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EFFECT OF PRESSURE ON HIGH TEMPERATURE DISSOLUTION

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ABSTRACT

The effect of pressure on high temperature dissolution has been investigated. Solubility of NiO in $Na_2O \cdot 2SiO_2$ glass was found to decrease with applied pressure, indicating that the entry rate of atoms from a solute into a solvent is decreased by increased pressure. The saturation concentration as measured with the electron beam microprobe is an accurate measurement of the liquidus concentration for a given temperature.

INTRODUCTION

Physical properties, such as compressive strength of clays and zirconia, have been enhanced by the application of pressure during a chemical reaction.[1-5] Chemical reactions can occur at lower temperatures under an applied pressure than under vacuum. Carruthers and Wheat[6] found mullite formation at 650°C in a china clay hot pressed during the dehydroxylation reaction with 30,000 psi. The process of dissolution can also be affected by an applied pressure.

The dissolution process consists of two steps, the entry of atoms of solute into the solvent and a subsequent diffusion of these atoms through the solvent. Either or both of these steps can be rate-controlling. These steps and their characteristics have been discussed previously.[7] When the migration of the solute atoms in the solvent is limited by the interfacial reaction, the expression for the concentration at any point contains error functions and a constant of proportionality.[8]

$$C = C_s \left[\operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}} \right) - e^{hx + h^2 Dt} \operatorname{erfc}\left(\frac{X}{2\sqrt{Dt}} + h\sqrt{Dt} \right) \right] \qquad (1)$$

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

$$\alpha(C_s - C_i) = -D \frac{\partial C}{\partial X} \qquad (2)$$

and C = concentration at any point

C_s = saturation coefficient

C_i = interface concentration

X = distance

D = diffusion coefficient

t = time

It is assumed here that the reaction is proportional to the chemical activity difference between the two phases. Simpson and Carter[9] used these equations to study the diffusion of oxygen in calcia-stabilized zirconia, taking into account the oxygen surface exchange.

The self-diffusion coefficient of lead has been shown to decrease with increased pressure by Hudson and Hoffman.[10] The other step in dissolution, the entry, will be shown here to be inhibited by an applied hydrostatic pressure.

The type of data obtained can be used to plot the liquidus of a phase diagram as a function of pressure. Schwerdtfeger[11] has shown that the saturation concentration as measured by the microprobe technique used in this study is an accurate measurement of a liquidus. He measured a portion of the liquidus in the Na_2O-SiO_2 system and found agreement to within 1% or better. The results of his work can be seen in Fig. 1. The dotted line shows the accepted liquidus of Kracek and the solid line shows Schwerdtfeger's determination. In the present work the NiO-$Na_2O \cdot 2SiO_2$ glass system was investigated and the effect or pressure on the entry rate demonstrated.

EXPERIMENTAL PROCEDURE

A. Materials

Powdered sodium disilicate glass and oxidized nickel spheres were used as the starting materials. The glass was made in the laboratory from silica flour and reagent grade sodium carbonate by melting and

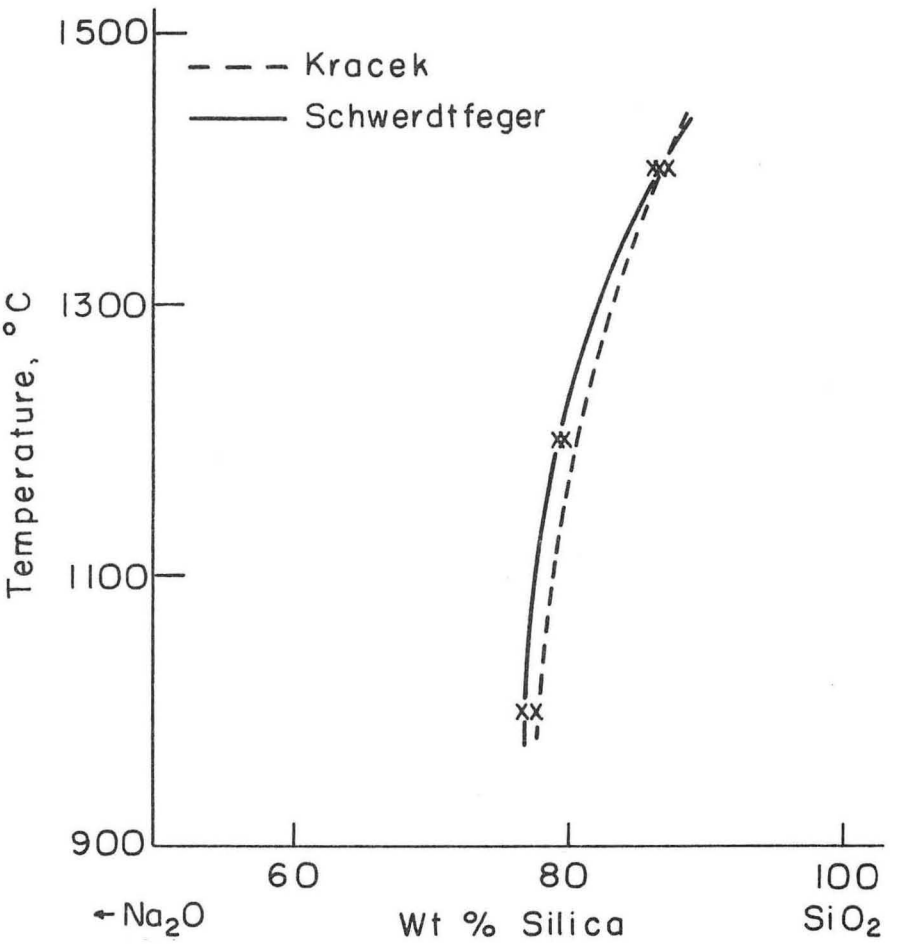

FIG. 1 PORTION OF LIQUIDUS CURVE OF SILICA IN THE SYSTEM $Na_2O \cdot SiO_2$.

(From K. Schwerdtfeger, J. Phys. Chem., 70 (7) 2131 (1966)

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refining in platinum crucibles in an inclined, rotating electric furnace at 1300°C. The glass was cast and then crushed and dry ground to -325 mesh and had a density of 2.57.

Commercially obtained nickel microspheres were oxidized at 800°C for one hour to provide a spherical source of NiO. The majority of the particles were about 100 microns in diameter.

B. Hot Pressing

The powdered glass was mixed with about 10% oxidized nickel spheres. Precise control of the composition was not necessary since microprobe work was done on isolated spheres within the matrix. The glass-oxidized nickel sphere mixture was hot pressed at 900°C for two hours at pressures ranging from zero to 1000 psi in a graphite die. A description of the hot-pressing arrangement has been given in a previous paper.[7]

The hot-pressed samples were sectioned and mounted in a clear casting resin. All samples were polished with a set of silicon carbide papers (240, 400, and 600 grit) and then finished on a series of diamond paste laps (6, 2, and 1/2 micron diamond). Carbon was vapor deposited on the finished samples to provide a conductive surface suitable for electron microprobe analysis.

C. Electron Microprobe

A Materials Analysis Company electron probe was used for the analysis of nickel. Characteristic radiation emitted by the nickel in the specimen was resolved by a properly positioned lithium fluoride crystal and the intensity was measured with a proportional detector. A

motor-driven gear mechanism moved the sample in a step-wise fashion relative to the electron beam. Integrated counts were taken at various intervals along the radius of an oxidized nickel sphere and into the glass sufficient to give a smooth curve of concentration as a function of distance. The beam diameter was 1μ and the depth of penetration was a maximum of 3μ. These values are small compared with the ∿100μ oxidized nickel particle size. The electron microprobe was equipped to take photographs of the X-ray image for any element from an oscilloscope. In order to minimize the instability of the alkali glass as a result of the electron beam, short counting times (10 sec.), a low sample current (0.02μA), a low voltage (15 KV), and a relatively heavy carbon coating were used. The stability obtained can be seen in Fig. 2.

All data obtained from the proportional counters were corrected for background, absorption, counter dead time and non-linearity, fluorescence, and atomic number. In this case the counter dead time, fluorescence, and atomic number corrections are negligible and the background can be accounted for by a simple subtraction. The absorption, however, requires more careful consideration. Detailed procedure and mass absorption coefficients were taken from Smith.[11]

RESULTS AND DISCUSSION

The composites pressed at zero, 250, and 1000 psi were examined in the microprobe and photographs were taken of the oscilloscope image of Ni around a sphere. The background concentration of nickel can be seen around an untreated oxidized sphere in Fig. 3. This background concentration was measured with the counter to be 0.2 $^{wt}/_{o}$ and a correction

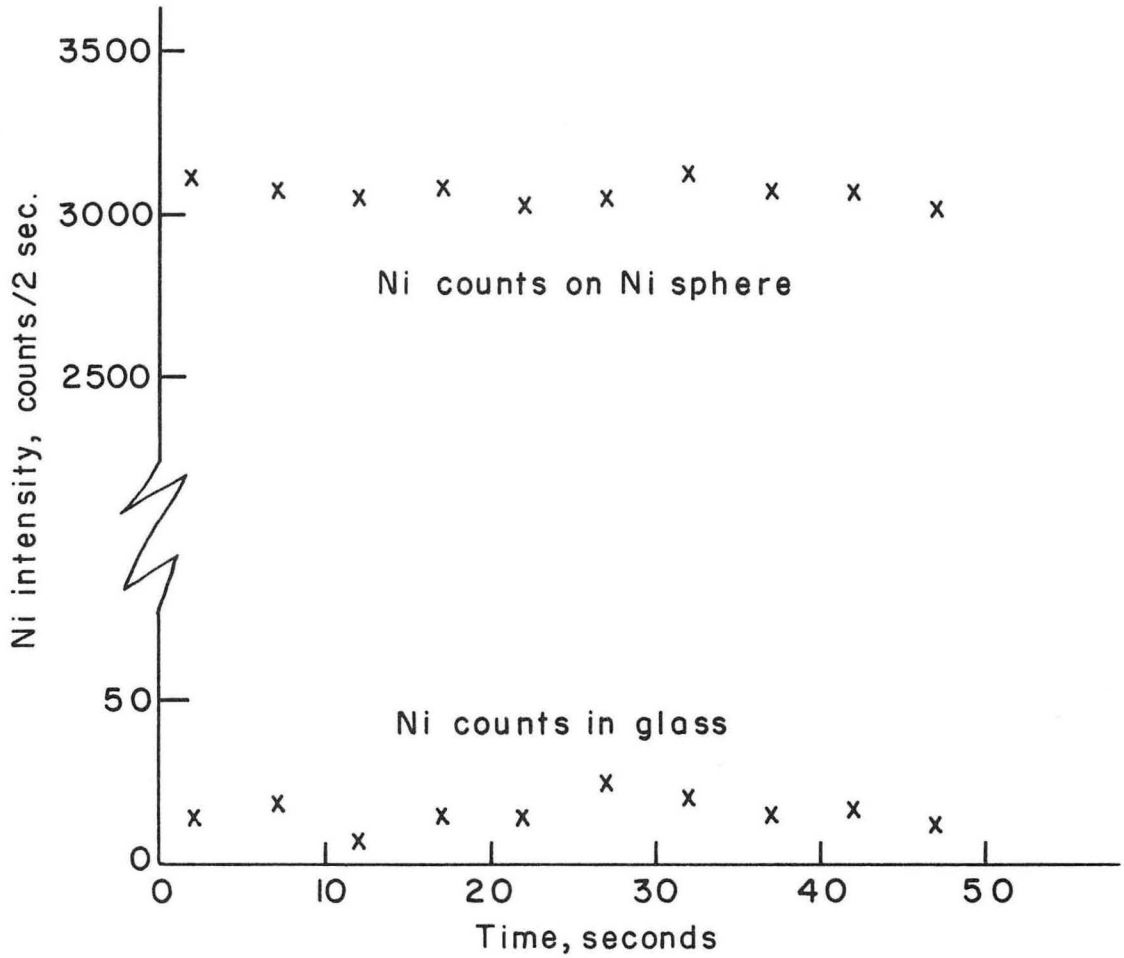

FIG. 2 EFFECT OF SURFACE DAMAGE ON COUNT RATE.

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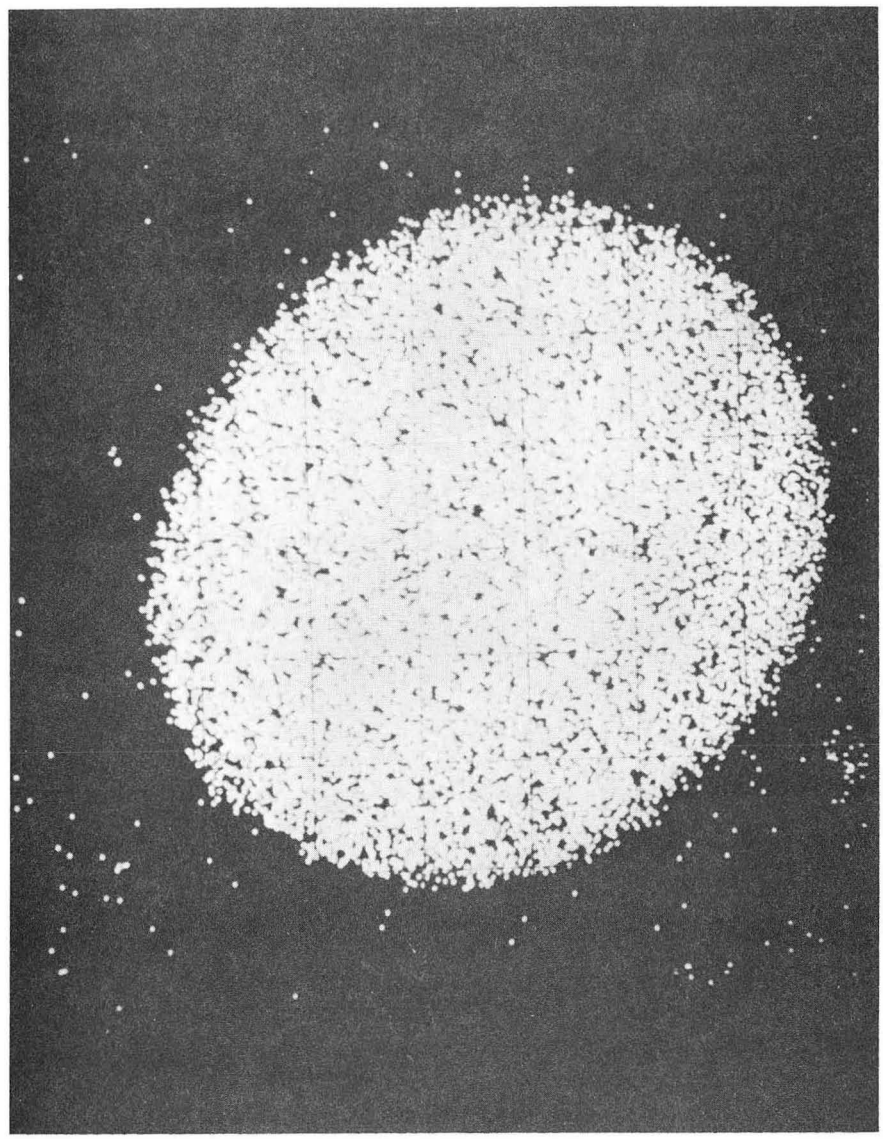

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Fig. 3 Oscilloscope photograph showing background Ni concentration about an untreated sphere.

was made for this in each of the following values. Figure 4 shows the nickel concentration around an oxidized nickel sphere in a composite that was treated at 900°C and zero pressure for two hours in vacuum. Measured concentrations here were 5.1, 4.7, 5.0, and 4.7 $^{wt}/_{o}$.

The Ni concentration around spheres in composites formed at 900°C for two hours in vacuum and at 250 psi and 1000 psi can be seen in Figs. 5 and 6, respectively. Measured concentrations were 2.6 $^{wt}/_{o}$ for the 250 psi sample and 0.4 $^{wt}/_{o}$ for the 1000 psi sample.

A composite was fabricated from sodium disilicate glass and nickel oxide particles to insure that the oxidized nickel spheres were actually acting as nickel oxide spheres. The composite was fabricated at 900°C for two hours and at zero pressure. The measured concentration in the matrix was found to be 4.7 $^{wt}/_{o}$, the exact agreement indicating that the oxidized nickel spheres truly did act as nickel oxide spheres in the composites. A concentration profile across the particle interface in the glass-nickel oxide composite can be seen in Fig. 7. The concentration gradient went from nickel oxide to glass in only eight microns. Differences in polishing characteristics between the nickel oxide and the glass contributed almost all of this.

Another sample was made in order to verify this polishing difference and to determine the method of material transfer. Oxidized nickel spheres and sodium disilicate particles were sintered at 750°C for two hours under zero pressure. The concentration gradient in this sample went from nickel oxide to glass in seven microns, verifying the polishing difference. A similar effect due to polishing differences was

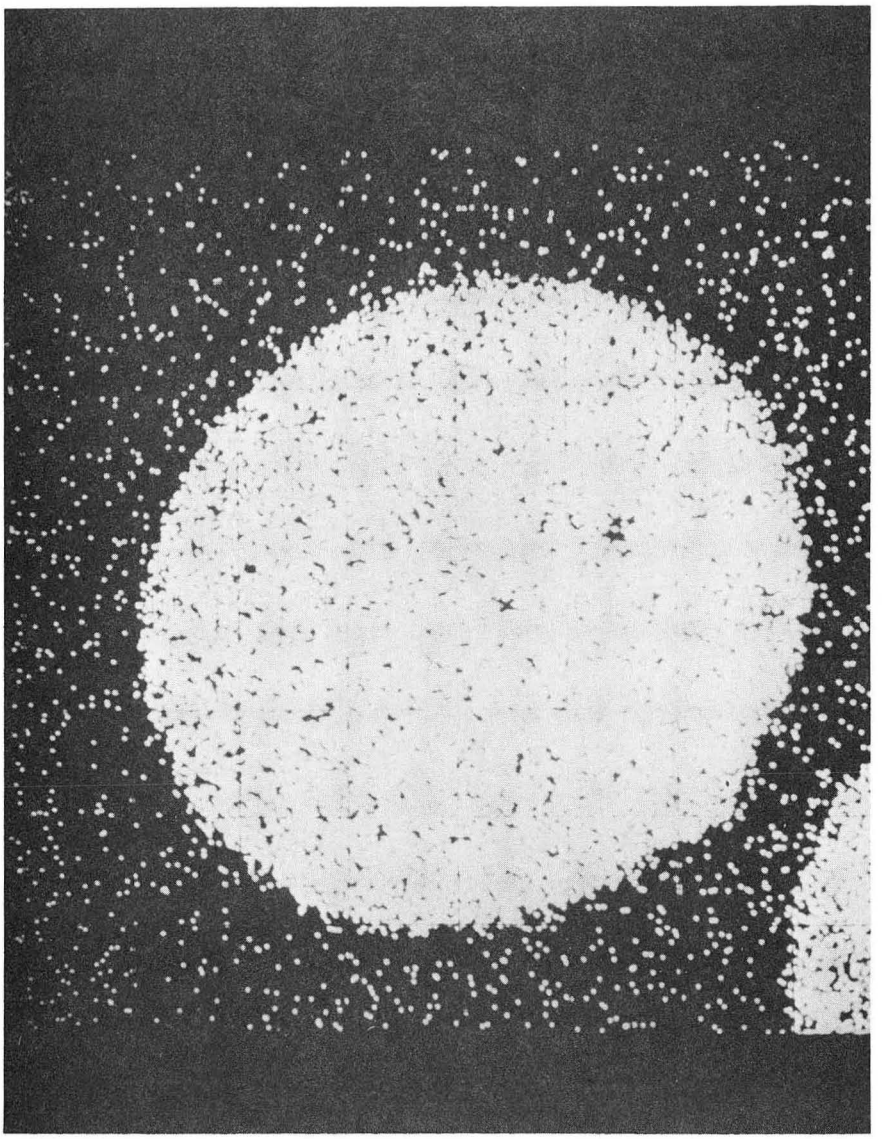

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Fig. 4 Oscilloscope photograph showing Ni concentration about a sphere in a composite formed at 900°C, zero psi, and 2 hrs.

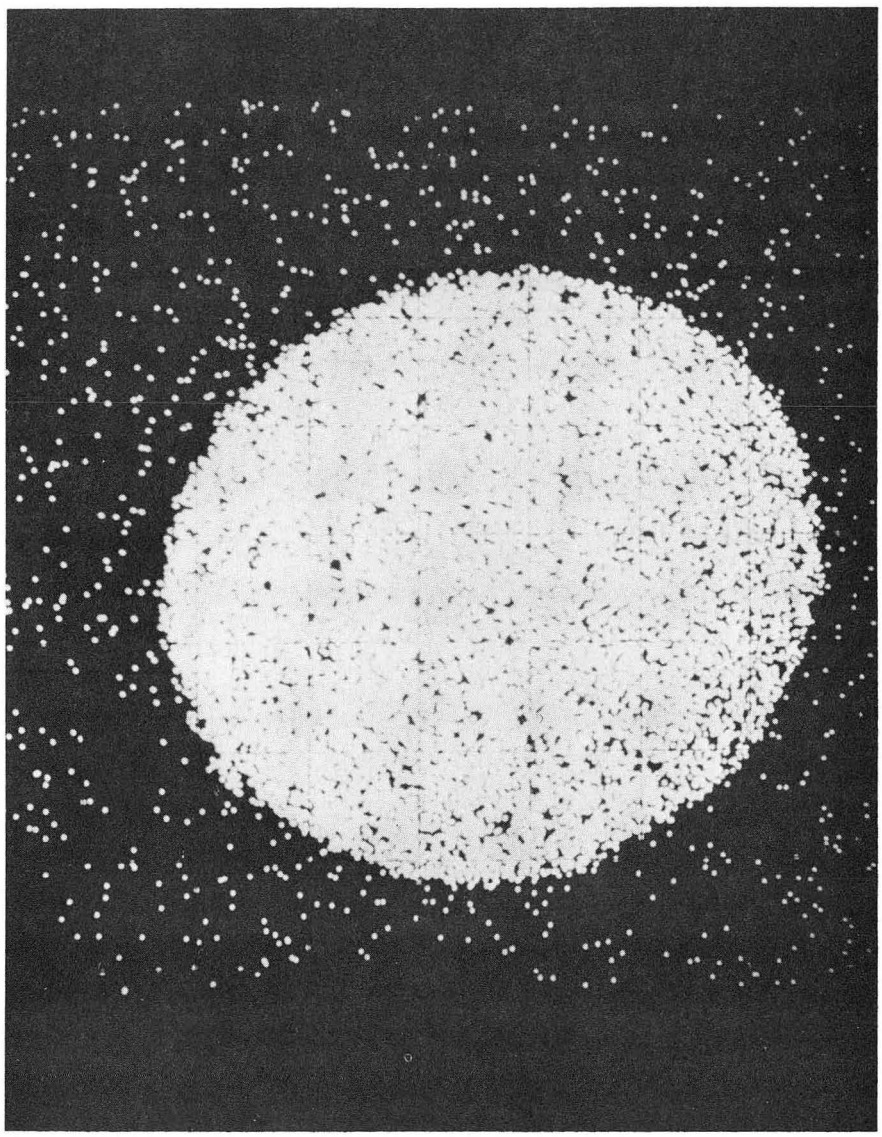

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Fig. 5 Oscilloscope photograph showing Ni concentration about a sphere in a composite formed at 900°C, 250 psi, and 2 hrs.

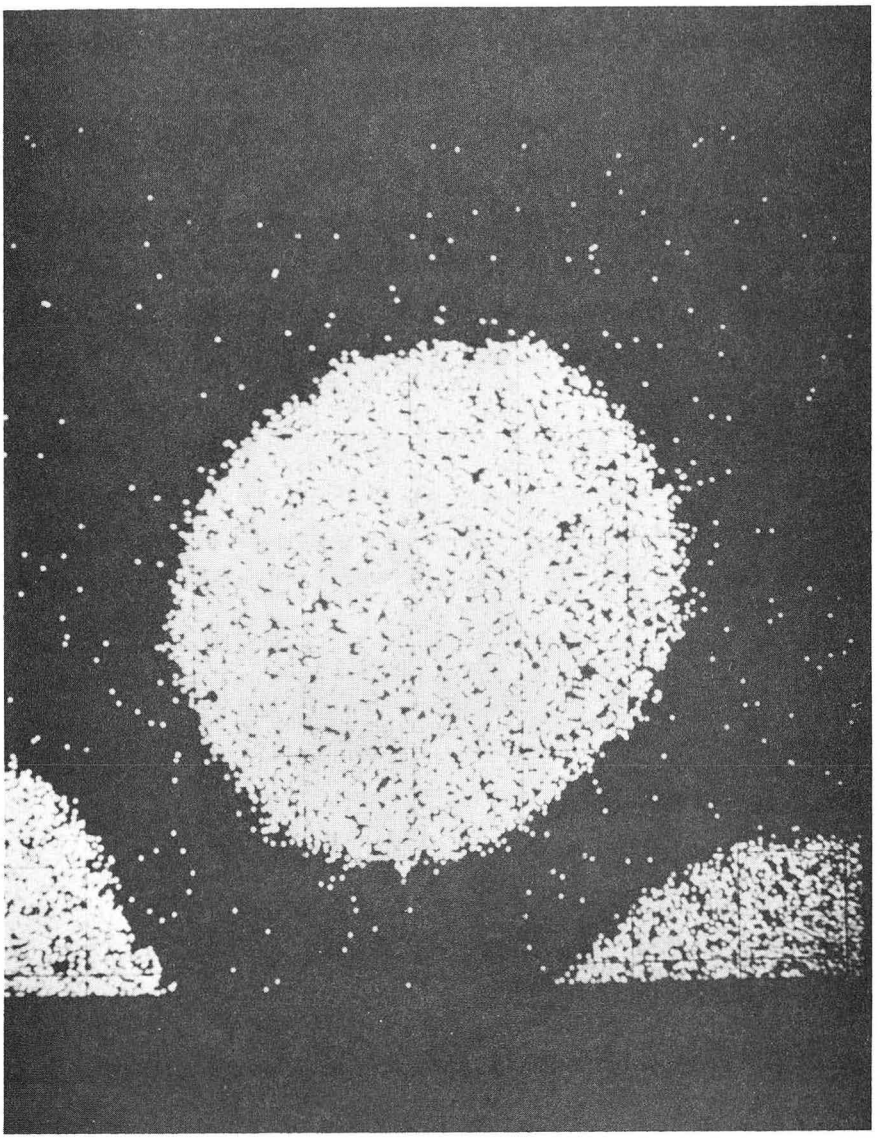

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Fig. 6 Oscilloscope photograph showing Ni concentration about a sphere in a composite formed at 900°C, 1000 psi, and 2 hrs.

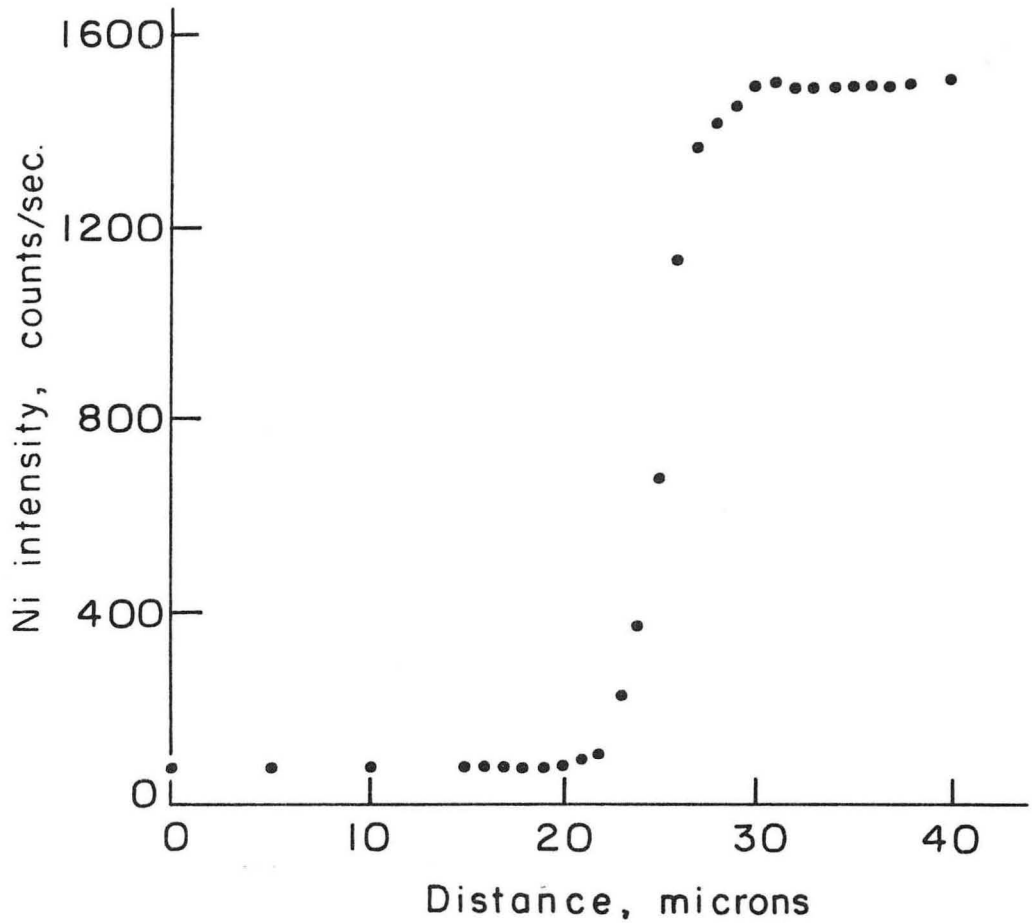

FIG. 7 CONCENTRATION PROFILE OF 900°C, ZERO PSI, 2 HOUR SAMPLE.

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seen in the Al_2O_3-sodium disilicate glass system.[7] The measured concentration of nickel oxide in the glass was 0.3 $^{wt}/_{o}$ indicating that surface diffusion provided almost no contribution to the mechanism of material transport from the oxidized nickel sphere into the glass matrix and that almost all of the transport away from the sphere occurs by bulk diffusion once the glass particles soften enough to provide a minimum fluidity.

As was seen earlier, the saturation concentration is an accurate measure of the concentration of the liquidus at a given temperature.[11] With a relatively long length of time at temperature, the saturation concentration will be reached and will be, in effect, the measured concentration in the matrix. A plot of these compositions as a function of pressure would therefore yield the liquidus as a function of pressure at a given temperature. This function can be seen in the non-equilibrium liquidus plotted in Figs. 8-9 and can be seen to be the correct shape as would be predicted from free energy considerations.

The free energy of a two-component system can be expressed as

$$dF = VdP - SdT + \mu_1 dn_1 + \mu_2 d(1-n_1) \qquad (1)$$

where

F = Gibbs free energy

V = volume

P = pressure

S = entropy

T = temperature

μ = chemical potential

n = mole fraction

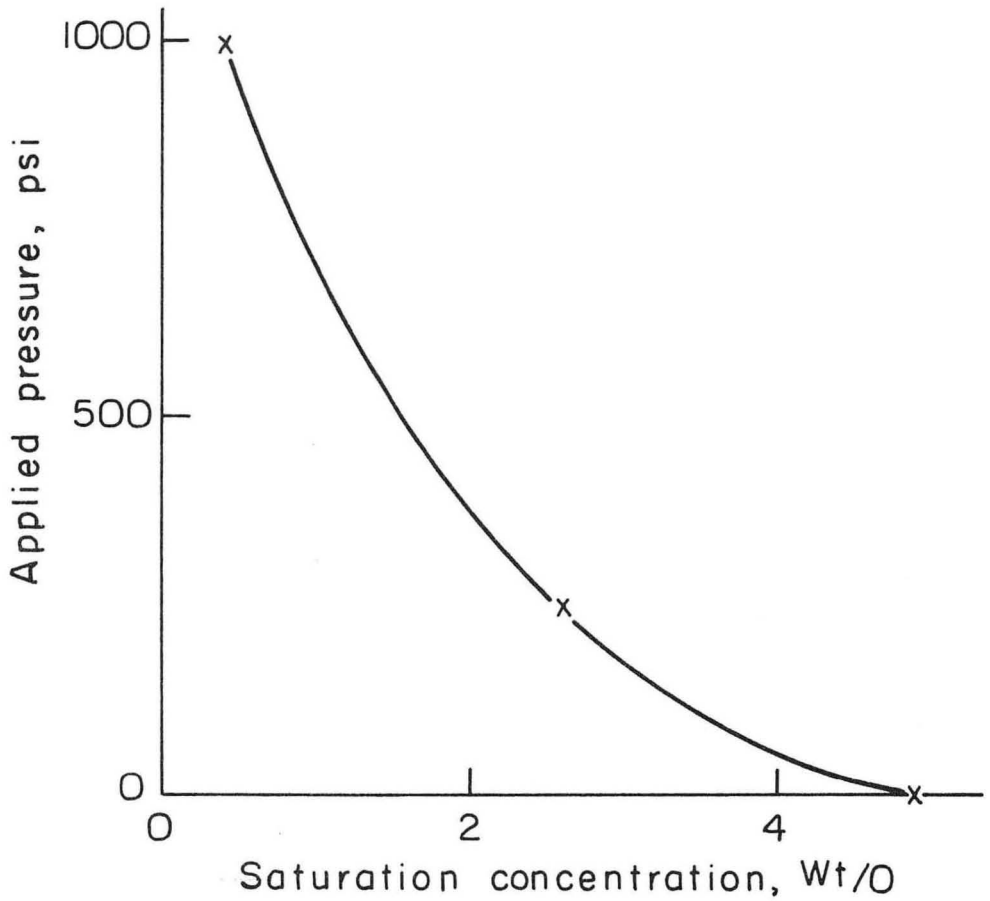

FIG. 8 EFFECT OF PRESSURE ON SATURATION CONCENTRATION.

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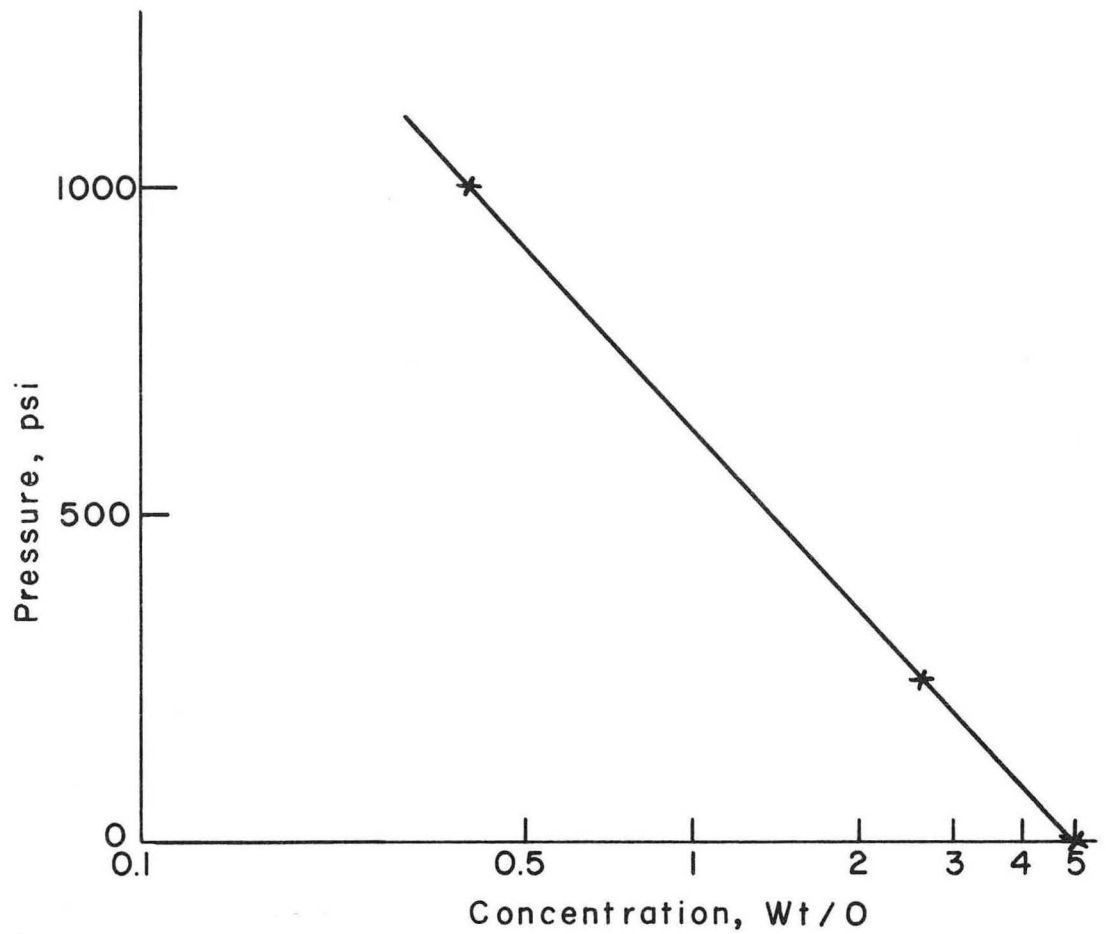

FIG. 9 EFFECT OF PRESSURE ON CONCENTRATION.

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Since the temperature is constant,

$$\frac{dF}{dn_1} = \frac{VdP}{dn_1} + (\mu_1 - \mu_2) \qquad (2)$$

Differentiating this,

$$\frac{d^2F}{dn_1^2} = \frac{Vd^2P}{dn_1^2} \qquad (3)$$

Therefore, the slope of a P-n diagram changes in a manner directly proportional to the change of slope of a F-n diagram. For a system like this that tends toward compound formation the shape of curve shown in Fig. 8 would be expected.

In all cases the concentration became constant deep in the matrix, indicating that the entry step was affected by the pressure. Had the diffusion step only been affected by the pressure, there would have been a concentration gradient in the matrix.

Another interesting point can be seen from the fact that the solubility decreases with pressure. This decrease would illustrate that in the hot pressing of two-phase systems, reaction between the two phases becomes less important as greater pressures are applied. Under high enough pressures two-phase systems actually are distinctly two-phase and the problem of a third, interfacial phase is minimized.

SUMMARY

The rate at which solute atoms enter the solvent has been shown to be dependent upon pressure. In the NiO-$Na_2O \cdot 2SiO_2$ system as the

pressure increases, the solubility of the NiO in the glass decreases and the system is truly two-phase. This would indicate that in the hot-pressing of two-phase systems, once a high enough pressure is reached, the problem of interference from a third, interfacial phase is minimized.

ACKNOWLEDGMENTS

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BIBLIOGRAPHY

1. A. C. D. Chaklader and M. N. Shetty, "Ceramic-Metal Composites by Reactive Hot Pressing," Trans. Met. Soc. AIME, 233 [7] 1440-43 (1965).

2. A. C. D. Chaklader and L. G. McKenzie, "Reactive Hot Pressing of Clays," Bull. Am. Ceram. Soc., 43 [12] 892-93 (1964).

3. A. C. D. Chaklader and V. T. Baker, "Reactive Hot Pressing: Fabrication and Densification of Non-Stabilized ZrO_2," Bull. Am. Ceram. Soc., 44 [3] 258-59 (1965).

4. P. E. D. Morgan and E. Scala, "The Formation of Fully Dense Oxides by Pressure Calcintering of Hydroxides," Department of Materials Science and Engineering, Cornell University, Ithaca, New York.

5. A. C. D. Chaklader, "Reactive Hot Pressing: A New Ceramic Process," Nature, 206 [April 24] 392-93 (1965).

6. T. G. Carruthers and T. A. Wheat, "Hot Pressing of Kaolin and of Mixtures of Alumina and Silica," Proc. Roy. Soc., #3, Fabrication Science, September 1965.

7. Mark A. Stett and R. M. Fulrath, "Chemical Reactivity in an Al_2O_3-Glass Composite," Lawrence Radiation Laboratory Report UCRL-16892 Rev., October 1966.

8. J. Crank, The Mathematics of Diffusion (Oxford Univ. Press, Oxford, 1956).

9. L. A. Simpson and R. E. Carter, "Oxygen Exchange and Diffusion in Calcia-Stabilized Zirconia," J. Am. Ceram. Soc., 49 [3] 139-144 (1966).

10. J. Hudson and R. Hoffman, "The Effect of Hydrostatic Pressure on Self-Diffusion in Lead," Trans. AIME, 221 [4] 761-68 (1961).

11. Klaus Schwerdtfeger, "Dissolution of Solid Oxides in Oxide Melts. The Rate of Dissolution of Solid Silica in Na_2O-SiO_2 and K_2O-SiO_2 Melts," J. Phys. Chem., 70 [7] 2131-37 (1966).

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