlling, solute atoms are relatively free to diffuse rapidly through the solvent. This condition results in a rapid drop in concentration followed by a constant solute concentration in the solvent as a function of distance due to rapid diffusivity. Consider the saturation concentration, as can be found from the proper phase diagram, as C_s and the concentration of the solute in the solvent adjacent to the solute as C_i. At zero time the level of C_i will be zero, and as time increases this level will increase non-linearly until equilibrium is reached and $C_i = C_s$. In this case, and in the following cases it is assumed that the temperature is constant and that at equilibrium the chemical activity of the solute in the solute is the same as the chemical activity of the solute in the solvent. The rate of entry of solute atoms into the solvent, R_e, is much less than

the rate of diffusion of solute atoms through the solvent, R_d.

When diffusion is rate controlling, solute atoms are free to enter the solvent, but are restricted in their movement through the solvent. This condition results in a build-up of the concentration at the interface followed by a gradual decrease in solute concentration as the solute atoms slowly diffuse through the solvent. At zero time C_i will be zero, but as time increases C_i will increase rapidly until it reaches C_s. During this time, however, the concentration profile will maintain an error function configuration. Once C_i reaches C_s, this configuration will change until at equilibrium the concentration of solute in solvent will be constant throughout the solvent.

The process of dissolution can be compared with the process of surface evaporation. Crank[1] has used this analogy and considered the mathematics of the process of evaporation from an infinite flat surface where diffusion is limited by an interfacial reaction. When the diffusion step is rate-controlling the concentration at any point in the vapor phase can be found by

$$C = C_s \operatorname{erfc} \frac{X}{2\sqrt{Dt}} \qquad (1)$$

where

C = concentration at any point

C_s = saturation concentration

X = distance

D = diffusion coefficient

t = time

When both steps have approximately the same rate constant, a combination of the two previous cases will be encountered. There will be a drop in concentration at the interface to a value of C_i which lies between C_s and the solvent concentration. The concentration will then gradually decrease with distance to the solute concentration in the solvent. As with the diffusion-controlled case, the interface concentration will increase until $C_i = C_s$ and then the concentration in the solvent will increase until C_s is reached at complete saturation of the solvent. When the diffusion of the solute atoms in the solvent is limited by the interfacial reaction, the expression for the concentration at any point in the solvent contains error functions and a constant of proportionality.

$$C = C_s \left[\operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}}\right) - e^{hx+h^2Dt} \operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}} + h\sqrt{Dt}\right)\right] \qquad (2)$$

where $h = \frac{\alpha}{D}$ and α is the interface reaction coefficient defined as

$$\alpha(C_s - C_i) = -D\frac{\partial C}{\partial X} \qquad (3)$$

In this case it is assumed that the reaction is proportional to the chemical activity difference between the two phases.

Simpson and Carter[2] used these equations to study the diffusion of oxygen in calcia-stabilized zirconia, taking into account the oxygen surface exchange. A probability plot for Eq. (1) will have $C/2C_s = 0.5$ for X=0 after interfacial equilibrium is established, while Eq. (2) will have $C/2C_s < 0.5$ for X=0 until the reaction ceases. Equation (2) will not yield a straight line, but the resulting curve will have a very large

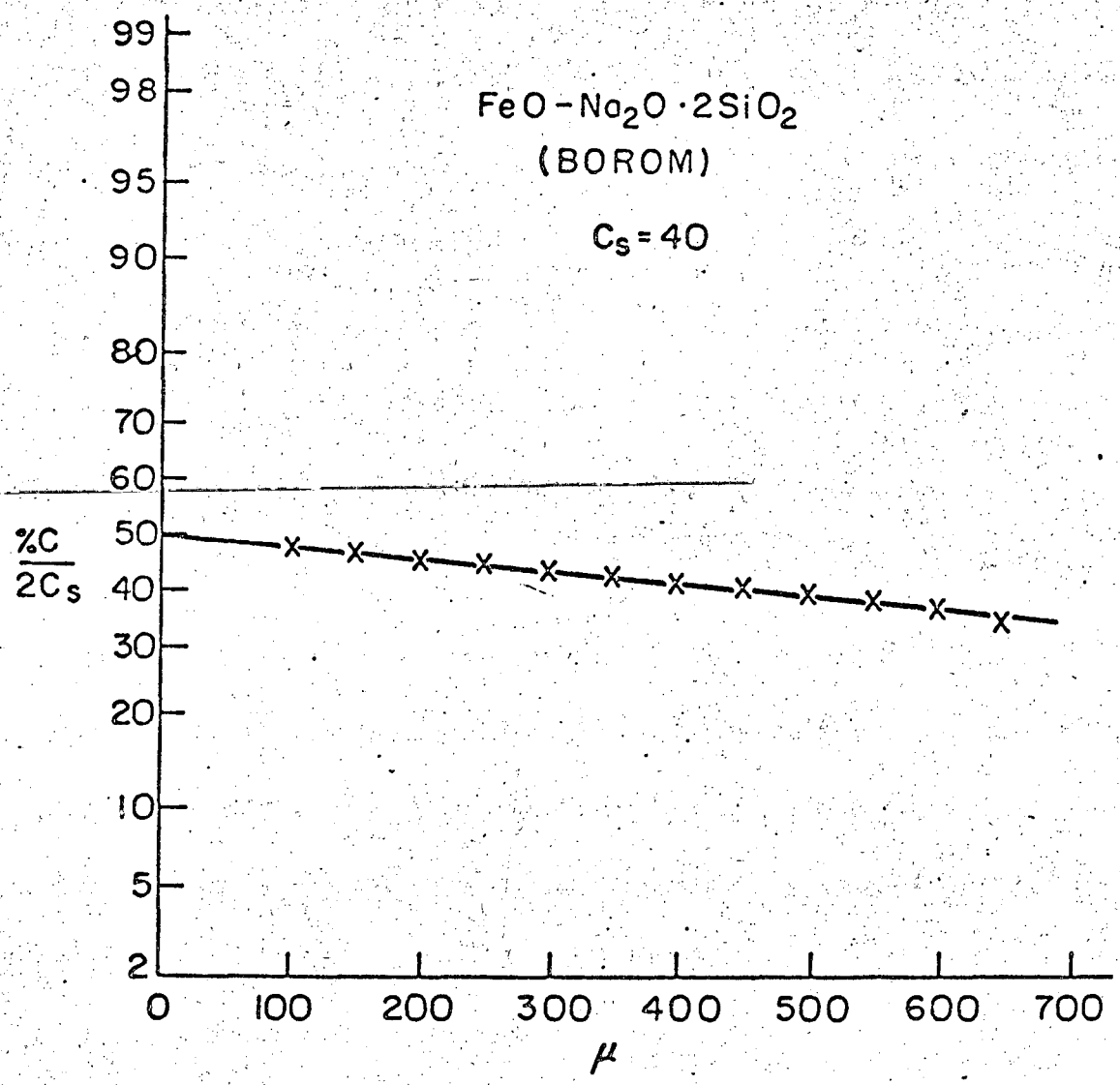
radius of curvature and curvature will not be detectable over an order of magnitude change in $C/2C_s$. This can be seen in Figs. 1 and 2 where microprobe data for reacting systems were plotted using this technique.

Dissolution of each of the oxides of iron in sodium disilicate glass was found by Borom[3] to be diffusion controlled. A plot of his data on probability paper (Fig. 1) for this system substantiates the fact that the dissolution is diffusion-controlled. Dorn, et al.[4] have also shown that Eq. (2) can be applied to several metallurgical cases such as the carburization and nitriding of several metals. They present graphical methods for the determination of the parameter h^2Dt, knowing the concentration ratio C/C_s, and the parameter hx.

The dissolution of single crystals of corundum was investigated by Reed and Barrett[5] who rotated rods of corundum in silicate melts. A weight loss was measured and dissolution rates were calculated from these data. The dissolution was found to increase with the speed of rotation and therefore it was concluded that the process was diffusion-controlled. In a later paper,[6] however, they observed a product layer which implied that they were looking at a surface reaction rather than just dissolution.

Busby and Eccles[7] also investigated the dissolution of corundum single crystals in several molten glasses. They, too, used weight loss data and calculated dissolution rates from these data. For two of the glasses they explained the corrosion profile in terms of diffusion, density currents in the glass, and surface tension phenomena.

Cooper and Kingery[8,9] studied the dissolution of various ceramic materials in a molten calcium aluminum silicate slag. They used the



MUB-13146

Fig. 1 Concentration profile in the $FeO-Na_2O \cdot 2SiO_2$ system (909±3°C, 50 hrs.)

rod rotation technique and measured the decrease in rod diameter and length. The dissolution, using these data, was considered to be controlled by transport in the molten silicate. Measurement of rod diameter before and after exposure, however, would not give separation of the entry rate from the rate of diffusion in the molten silicate in a stagnate system.

The Al_2O_3-$Na_2O \cdot 2SiO_2$ system is an example of one in which the entry step plays a more important role. A polished piece of sapphire was heated to 900°C with sodium disilicate glass resting on top of it. The Al_2O_3 and glass were held there under no pressure for two hours and then cooled rapidly. Materials and equipment were discussed previously.[10] The Al_2O_3-glass interface was then microprobed and the alumina concentration plotted on probability paper (Fig. 2). It can be seen from the ordinate intercept that for these conditions the dissolution process is not purely diffusion-controlled. This may be true either because the initial build-up of C_i to C_s is relatively sluggish in this system or because dissolution in this system is influenced by the entry step at all times. In either case, for these conditions, attempts at controlling properties in this system must take into account the influence of the entry step and not rely upon diffusion as being the only step influencing the process.

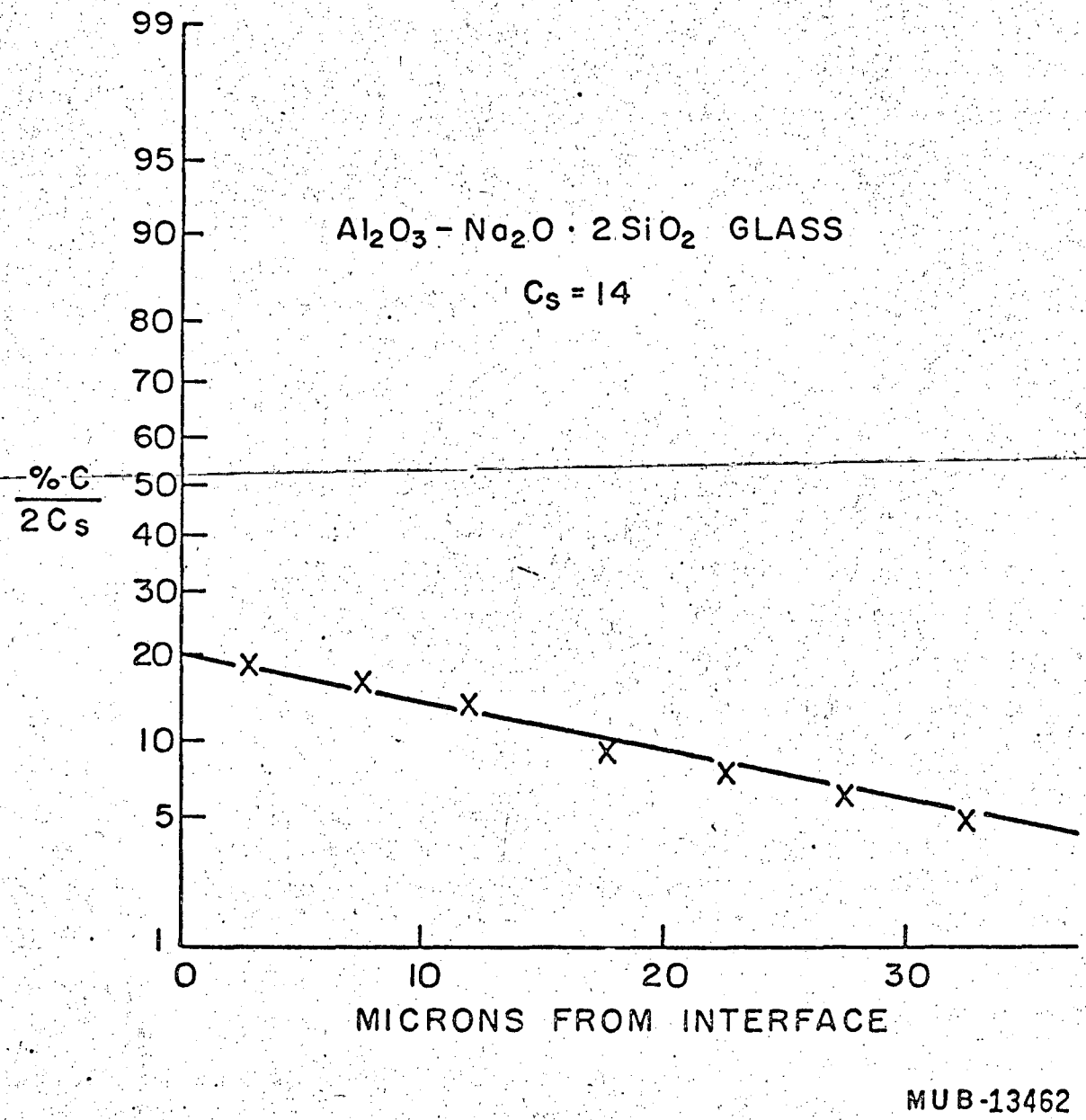


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Fig. 2 Concentration profile in the Al_2O_3-$Na_2O \cdot 2SiO_2$ system (900°C, 2 hrs.)

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