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INTERDIFFUSION AND MOVING BOUNDARIES IN NiO-CaO AND NiO-MgO SINGLE CRYSTAL COUPLES

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Publication Date
1969-10-01

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Marvin Appel and Joseph A. Pask

October 1969

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INTERDIFFUSION AND MOVING BOUNDARIES IN NiO-CaO AND NiO-MgO SINGLE CRYSTAL COUPLES

Marvin Appel and Joseph A. Pask

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ABSTRACT

October 1969

For single crystal NiO-CaO and NiO-MgO diffusion anneals in air in the temperature range 1300-1600°C, the diffusivity was found to be exponentially dependent on the Ni concentration. Diffusion proceeded more rapidly in the NiO-rich phase resulting in movement of the phase boundary between the diffusing crystals and growth of the NiO at the expense of the other crystal. If the two crystals were of different crystallographic orientation, the orientation of the volume swept out transformed to that of the growing crystal. The chemical diffusivities for NiO-CaO interdiffusion were found to be

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Based in part on a thesis submitted by Marvin Appel for the Ph.D. degree in materials science at the University of California, Berkeley, June 1968.

Supported by the United States Atomic Energy Commission under Contract W-7405-eng-48.

At the time this work was done the writers were, respectively, research assistant and professor of ceramic engineering, Department of Materials Science and Engineering, College of Engineering, and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California 94720.

Presented at the Twenty-second Pacific Coast Regional Meeting, The American Ceramic Society, Seattle, Washington, October 17, 1969 (Basic Science Division).

$$\tilde{D}_{NiO} = 0.231^{+.395}_{-.145} \exp\left(-\frac{72{,}090 \pm 3380}{RT}\right) \text{cm}^2/\text{sec}$$

$$\tilde{D}_{CaO} = 13.9^{+162}_{-12.7} \exp\left(-\frac{93{,}800 \pm 8630}{RT}\right) \text{cm}^2/\text{sec}$$

Current theoretical and experimental attacks on the nature of Darken's analysis of a moving phase boundary are discussed as is its inapplicability to ionic systems with rigid anion lattices.

I. INTRODUCTION

Interdiffusion of cations in stoichiometric and non-stoichiometric oxides may give rise to phase boundary motion and crystallographic reorientation. These phenomena have practical applications to the understanding of grain growth and sintering.

NiO, CaO and MgO provide good materials for such a study since single crystals are available. Their crystal structures are variants of the NaCl structure. Mitoff[1] has shown that NiO is non-stoichiometric in air. There is a finite concentration of Ni^{+3} proportional to $(P_{O_2})^{1/6}$ and equal to 4×10^{-4} atoms per ion pair at 1400°C. The maintenance of electrovalent neutrality requires that one cation lattice vacancy exists for every two trivalent nickel ions present. CaO and MgO are stoichiometric.

Diffusion in ionic systems has been discussed extensively in the literature.[2-6] Diffusion in these oxides is dependent upon the presence of vacancies since the activation energies for other mechanisms--ring, interstitial, etc.--are too high. Vacancy sites are formed as thermally-created Schottky defects or by the presence of trivalent impurities or trivalent nickel ions. The activation energies for the formation of Frenkel defects in NiO, CaO, and MgO are very high, so that the Frenkel defect concentrations are negligible in comparison with the Schottky defect concentrations.

Wartenberg and Prophet[7] report a complete series of solid solutions for MgO and NiO for all compositions and temperatures. This analysis is consistent with Hahn and Muan,[8] who used X-ray diffraction to determine that NiO-MgO solid solutions are ideal for all compositions at low

pressures of oxygen. The lattice parameters of the pure substances are 4.203 Å and 4.172 Å for MgO and NiO, respectively.

Blank and Pask[9] have reviewed the diffusion studies in the NiO-MgO system reported in the literature. They showed experimentally that there can be a moving boundary in oxide systems, even though a one-for-one counterdiffusion is necessary across any plane perpendicular to the direction of diffusion for diffusing species of equivalent charge in order to maintain a charge balance. For an NiO-MgO diffusion anneal in air, they found an exponential dependence of the chemical diffusivity on nickel content and motion of the plane of 25 a/o Ni content. In vacuum, where there was no concentration-dependence of the chemical diffusivity, no motion of the 25 a/o Ni plane occurred.

NiO and CaO exhibit a limited solid solubility with no intermediate compound formation. Tikkanen[10] and more recently Smith et al.[11] have determined phase diagrams primarily by X-ray diffraction measurements of lattice parameters. The lattice parameter of CaO is 4.797 Å. The present diffusion study provides additional information on this phase diagram. Reports of diffusion studies in the literature in this system have been limited.

The objective of this study has been to provide a fundamental understanding of the diffusion characteristics and the phenomenon of phase boundary motion exhibited in the NiO-MgO and NiO-CaO systems on annealing in air.

II. EXPERIMENTAL PROCEDURE

Single crystals of MgO, CaO and NiO were used in this study.* Their spectroscopic analyses are listed in Table I. Preliminary diffusion anneals made with single crystals pressed in powder were abandoned because they produced erratic results which were attributed to lack of consistently reliable contacts between the powder and single crystal.

Diffusion couples of NiO-MgO and NiO-CaO were prepared by placing one crystal on top of another, measuring 0.5-1 cm on a side, with a 210 gram platinum weight load to promote good crystal-crystal contact. The crystals were offset from one another to aid in the location of the original phase boundary. This assembly was placed on a platinum foil in a high-purity Al_2O_3 crucible. Specimens with (100) faces were prepared by cleaving; those with (110) faces, by sawing. In all cases, the contact surfaces were slightly polished (2 min on a fine diamond lap, 2 min on an extra-fine diamond lap, and 2 min with 1000 grit SiC loose abrasive in an ethanol slurry) so as to improve contact but not change the surface characteristics significantly.

Diffusion anneals were made in air at the test temperatures and times indicated in Table II. The furnace was heated with vertical $MoSi_2$ hairpins, monitored and controlled by a Leeds and Northrup Speedomax H recorder-controller. The control thermocouple, Pt vs Pt-10% Rh, was placed near a hairpin. Another thermocouple placed 1/2" underneath the specimen in the center of the hot zone was used to measure

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* Single crystals of MgO and CaO were obtained from Muscle Shoals Electrochemical Corporation, P.O. Box 87, Tuscumbia, Alabama; NiO, from Marubeni-Iida American, Inc., 650 California St., San Francisco, Calif.

the specimen temperature. At no time was it found to deviate by more than 3°C from the average temperature for the course of the anneal. The diffusion assembly was introduced into the furnace at temperature, and the sample always reached thermal equilibrium within 1/2 h. After the anneal the sample cooled within the furnace with the power off since the thermal shock associated with immediate extraction frequently caused the welded crystals to break apart. In all cases, the furnace temperature dropped below 1000°C within 2-1/2 h and was below 300°C within 12 h.

Following the diffusion anneal, the welded crystals were sectioned perpendicular to the original interface with a diamond saw. The sectioned specimen was then polished to optical quality (2 min on a fine diamond lap, 2 min on an extra-fine diamond lap, 5-10 min on 600 grit SiC paper, 2 min on 4/0 paper, 4-8 min on a 6 μ diamond lap, and 5 min with Linde A 0.3 μ Al_2O_3 in an ethanol slurry), and carbon was vacuum-deposited to improve its surface conductivity in preparation for the electron microprobe analyzer.

Prior to microprobing, the surface conductivity was further enhanced by painting those portions which were not of interest with a slurry of carbon in ethanol. A Materials Analysis Company Model 400 electron microprobe analyzer was used to determine the concentration vs distance profiles across the crystal-crystal interfaces.

The nominal beam size was 1 μ, although resolution was probably in the range of 2-5 μ. In every case, two spectrometers were employed simultaneously to record the concentrations of both cations at every point. The specimens were always sufficiently large so that infinite

diffusion theory could be applied in the analysis of the profiles. The undiffused portions of the specimens served as internal standards representing spectrometer count rates in the pure oxides.

Laue back-reflection X-ray photographs were taken of all the specimens to determine the deviation of the microprobe path from the true normal of the crystal-crystal interface. This deviation resulted when the specimens were sawed not exactly normal to the interface, and never exceeded 10°.

Frazer, et al.[12] have written computer programs which correct the raw microprobe data for dead time, drift, background, absorption, and fluorescence if any. These programs were modified to suit the Radiation Laboratory computer facilities and additional programs were written and incorporated which converted the concentrations into mole fractions, made the corrections in distance indicated by the Laue photographs, and used a Cal-Comp plotter to plot automatically the concentration vs distance profiles.

The concentration-distance coordinates were taken manually directly from the Cal-Comp plots and punched on computer data cards. Computer programs were written which used this data to determine the Boltzmann-Matano interface and the concentration-dependent or independent chemical diffusion coefficients.

III. MATHEMATICAL ANALYSIS

If the diffusivity is a function of the concentration of the diffusing species, Fick's 2nd law for the one-dimensional case

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\,\frac{\partial c}{x}\right) \qquad (1)$$

is an inhomogeneous differential equation. For the case of counter-diffusion in two semi-infinite solids, Matano[13] has modified a solution originally presented by Boltzmann[14] to give the chemical diffusivity $\tilde{D}$ as a function of concentration, distance, and time (c, x, t). The Boltzmann-Matano solution involves the determination of an "interface" across which there has been a zero net flux of atoms of the counter-diffusing species. This defines x = 0 for the solution and is determined by the condition

$$\int_0^{c_o} x\,dc = 0 \text{ for } -\infty<x<\infty. \tag{2}$$

The diffusivity is given by

$$\tilde{D}(c') = -\frac{1}{2t}\left(\frac{dx}{dc}\right)_{c=c'} \int_0^{c'} x\,dc \tag{3}$$

The Boltzmann-Matano solution may not be applied to a system containing two or more phases, since the concentration vs distance profile is discontinuous at the phase boundary or boundaries and the required mathematical operations of integration and differentiation may not be performed. Jost[15] and Heumann[16] have developed qualitative solutions which overcome this difficulty. Appel[17] presented a quantitative solution where, for the two phase case, Eq. (2) becomes

$$\int_0^{c_{1e}} x\,dc + \int_{c_{2e}}^{c_o} x\,dc + (c_{2e} - c_{1e})\,X = 0 \tag{4}$$

where c_{1e} and c_{2e} are the respective equilibrium concentrations at the phase boundary and X is the distance the boundary has moved. x and X are measured either positive or negative from the x = 0 plane. For a given concentration, c', $\tilde{D}(c')$ is given by Eq. (3) for the region to the left of the discontinuity, and

$$\tilde{D}(c') = -\frac{1}{2t}\left(\frac{dx}{dc}\right)_{c=c'} \left[\int_0^{c_{1e}} x\,dc + \int_{c_{2e}}^{c'} x\,dc + (c_{2e} - c_{1e})\,X\right] \quad (5)$$

for the region to the right of the discontinuity. In the above expressions, t represents the time of the diffusion anneal.

The chemical diffusivity, $\tilde{D}$, is that one defined by Fick's 1st law

$$J = -\tilde{D}\frac{\partial c}{\partial x} \quad (6)$$

where J is the atom flux.

Smigelskas and Kirkendall[18] have shown experimentally that when the diffusivity is a function of concentration, the two counterdiffusing species in a metal-metal couple may move at different speeds, so that the original boundary between them and inert markers lying on the boundary move and no longer coincide with the Boltzmann-Matano interface.

Darken[19] developed a theoretical analysis of the Kirkendall effect which relates $\tilde{D}$ and v, the velocity of the inert markers at a constant composition to the intrinsic diffusivities, D_1 and D_2, of the individual, counterdiffusing species at that composition. The relationships are

$$\tilde{D} = D_1N_2 + D_2N_1 \quad (7)$$

$$v = (D_1 - D_2) \frac{\partial N_1}{\partial x} \tag{8}$$

where N_1 and N_2 are the atomic fractions of the respective species, subject to $N_1 + N_2 = 1$. When the controlling physical process involved is diffusion, $c = c(xt^{-1/2})$ and $v = X/2t$.

D_1 and D_2 are related to the tracer diffusivities, the diffusivities of radioactive tracer atoms in matrices of their own species (e.g., radioactive gold in gold), by

$$D_1 = D_1^* \left(1 + \frac{d \ln \gamma_1}{d \ln N_1}\right) \tag{9}$$

where D_1^* is the tracer diffusivity and γ_1 is the activity coefficient of component 1 at the concentration represented by N_1. For ideal solutions, $\gamma_1 = 1$ for all N_1 and $D_1 = D_1^*$; likewise, $D_2 = D_2^*$.

Darken's analysis is phenomenological and does not resort to any discussion of mechanisms. Therefore, it should be applicable to diffusion in any state--gas, liquid, or solid. In experiments involving seven different pairs of binary gas diffusion couples, McCarthy and Mason[20] found that Darken's analysis was not valid. The measured diffusivities were found to be related by equations derived from the kinetic theory of gases,[21,22] which are of a different form than Darken's equations.

Birchenall[23] and Vignes and Birchenall[24] have considered the problem from a fundamental viewpoint and believe Darken's equations to be basically incorrect for oxides also. According to them, there is one,

and only one, independent interdiffusion coefficient, the chemical diffusivity $\tilde{D}$, which completely describes the diffusion. D_1 and D_2 are essentially meaningless quantities, since there is no physical significance attached to a plane of constant composition on which inert markers lie.

Unfortunately, a kinetic theory of solids does not exist. Shewmon[25] discusses the various attempts which have been made to test Darken's analysis in solids. All attempts to date have suffered from very large experimental errors, and while the results agree with the analysis within those errors, they are by no means conclusive.

IV. RESULTS AND DISCUSSION

(1) Diffusion Profiles

(A) The NiO-MgO System: Typical profiles for this system are shown in Fig. 1. They are continuous since there is complete solid solution. An interface exists because a (110) MgO face was in contact with a (100) NiO face. Profiles for the same system under identical conditions but with oriented (100) faces in contact were an exact duplicate; the crystal-crystal interface, however, disappeared. These results provide experimental proof that the diffusion rate is independent of the crystallographic direction in cubic crystals. Nye[26] presents a theoretical proof.

Each of the profiles, for Ni and Mg, were analyzed independently, as discussed in Section III, to give $\tilde{D}$. As reported by Blank and Pask,[9] these diffusivities were always found to vary exponentially with Ni concentration. Since the diffusivity is also proportional to the vacancy concentration, it follows that the vacancy concentration varies

exponentially with total nickel concentration. Similar effects have been observed by Zintl[27] and Werner.[28] Zintl investigated cation lattice vacancies as a function of composition in Co_xO-MgO solid solutions and found that the vacancy concentration varied exponentially with cobalt concentration. Werner measured electrical conductivity in (Cu,Ag)S solid solutions as a function of copper composition. (Cu,Ag)S is a pure ionic conductor where electrical conductivity occurs by vacancy diffusion of the cations. The vacancy concentration depends on the fraction of Cu^{+2} present. He found that the electrical conductivity varied exponentially with copper concentration; which is to say, the vacancy concentration varied exponentially with copper concentration. These three effects are all manifestations of the same phenomenon. A small addition of the potentially-oxidizable ion present in the lattice will result in greater oxidation and formation of vacancies. Furthermore, since $Ni_{\square} \alpha e^{B[Ni]} \alpha e^{-\Delta H_f/RT}$, the heat of formation of a vacancy, ΔH_f, will decrease linearly with increasing nickel concentration. An ordered array of vacancies will have a lower energy per vacancy than will an isolated vacancy in the ordered crystal lattice. The vacancies interact with one another to lower the total energy of the system.

The total amount of Ni^{+3}, however, is small, the mole fraction being about 10^{-4} or less. This is indicated by the fact that the Ni and Mg profiles are complementary within experimental error. It may also be assumed that the NiO was at thermodynamic equilibrium with respect to its Ni^{+3} concentration throughout the course of the diffusion anneals since Mitoff[1] reports equilibrium with respect to thermal conductivity in times less than 2 h for temperatures in excess of 1300°C.

The $\tilde{D} = Ae^{B[Ni]}$ dependence was evaluated for three NiO-MgO diffusion couples--two at 1346°C for 173.26 h and one at 1342°C for 236:54 h. A and B were determined for each couple by a least-squares analysis and then a weighted average was taken of all three with weights inversely proportional to the individual variances. It was found that

$$\tilde{D} = 7.19 \times 10^{-12} \exp \{(4.31 \pm 0.11) [Ni]\} \text{ cm}^2/\text{sec} \qquad (10)$$

where [Ni] is expressed in atomic fraction Ni. In an analysis of just the nickel profiles in MgO single crystals, Blank and Pask[9] found that

$$\tilde{D} = 7.6 \times 10^{-12} \exp \{5.37 [Ni]\} \text{ cm}^2/\text{sec} \qquad (11)$$

at 1370°C and that B was constant between 1200 and 1400°C. They also found that the activation energy for diffusion was 45.5 kcal/mol and remained constant for all compositions.

From Eq. (1) it is seen that $\tilde{D}$ varies between 7.19×10^{-12} and 4.87×10^{-11} cm²/sec in going from pure MgO to pure NiO. This variation is less than an order of magnitude, so an average value of $\tilde{D}$ could be calculated. It was found to be 4.07×10^{-11} cm²/sec.

Choi and Moore[29] found that radioactive Ni^{+2} tracer diffusion in NiO was described by the equation $D = 1.83 \times 10^{-3} \exp\left(-\frac{45,600}{RT}\right)$, so that $D_{1345°C} = 1.21 \times 10^{-9}$ cm²/sec. For radioactive Mg^{+2} tracer diffusion in MgO, Lindner and Parfitt[30] found $D = 0.249 \exp\left(\frac{-79,000}{RT}\right)$, so that $D_{1345°C} = 4.86 \times 10^{-12}$. It is seen that the average value obtained in this study for the bulk interdiffusion lies between these two, as

expected. Wuensch and Vasilos[31] measured Ni^{+2} tracer diffusion in MgO and determined $D = 1.80 \times 10^{-5} \exp\left(-\frac{48,500}{RT}\right) = 4.84 \times 10^{-12}$ at 1345°C which is in good agreement with Lindner and Parfitt's determination for Mg^{+2} in MgO. In Blank and Pask's experiments, single crystals of MgO were embedded in NiO powder and the concentration profiles were measured only for Ni in the single crystal. Their determination, $\tilde{D} = 1.70 \times 10^{-5} \exp\left(-\frac{42,800}{RT}\right) = 2.70 \times 10^{-11}$ at 1345°C is slightly lower than that of this study, 4.07×10^{-11} cm^2/sec, as would be expected if the higher diffusivity regions in the NiO were not included.

The diffusion in these couples was of the extrinsic type since the MgO single crystals contained 0.015% Al as an impurity. The number of lattice cation vacancies from this source is greater than the number created thermally.[9]

(B) <u>The NiO-CaO System</u>: Typical profiles for this system are shown in Fig. 2. Discontinuities exist at the crystal interface because of limited solid solutions. The finite resolution of the electron microprobe beam caused the sharp discontinuities at the phase boundary to appear experimentally as non-vertical lines. The effect of this on calculations involving these results is negligible, since the deviations from straight, vertical lines are sufficiently small.

Each of the profiles, for Ni and Ca, was analyzed independently. The low mutual solubilities of NiO and CaO prevented a determination of the constants in the $\tilde{D} = Ae^{B[Ni]}$ dependence, but since the concentration span was never very great, averages could be taken for the respective diffusivities in each phase. Furthermore, since the mole fraction of Ni^{+3} (and thus lattice vacancies) is small, the diffusion profiles for

Ni and Ca are mirror images reflected about the Ni = Ca = 0.25 atomic fraction composition line. $\tilde{D}$ for Ni should then equal $\tilde{D}$ for Ca at each composition plane. The experimental data were averaged accordingly in each matrix.

Table II lists the experimentally-determined average diffusivities. These values were then fitted to equations of the form $\tilde{D} = D_o e^{-\Delta H/RT}$ (Fig. 3) to obtain the respective pre-exponential terms and activation energies. The results of a least-square analysis are shown in Table III; the indicated respective limits represent one standard deviation of the calculated values.

The coefficients for the CaO matrix are for intrinsic diffusion rather than extrinsic diffusion. There are more thermally created lattice vacancies (Schottky defects) than there are vacancies due to the presence of impurities of valence greater than +2. Consequently, the concentration of vacancies is temperature-dependent and is part of ΔH, rather than being a temperature-independent component of D_o. For intrinsic diffusion,

$$\Delta H = \Delta H_m + \Delta H_s/2 \qquad (12)$$

where ΔH_m is the heat of motion and ΔH_s is the heat of formation of a Schottky defect.

Lindner[32] has determined the intrinsic tracer diffusion of Ca^{+2} in CaO to be $D = 0.4 \exp\left(-\frac{81,000}{RT}\right)$ while Gupta and Weirick[33] have determined the extrinsic diffusion to be $D = 1.95 \times 10^{-7} \exp\left(-\frac{34,020}{RT}\right)$ so that ΔH_s = 94,000 cal/mol = 4.07 ev/defect for pure CaO. On

theoretical grounds, Yamashita and Kurosawa[34] have predicted Schottky defect heats of formation of 3-5 ev in CaO. The agreement is good. For an assumed heat of formation of 4 ev, the equilibrium concentration of cation vacancies at the lowest temperature of the anneals, 1342°C, is given by

$$N_{Ca} = \left(e^{-4x23,100/1.99x1615}\right)^{1/2} = 5.4 \times 10^{-7} \qquad (13)$$

where N_{Ca} is the mole fraction of calcium ion lattice vacancies. The spectroscopic analyses listed in Table I do not show the presence of any trivalent or quadrivalent impurities with greater concentrations.

The activation energy for interdiffusion in the CaO matrix, 93.80 ± 8.63 kcal/mol, is in fair agreement with the self-diffusivity for Ca^{+2} in CaO, 81.0 kcal/mol. No data exists for the activation energy for self-diffusion of Ni^{+2} in NiO in air but it should be less, since there are always excess cation vacancies available due to the presence of Ni^{+3}. The activation energy for self-diffusion of Ni^{+2} in NiO in air is probably very close to the activation energy for interdiffusion determined in this study, 72.09 ± 3.38 kcal/mole.

(2) Moving Phase Boundaries

(A) The NiO-MgO System: A photomicrograph of a polished cross-section of the NiO-MgO diffusion couple with composition profile of Fig. 1, but with oriented (100) faces in contact, is shown in Fig. 4. The original boundary is obliterated except for a line of elongated pores arising from the original imperfect matching of the two crystals. This line of pores is identifiable as the site of the original boundary

by its coincidence with the portion of the edge of the MgO crystal which was offset and because the cation concentration at this line is identical to that at the Boltzmann-Matano interface (30.4 a/o Ni and 19.8 a/o Mg, which adds to 50 a/o total cation concentration within experimental error) as determined by the computer analysis.

Figure 5 is a photomicrograph of the couple with a NiO (100) face in contact with a (110) MgO face whose diffusion profiles are also represented by Fig. 1. In this case the crystal offset is reversed and the phase boundary has clearly moved into the MgO crystal. To determine what happens to the crystallographic orientation of the volume swept out by the moving boundary, another diffusion anneal of a similar couple was made at 1342°C for 236:54 h. The boundary moved 51.4 μ into the MgO. The crystals broke apart at this interface. Laue back-reflection X-ray diffraction photographs of the new surfaces showed that the crystallographic orientation of the material swept out by the boundary changed from (110) to (100).

This movement is not generated by differences in surface energies at the interface. On the basis of thermal stabilities (at 1700°K, Coughlin[35] reports that ΔF for MgO is -91.3 kcal/mol and for NiO, -20.0 kcal/mol; also NiO decomposes rapidly in vacuum at temperatures greater than 1400°C) NiO would be expected to have a lower surface free energy than MgO. Then, the usual driving force for grain growth would have caused the boundary to move into the NiO, instead of into the MgO as was found here.

(B) The NiO-CaO System: A photomicrograph of a polished cross-section of the NiO-CaO couple, whose diffusion profiles are represented by Fig. 2, is shown in Fig. 6. The phase boundary remains because of limited solid solubility, but it has moved into the CaO as indicated by its curvature at the offset. The black area is due to material lost during polishing; it can thus be seen that the tip of the curved interface coincides with the offset CaO surface which also coincides with the Boltzmann-Matano interface.

In any diffusion-controlled process, $c = c(xt^{-1/2})$ only, so that at the Boltzmann-Matano interface, where $x = 0$ for all t, the concentration is invariant. Table II lists the independently-determined concentrations of each cation at the respective Boltzmann-Matano interfaces for each diffusion anneal. Within experimental error, the sum of the cation concentrations is 0.500 mole fraction; also the concentrations are constant at a given temperature.

The experimentally determined average velocities of phase boundary motion are listed in Table II and plotted as a function of the inverse absolute temperature in Fig. 7. A least squares analysis gives the equation listed in the figure. The activation energy of 61 ± 9 kcal/mol is close to the value of 72 ± 3 kcal/mol determined for interdiffusion in the NiO matrix. This agreement suggests that the boundary motion is primarily governed by the diffusion in the matrix that has the higher diffusivities.

The instantaneous velocity of the boundary at a given time can be mathematically calculated by equating the difference in the diffusion fluxes in the two phases at the interface to the rate of transfer of

material to the growing phase.

(C) Mechanisms: Diffusion experiments with oxide systems have indicated that essentially a rigid anion lattice is maintained. Oishi and Kingery[36] and O'Keefe and Moore[37] have shown that the oxygen diffusivities in MgO and NiO, respectively, are many orders of magnitude lower than the diffusivities of the corresponding cations. Also, Carter[38] has shown with the aid of markers that the oxygen anion lattices are rigid during interdiffusion in the $MgO-Al_2O_3$ and $MgO-Fe_2O_3$ systems. Since there is no net flux of oxygen atoms, a one-for-one exchange of cations of equivalent charge must occur at each plane normal to the diffusion direction in order to maintain a charge balance. The original interface then becomes the mass balance plane and corresponds to the Boltzmann-Matano interface which is indicated in Figs. 1 and 2. The requirement for maintenance of electroneutrality means that at each plane D(Ni) = D(Ca) or D(Ni) = D(Mg). The diffusion rate at each plane, however, may be different due to any variations in vacancy concentrations that may exist.

The observed moving boundary, thus, is not a Kirkendall marker in the sense that the term is used by Kirkendall[18] and Darken,[19] for its movement does not result from an unequal counterdiffusion at a given plane. Darken's analysis therefore cannot be applied to ionic systems of this type, since the species do not counterdiffuse independently of one another. Equations (7) and (8) consequently are inoperative since in this case $D_1 = D_2 = \tilde{D}$.

It is possible, however, to apply a Darken's analysis approach using Eqs. (7) and (8) to calculate the pseudo intrinsic diffusivities

D(Ni) and D(Ca) or D(Mg) if the assumption is made that D(Ni) is not equal to D(Ca) or D(Mg) at a given point. Such calculations were made using the $\tilde{D}$ and v data obtained in this study.[39] These calculations indicated that in regions where the nickel concentration was large, D(Ni) was large and negative. Thus, although mathematical treatment is possible, the values obtained are meaningless on the basis of the proposed mechanism or model wherein D(Ni) must equal D(Ca) or D(Mg) at a given concentration.

The driving force for the phase boundary motion arises from the difference in the chemical diffusivities in the portions of the phases adjoining the boundary; in this case diffusion in the NiO-rich phase is more rapid than either in the MgO-rich or CaO-rich phases. The MgO or CaO concentration on the NiO side of the boundary thus tends to deplete more quickly than the NiO concentration on the MgO or CaO side of the boundary. This situation leads to a continuous reaction at the interface in order to maintain equilibrium compositions resulting in the movement of the boundary into the MgO or CaO phase. Without a net oxygen flux, this movement involves a rearrangement and a transfer of oxygen anions to the growing phase at the boundary. This rearrangement or reaction occurs more rapidly than the diffusion; for otherwise, the (100) vs (100) and (100) vs (110) diffusion profiles in the NiO-MgO couples would not be identical and continuous, and the compositions at the phase boundary in the NiO-CaO couples would not be constant with time at a given temperature.

(3) NiO-CaO Phase Diagram

Short and Roy[40] have shown that diffusion data can be used to yield information on equilibrium phase diagrams. The concentrations in the respective phases at the phase boundary represent the equilibrium solubilities for the annealing temperature when the reactions are faster than the diffusivities. The equilibrium molar solubilities of CaO in NiO and NiO in CaO found for the air diffusion anneals in this study are listed in Table II and shown in Fig. 8. The figure shows the superimposed phase diagrams for the NiO-CaO system published by Tikkanen[9] and more recently by Smith et al.[11] The reasons for the lack of agreement between the three studies were not resolved.

V. CONCLUSIONS

1. In an air diffusion anneal of two semi-infinite solids, NiO and MgO or NiO and CaO, the variable vacancy concentration due to the varying content of Ni^{+3} with varying total NiO content causes the diffusivity to be concentration-dependent. Therefore, diffusion proceeds more rapidly in NiO-rich regions.

2. For NiO-MgO anneals in air, the dependence of the chemical diffusivity is

$$\tilde{D} = 7.19 \times 10^{-12} \exp \{(4.31 \pm 0.11)[Ni]\} \ \ cm^2/sec \qquad (10)$$

where [Ni] is expressed as atomic fraction Ni. This form of the dependency is due to the exponential dependence of Ni^{+2} vacancy concentration on Ni content, which in turn is due to the lower energy per vacancy when there are many vacancies present in the lattice.

3. The difference in the chemical diffusivities in the phases at the boundary will cause the phase boundary to move into the CaO in an NiO-CaO anneal and into the MgO in an NiO-MgO anneal when the faces originally in contact are of different crystallographic orientation. In the case of NiO-MgO diffusion anneals, no phase boundary exists when like crystallographic orientations are in contact. For an NiO-CaO anneal, the motion of the phase boundary is governed by the equation

$$v = 0.044^{+.651}_{-.041} \exp\left(-\frac{60{,}910 \pm 9340}{RT}\right) \text{ cm/sec} \qquad (14)$$

This result agrees with the measured activation energy in the NiO matrix indicating that the boundary motion is governed primarily by diffusion in the matrix exhibiting faster diffusivities.

4. When crystals of diverse crystallographic orientations are annealed in contact, the volume swept out by the moving boundary changes its orientation to conform to that of the growing crystal. Grain growth occurs.

5. The observed phase boundary motion is not a Kirkendall effect in the classical sense. In ionic solids with rigid anion lattices, electroneutrality requires that the respective intrinsic diffusivities of the two counterdiffusing cation species be equal at a given plane perpendicular to the direction of diffusion. Darken's analysis cannot be applied to such systems.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to Professor J. E. Dorn for discussions on the mathematics of diffusion.

This work was done under the auspices of the United States Atomic Energy Commission.

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Table I. Spectroscopic Analyses

Impurity (Reported as w/o oxide)	MgO	CaO	NiO
Mg	P.C.	0.04	0.001
Al	0.015	<0.002	<0.003
Si	Undetected	<0.002	<0.005
Ca	0.04	P.C.	0.001
Ti	Not analyzed	<0.005	<0.003
Cr	0.001	<0.0005	<0.001
Mn	Undetected	<0.0005	<0.001
Fe	0.008	<0.003	<0.005
Co	Not analyzed	<0.003	<0.01
Ni	<0.002	<0.001	P.C.
Cu	0.001	0.001	<0.0005
Sr	Not analyzed	0.015	Undetected
Sn	Not analyzed	<0.005	<0.01
Ba	Not analyzed	0.002	<0.001
W	Not analyzed	Undetected	Undetected

The analyses were performed by the American Spectrographic Laboratories, Inc., 557 Minna Street, San Francisco, California.

Table II. Data for Interfaces and Average Diffusion Coefficients in NiO-CaO and NiO-MgO Systems in Air

Temp °C	Time hrs	Mole Fractions at Boltzmann-Matano Interfaces		Mole Percent at Phase Boundary		Phase Boundary Velocity x 10^{10} cm/sec	Average Diffusion Coefficients in	
		Ca	Ni	CaO in NiO	NiO in CaO		NiO Matrix	CaO Matrix
1346	173:26	.0402	.4608	7.4	2.6	2.92	3.97×10^{-11}	7.13×10^{-12}
1352	122:35	.0372	.4621	6.7	6.6	3.22	5.34×10^{-11}	1.91×10^{-12}
1352	251:59	.0412	.4590	6.7	6.6	2.96	5.14×10^{-11}	2.65×10^{-12}
1410	97:57	.0613	.4376	8.7	7.9	4.47	7.77×10^{-11}	6.63×10^{-12}
1420	170:42	.0456	.4531	9.0	8.2	7.16	1.32×10^{-10}	7.41×10^{-12}
1423	266:37	.0485	.4516	9.1	8.3	5.08	1.06×10^{-10}	2.29×10^{-11}
1481	169:10	.0569	.4421	12	5.0	12.11	2.44×10^{-10}	1.95×10^{-11}
1481	169:10	.0507	.4493	11	6.6	5.05	2.33×10^{-10}	2.37×10^{-11}
1524	47:48	.0663	.4355	14	6.4	34.12	3.93×10^{-10}	4.97×10^{-11}
1527	171:53	.0504	.4507	16	6.5	12.49	3.55×10^{-10}	7.98×10^{-11}
1527	123:03	.0629	.4373	14	5.4	23.82	4.83×10^{-10}	7.27×10^{-11}
		Mg	Ni				NiO Matrix	MgO Matrix
1346	173:26	.1872	.3156				4.07×10^{-11}	
1346	173:26	.1984	.3040					
1342	236:54	.1961	.3034					

Table III. D_o and ΔH for the Diffusivities for the NiO-CaO System

	D_o	ΔH(kcal/mol)
NiO Matrix	$0.230^{+.395}_{-.145}$	72.09 ± 3.38
CaO Matrix	$13.9^{+162}_{-12.7}$	93.80 ± 8.63

FIGURE CAPTIONS

Fig. 1. Diffusion profiles for (100) NiO face in contact with (110) MgO face.

Fig. 2. Diffusion profiles for NiO-CaO couple with (100) faces in contact.

Fig. 3. Chemical diffusivities in NiO-CaO system: averages for respective matrices.

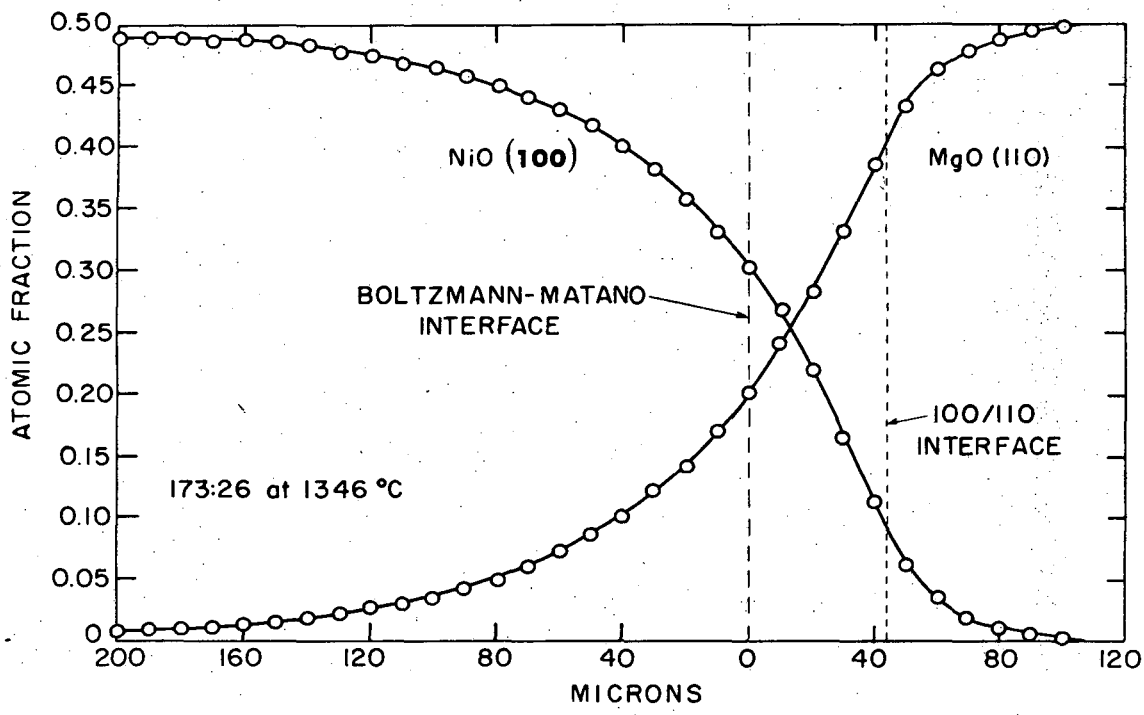
Fig. 4. Micrograph of NiO-MgO diffusion couple with (100) faces in contact. The leftmost line of pores corresponds to the original interface. (X100)

Fig. 5. Micrograph of NiO-MgO diffusion couple with (100) NiO face in contact with (110) MgO face. (X100)

Fig. 6. Micrograph of NiO-CaO diffusion couple with (100) faces in contact. (X100)

Fig. 7. Velocity of phase boundary motion in NiO-CaO diffusion couples with (100) faces in contact.

Fig. 8. NiO-CaO phase diagram.



XBL 686-923

Fig. 1

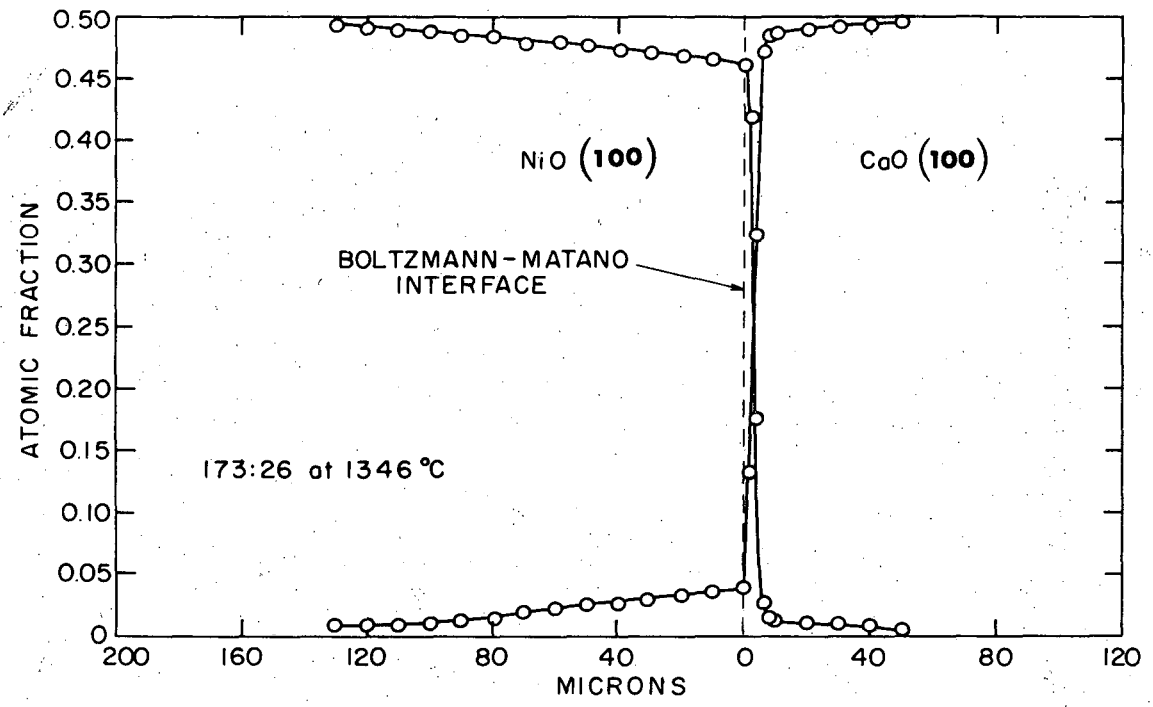


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Fig. 2

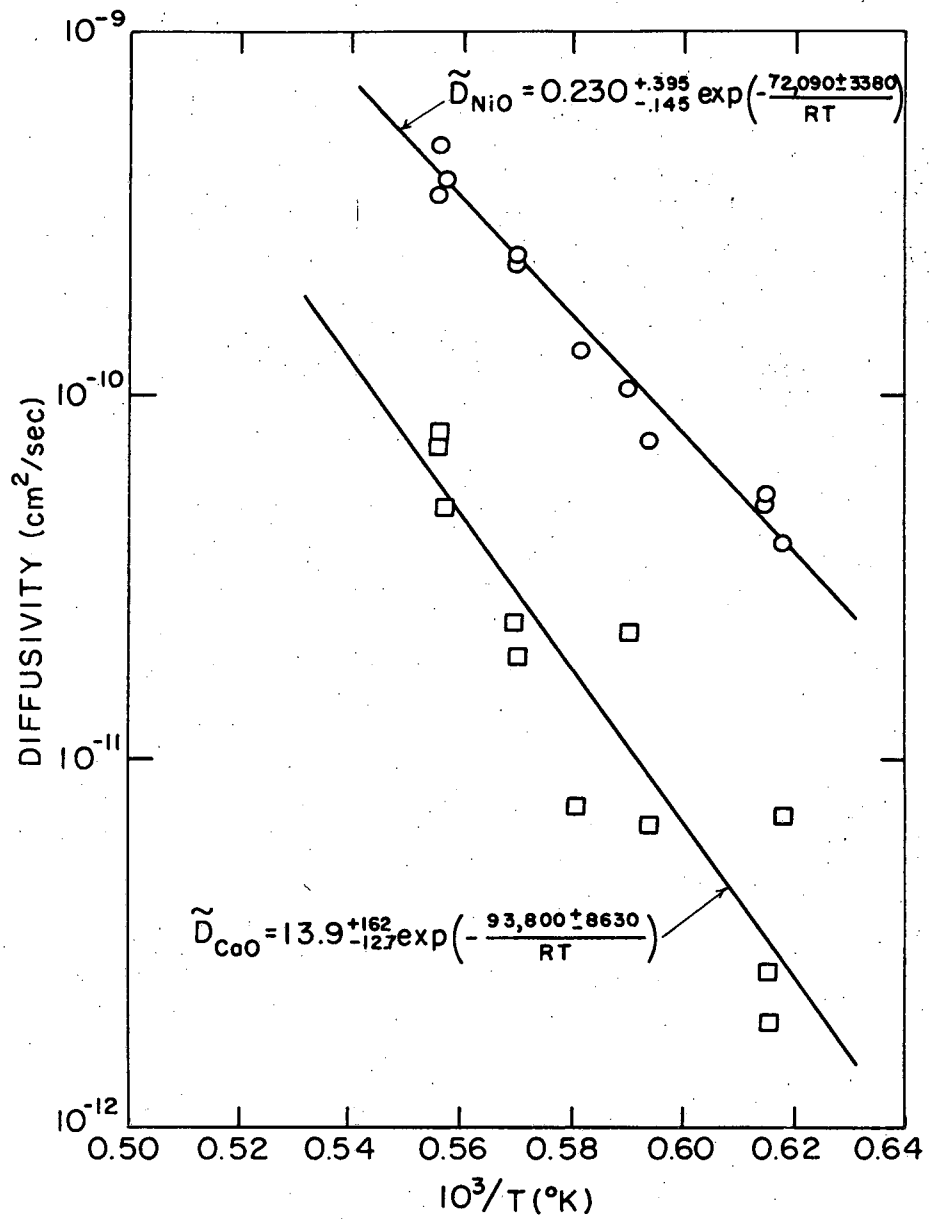

Fig. 3

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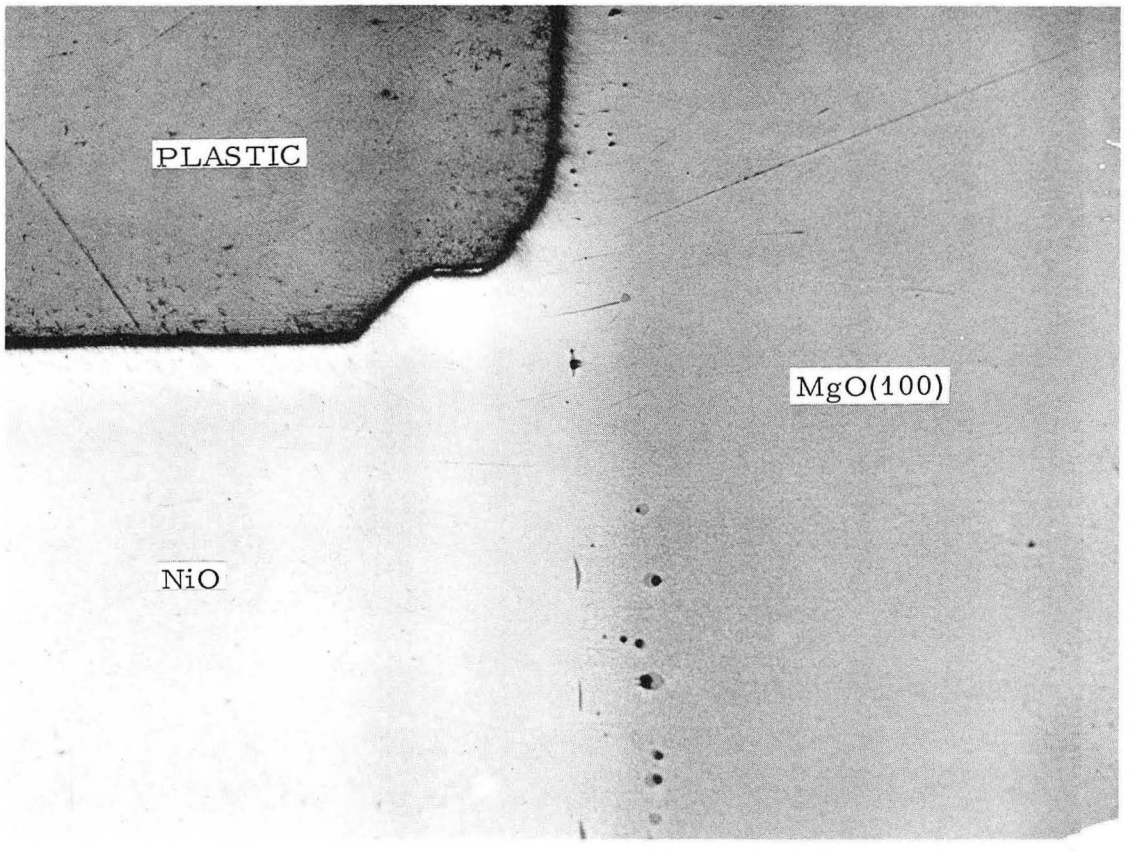

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Fig. 4

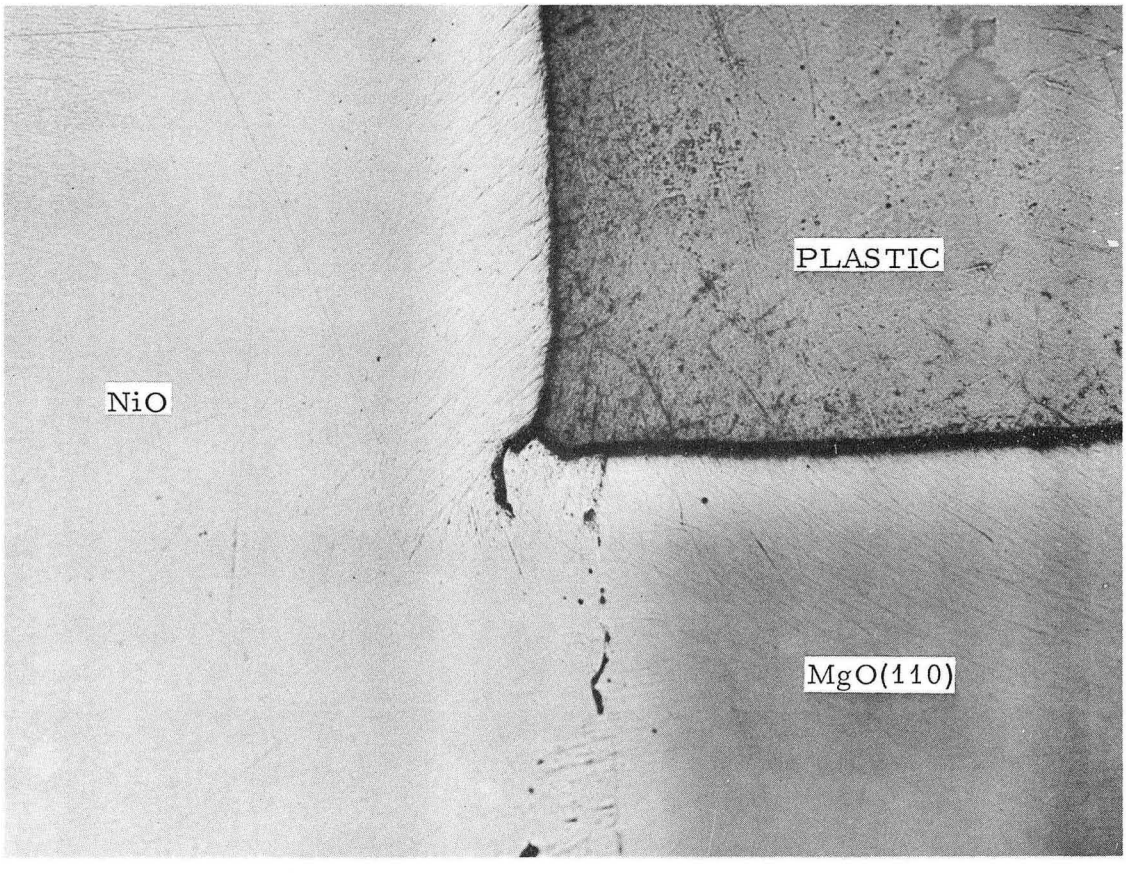

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Fig. 5

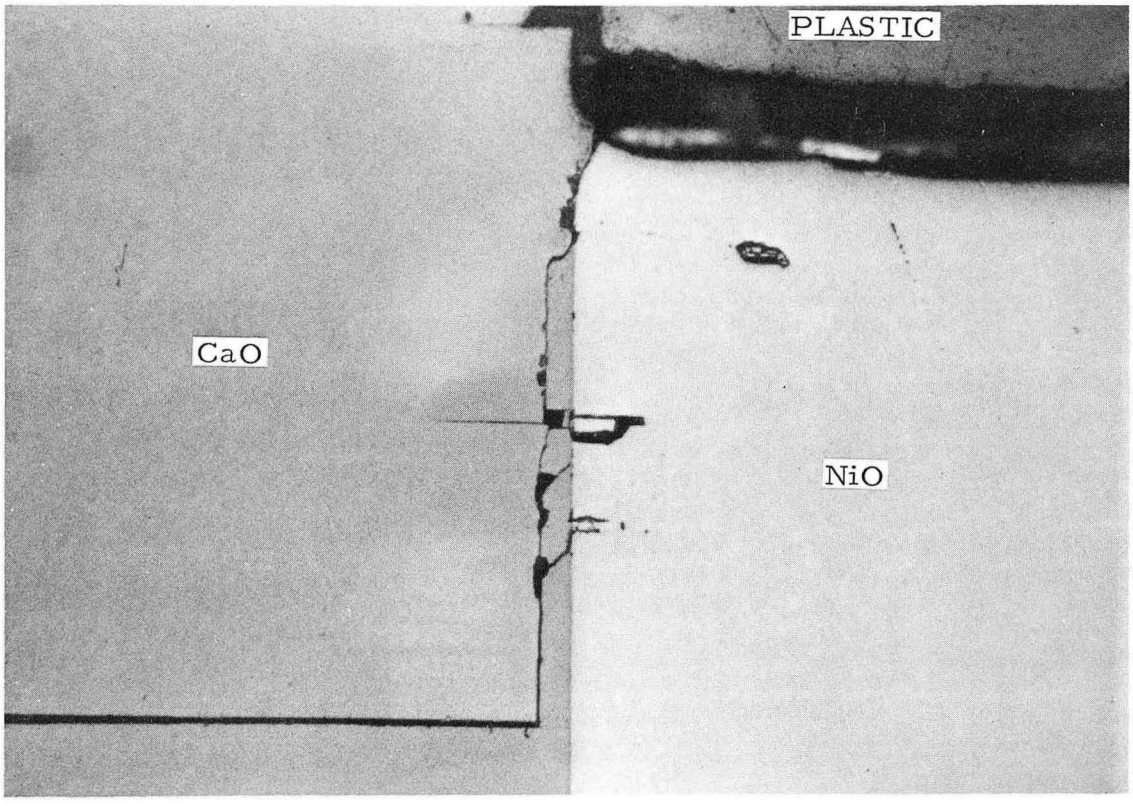

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Fig. 6

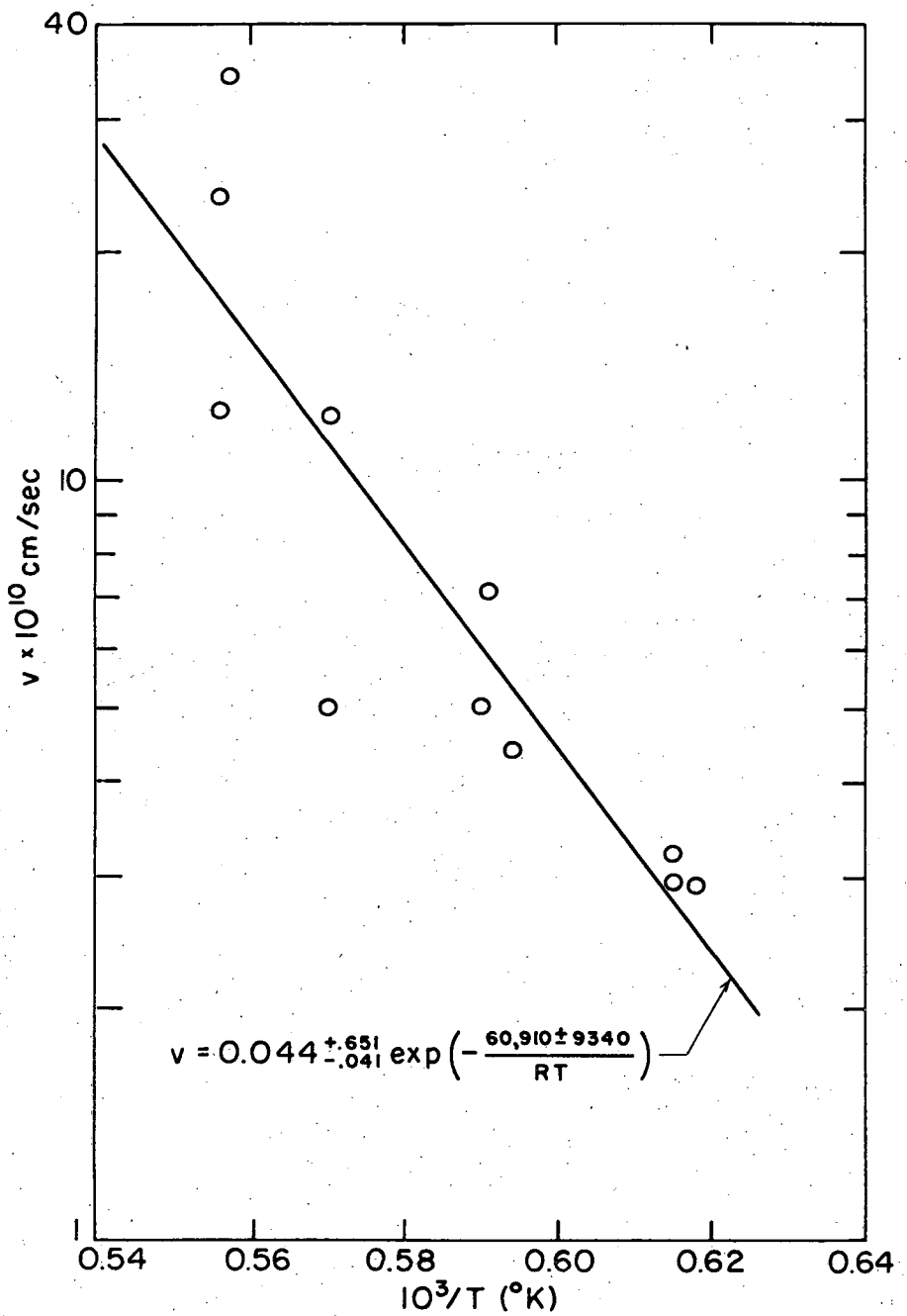
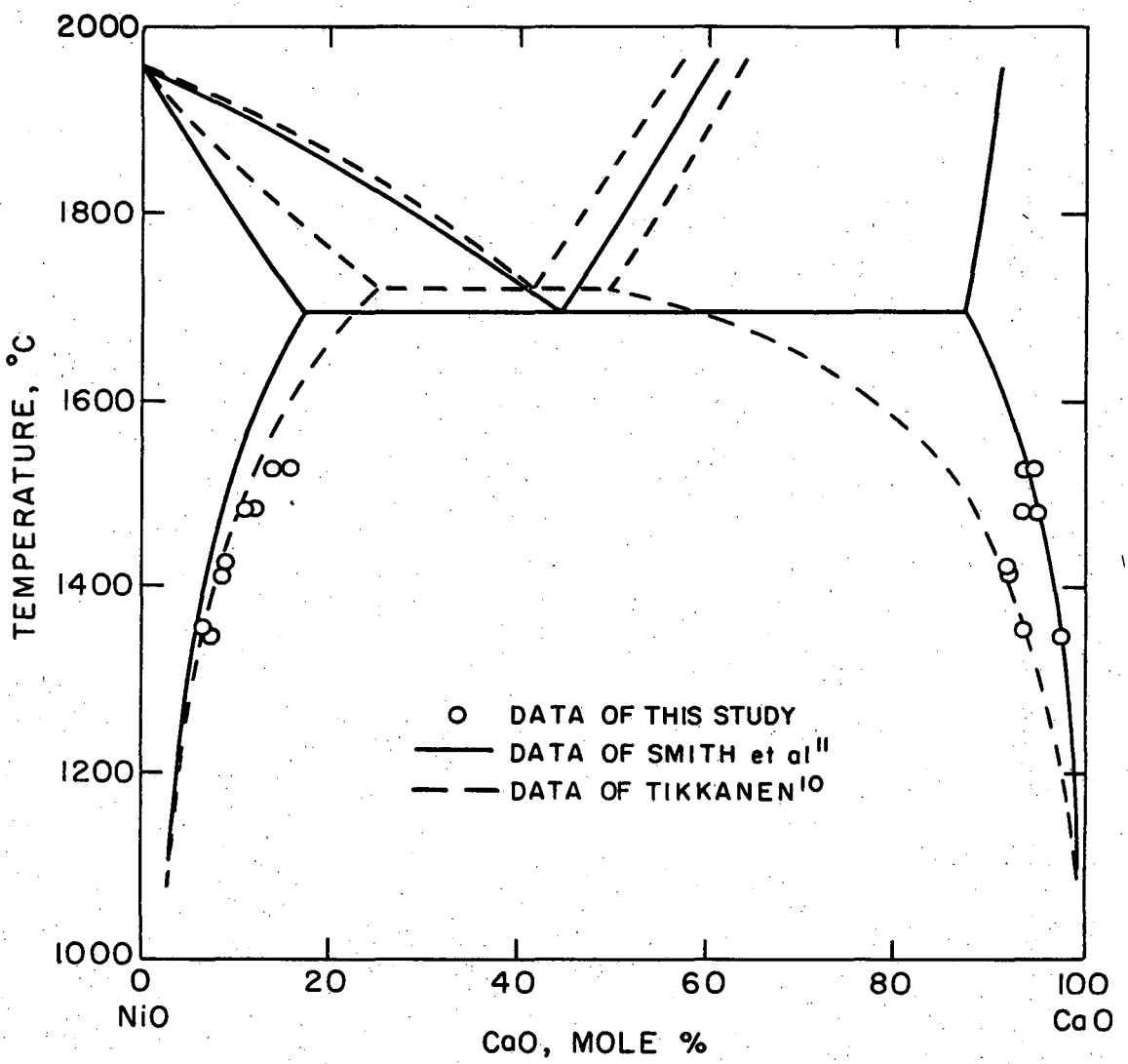


Fig. 7

XBL 686-925



XBL 699-5673

Fig. 8

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