Kinetic decomposition of Ni_2SiO_4 in oxygen potential gradients

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Nickel orthosilicate (Ni_2SiO_4) has been found to decompose into its component binary oxides in oxygen potential gradients at 1373 K. Nickel oxide was formed at the high oxygen potential boundary, while silica was detected at the low oxygen potential side. Significant porosity and fissures were observed near the Ni_2SiO_4/SiO_2 interface and the SiO_2 layer. The critical oxygen partial pressure ratio required for decomposition varied from 1.63 to 2.15 as the oxygen pressures were altered from 1.01×10^5 to 2.7×10^{-4} Pa, well above the dissociation pressure of Ni_2SiO_4. Platinum markers placed at the boundaries of the Ni_2SiO_4 sample indicated growth of NiO at the higher oxygen potential boundary, without any apparent transport of material to the low oxygen potential side. However, significant movement of the bulk Ni_2SiO_4 crystal with respect to the marker was not observed. The decomposition of the silicate occurs due to the unequal rates of transport of Ni and Si. The critical oxygen partial pressure ratio required for decomposition is related both to the thermodynamic stability of Ni_2SiO_4 with respect to component oxides and the ratio of diffusivities of nickel and silicon. Kinetic decomposition of multicomponent oxides, first discovered by Schmalzried, Laqua, and co-workers [H. Schmalzried, W. Laqua, and P. L. Lin, Z. Natur Forsch. Teil A **34**, 192 (1979); H. Schmalzried and W. Laqua, Oxid. Met. **15**, 339 (1981); W. Laqua and H. Schmalzried, *Chemical Metallurgy—A Tribute to Carl Wagner* (Metallurgical Society of the AIME, New York, 1981), p. 29] has important consequences for their use at high temperatures and in geochemistry.

I. INTRODUCTION

Recently increasing attention is being focused on the possible use of multicomponent ceramics as structural materials in high-temperature systems. The effect of both chemical and thermal gradients on the stability of multicomponent ceramic structures needs to be understood clearly before they could be used in practice. Schmalzried, Laqua, and co-workers[1-3] have shown that homogeneous oxide solid solutions can exhibit demixing, and ternary oxide compounds undergo decomposition in oxygen potential gradients. They have also suggested that the oxide crystal itself can be shifted toward the higher oxygen potential with respect to a fixed frame under certain conditions. Measurements have been reported on demixing in a (Mg, Co)O solid solution[1,2] and decomposition of cobalt and nickel titanates[2,3] in oxygen potential gradients.

Jacob[4] has shown that β-alumina—a superionic conductor—undergoes decomposition to Al_2O_3 and $NaAlO_2$ at the electrodes in an oxygen potential gradient, provided an external circuit is available for electron flow. The decomposition occurs at oxygen potentials well within the stability field of β-alumina. Field-induced composition changes in a sodium borate glass has been reported during electrolysis by Baucke and Duffy.[5]

Sodium ions move toward the cathode and oxygen to the anode by boron coordination switching. As a consequence, sodium-depleted glass is formed near the anode.

This study examines whether the silicates, which, unlike the titanates studied earlier, are almost stoichiometric compounds, also exhibit kinetic decomposition. It is known from self-diffusion measurements that the divalent cations are much more mobile than either oxygen or silicon in silicate structures.[6,7] Platinum markers placed on the sample indicate the direction of mass transport. The choice of Ni_2SiO_4 was dictated by the availability of accurate thermodynamic data for this compound.[8]

II. EXPERIMENTAL DETAILS
A. Materials

Nickel orthosilicate was prepared from high-purity silicic acid and nickel sulfate. Both compounds were heated separately in flowing argon up to 1400 K, and their respective mass losses were determined. An intimate mixture of the two compounds in the appropriate ratio was then heated to 1200 K in a platinum crucible under an atmosphere of argon. After quenching the mixture was ground under acetone, pelletized, and fired at 1750 K. The cycle of quenching, grinding, pelletizing,

and firing at 1750 K was repeated four times. The sample was held at 1750 K for a total of 5 days. The x-ray diffraction indicated that the product was single phase. Disks having 94.7% theoretical density, and approximately 13 mm in diameter and 3 mm thick were prepared by double end compression in a steel die and subsequent sintering. Both sides of the disk were polished with diamond paste. Platinum markers were attached to both sides of some disks by hot pressing grids of platinum wires at 1750 K.

B. Apparatus and procedure

A schematic diagram of the apparatus is shown in Fig. 1. The disk of Ni_2SiO_4 was held in an assembly of alumina tubes arranged such that two separate gases could be independently equilibrated with each side of the disk. The gas-tight seal between the disk and alumina tube was obtained by placing platinum O-rings between them. The assembly was held together under pressure by a system of springs attached to the brass heads at the cold ends of the outer alumina tube. The entire assembly was suspended in a vertical resistance furnace, with the Ni_2SiO_4 disk placed in the constant temperature zone.

Separate streams of gases were passed on each side of the Ni_2SiO_4 disk at flow rates varying from 1.5–3 ml s^{-1}. The high-purity gases were dried prior to their introduction into the high-temperature system. The high oxygen partial pressures were established by mixing pure oxygen and argon in the required ratio. To establish low oxygen partial pressures over the Ni_2SiO_4 disk,
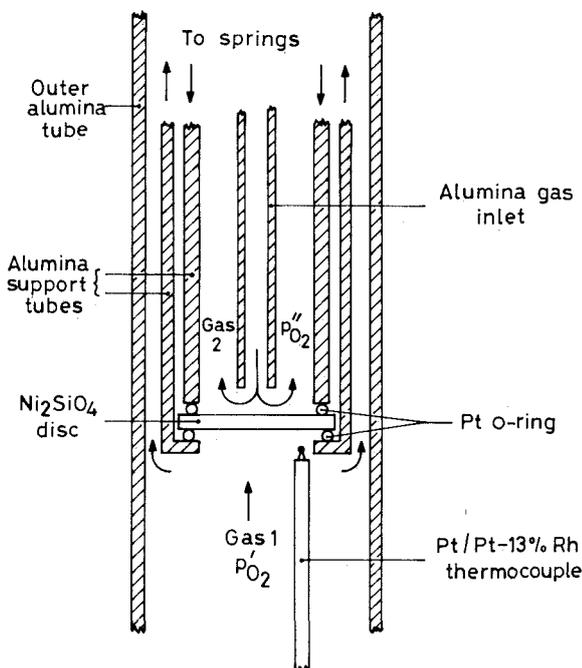
mixtures of $CO + CO_2$ of known composition were used. The mixtures were prepared by mixing component gas streams at preset flow rates in a glass tower filled with beads. In most of the experiments, oxygen partial pressure at one side of the Ni_2SiO_4 disk was held constant at either 1.01×10^5 or 1.89×10^{-3} Pa, while the partial pressure on the other side was varied systematically. The temperature of the Ni_2SiO_4 disk was measured by a $Pt/Pt-13\%$ Rh thermocouple placed 3 mm below it.

The Ni_2SiO_4 disks were placed in oxygen potential gradients established by two separate gas streams for 400–600 ks at 1373 K. At the end of the experiment, the disks were removed from the apparatus and their flat surfaces were examined by optical and scanning electron microscopy as well as x-ray diffraction. The disks were then sectioned and composition variation across them was determined by electron probe microanalysis (EPMA).

III. RESULTS

Examination of the Ni_2SiO_4 disks indicated that the silicate decomposed into its component oxides when the ratio of the partial pressures of oxygen at the two flat surfaces of the sample exceeded a critical value. Unlike in a normal chemical decomposition where the products are in close proximity, decomposition in oxygen potential gradient produced a layer of NiO at the high oxygen potential side of Ni_2SiO_4 and another layer of SiO_2 at the low oxygen potential boundary as indicated in Fig. 2. A large number of pores and fissures were seen in the SiO_2 layer. The NiO/Ni_2SiO_4 interface was much smoother than the SiO_2/Ni_2SiO_4 interface. The thickness of the decomposed regions of NiO and SiO_2 increased with the

FIG. 1. Schematic diagram of the apparatus.
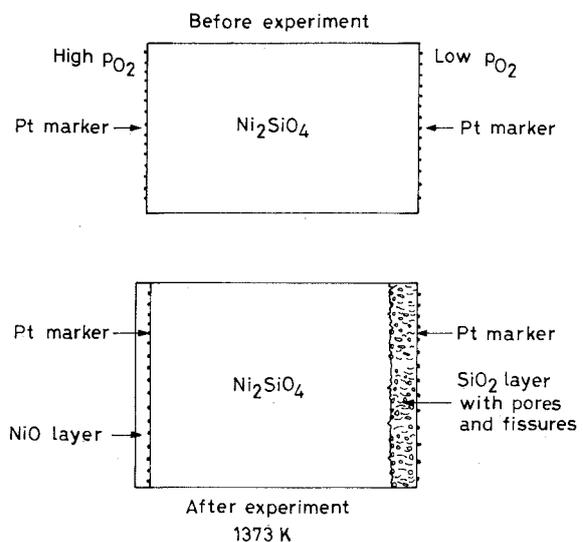
FIG. 2. Appearance of the Ni_2SiO_4 disk before and after kinetic decomposition at 1373 K.

absolute value of the oxygen potential difference established at the two flat surfaces of the Ni_2SiO_4 disk. When the ratio of partial pressures of oxygen on either side of Ni_2SiO_4 was less than a critical value, the chemical composition of the disk remained uniform throughout. There was no change in the appearance of the disk or position of the markers on exposure to small oxygen potential gradients below the critical value.

In experiments where decomposition of Ni_2SiO_4 was observed, the Pt marker placed initially at the high oxygen potential boundary was found to be buried inside the NiO layer near the NiO/Ni_2SiO_4 boundary. There was some movement of the Ni_2SiO_4 phase outward toward the high oxygen potential relative to the marker when large oxygen potential gradients were imposed on the sample. However, the distance of crystal movement was of the same order of magnitude as the roughness of the NiO/Ni_2SiO_4 interface precluding accurate measurement. The growth of the NiO layer past the inert marker suggests transport of nickel ion from the low oxygen potential region to the high oxygen potential side. The Pt marker at the low oxygen potential boundary remained at the outer surface of the sample during exposures at 1373 K.

Details of oxygen partial pressure, exposure time, and phases identified after exposure to the oxygen potential gradient at 1373 K are summarized in Table I. In experiments in series A, where the higher oxygen partial pressure was held at 1.01×10^5 Pa, the critical ratio of oxygen partial pressures for the onset of decomposition

was 1.63. In series B, where the higher oxygen potential was set at 1.89×10^{-3} Pa using $CO_2 + CO$ mixtures, the critical oxygen partial pressure ratio was found to be 2.16. The exact value of the critical oxygen partial pressure ratio for the onset of decomposition therefore appears to be a function of the average oxygen potential seen by the silicate. A typical compositions profile across the Ni_2SiO_4 disk obtained using EPMA is shown in Fig. 3.

IV. DISCUSSION

The oxygen partial pressure corresponding to the dissociation of Ni_2SiO_4 according to the reaction

$$Ni_2SiO_4(\text{olivine}) \rightarrow 2Ni(s) + SiO_2(\text{quartz}) + O_2(g) \tag{1}$$
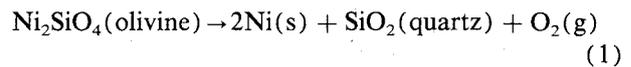
is 7.34×10^{-5} Pa at 1373 K.[8] The oxygen partial pressures used in this study are above the dissociation pressure by more than an order of magnitude. Therefore chemical decomposition of Ni_2SiO_4 is not expected under the present experimental conditions. Also Ni_2SiO_4 is thermodynamically more stable than its binary component oxides at 1373 K. For the reaction[8]

$$NiO(\text{r.s.}) + SiO_2(\text{quartz}) \rightarrow Ni_2SiO_4(\text{olivine}), \tag{2}$$
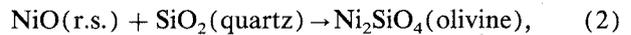
$$\Delta G_2^0 = -13\,050 + 5.67T(\pm 100)J\,\text{mol}^{-1}. \tag{3}$$

The decomposition of Ni_2SiO_4 observed in this study therefore appears surprising at first sight. An important aspect of this decomposition is its morphology; the products of decomposition are physically separated and

TABLE I. Summary of experimental data at 1373 K.

Expt. No.	$\left(\dfrac{P_{CO_2}}{P_{CO}}\right)'$	$\left(\dfrac{P_{CO_2}}{P_{CO}}\right)''$	P_{O_2}' (Pa)	P_{O_2}'' (Pa)	$\dfrac{P_{O_2}'}{P_{O_2}''}$	t,ks	Phases (EPMA and x-ray diffraction)	$\left(\dfrac{P_{O_2}'}{P_{O_2}''}\right)_{crit}$
A1			1.01×10^5	9.06×10^4	1.12	500	Ni_2SiO_4	
A2			1.01×10^5	7.42×10^4	1.36	500	Ni_2SiO_4	
A3			1.01×10^5	6.20×10^4	1.6	600	Ni_2SiO_4	
A4	Ar + O₂ mixture	Ar + O₂ mixture	1.01×10^5	6.18×10^4	1.63	600	NiO', Ni_2SiO_4, SiO_2''	1.63
A5			1.0×10^5	6.14×10^4	1.65	500	NiO', Ni_2SiO_4, SiO_2''	
A6			1.01×10^5	3.54×10^4	2.85	400	NiO', Ni_2SiO_4, SiO_2''	
A7			1.01×10^5	1.93×10^3	5.23	400	NiO', Ni_2SiO_4, SiO_2''	
A8			1.01×10^5	4.17×10^3	24.2	400	NiO', Ni_2SiO_4, SiO_2''	
B1	228	180	1.89×10^{-3}	1.18×10^{-3}	1.60	400	Ni_2SiO_4	
B2	228	174	1.89×10^{-3}	1.10×10^{-3}	1.72	500	Ni_2SiO_4	
B3	228	158	1.89×10^{-3}	9.12×10^{-4}	2.08	600	Ni_2SiO_4	
B4	228	156	1.89×19^{-3}	8.89×10^{-4}	2.13	600	Ni_2SiO_4	
B5	228	154	1.89×10^{-3}	8.665×10^{-4}	2.18	500	NiO', Ni_2SiO_2, SiO_2''	2.16
B6	228	140	1.89×10^{-3}	7.16×10^{-4}	2.64	400	NiO', Ni_2SiO_4, SiO_2''	
B7	228	86	1.89×10^{-3}	2.70×10^{-4}	7.02	400	NiO', Ni_2SiO_4, SiO_2''	
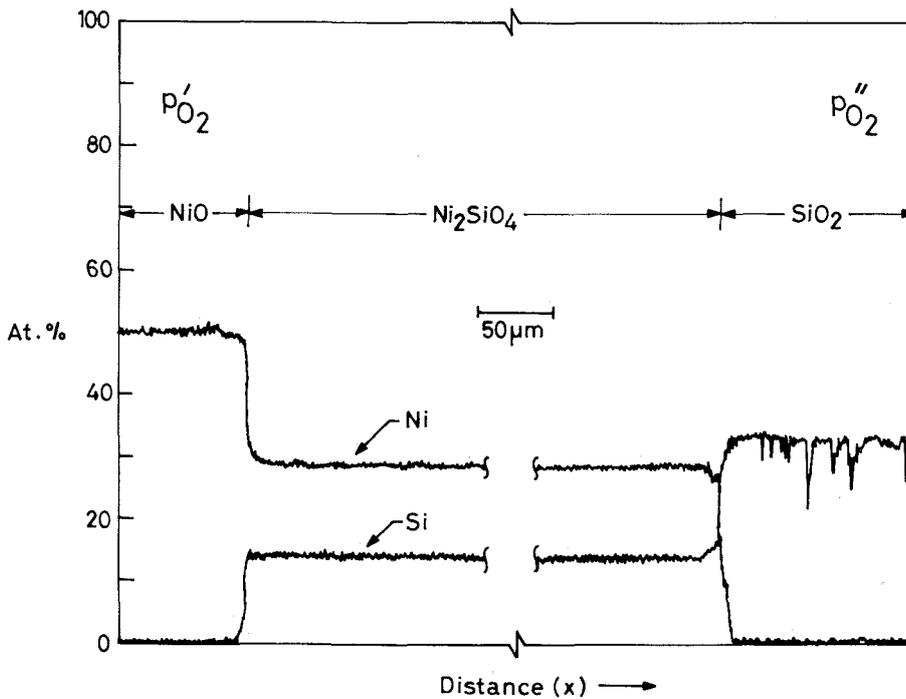
FIG. 3. Composition profile across the Ni₂SiO₄ disk after kinetic decomposition obtained by EPMA.

appear at the extremities of the sample.

Mobile species in ionic crystals move under the action of electrochemical potential gradients. Local equilibrium cationic vacancy or interstitial concentrations in transition metal oxides depend on the oxygen potential. The exact functional dependence is determined by the majority point defects present in the system. When an isothermal oxygen potential gradient is imposed on the Ni_2SiO_4 sample, it induces a vacancy (or interstitial) gradient in the cationic sublattices. As a result of this gradient, cations are transported to the oxide surface exposed to the higher oxygen potential with coupled transport of electron holes in the opposite direction. The direction of fluxes and movement of the bulk sample are indicated in Fig. 4. If the mobility of one of the cationic species in multicomponent oxide is higher than that of the others, there is preferential flux of that species until a steady state is attained. Applying the analysis of Schmalzried and Laqua[1–3] to the orthosilicate composition, quantitative mathematical relations can be developed for the critical oxygen potential gradient required to initiate decomposition and the steady-state velocity of the Ni_2SiO_4 crystal.

The flux of an ionic species such as Ni^{2+} (J_{Ni}) in a potential gradient in the x direction is given by

$$J_{Ni} = \frac{-C_{Ni}D_{Ni}}{RT} \frac{\partial}{\partial x} (\mu_{Ni^{2+}} + Z_{Ni^{2+}}\mathscr{F}\phi), \quad (4)$$

where the driving force is the electrochemical potential, composed of a chemical term ($\mu_{Ni^{2+}}$) and an electrical field contribution ($Z_{Ni^{2+}}\mathscr{F}\phi$), where Z is the charge of

the ion, $\mathscr{F}$ is the Faraday constant, and ϕ is the electric potential. The symbols C_{Ni} and D_{Ni} in Eq. (4) denote the concentration (in moles per unit volume) and diffusion coefficient of Ni^{2+} ions in Ni_2SiO_4. In general, diffusivities of the cations in ternary oxides are not only functions of total pressure and temperature, but also vary with the chemical potentials of one of the component oxides (NiO or SiO_2) and oxygen. The functional dependencies are determined by the type of disorder. In the following treatment, average diffusion coefficients are used.

Applying the principle of local equilibrium, the chemical potentials of ionic species can be written in terms of the chemical potentials of neutral species and electronic defects as follows:
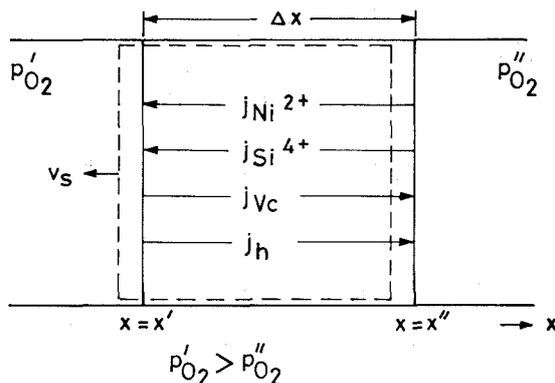
FIG. 4. The directions of fluxes of cations, vacancies, and electron holes in Ni_2SiO_4 when exposed to an oxygen potential gradient. Here Δx = the thickness of Ni_2SiO_4 and v_s = steady-state velocity.

$$Ni + 2h \rightarrow Ni^{2+}, \quad \mu_{Ni} + 2\mu_h = \mu_{Ni^{2+}}, \qquad (5)$$
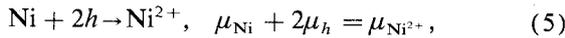
where h represents an electron hole. Since Ni_2SiO_4 is a semiconductor, $-dF\phi = d\mu_h$ and Eq. (4) reduces to

$$J_{Ni} = \frac{-C_{Ni}D_{Ni}}{RT}\frac{\partial\mu_{Ni}}{\partial x}. \qquad (6)$$

Similarly the flux of silicon is given by

$$J_{Si} = \frac{-C_{Si}D_{Si}}{RT}\frac{\partial\mu_{Si}}{\partial x}. \qquad (7)$$

The chemical potentials of Ni and Si can be expressed in terms of chemical potentials of the corresponding oxides and oxygen. By virtue of the formation reactions for binary oxides, we have

$$Si + O_2 \rightarrow SiO_2, \quad Ni + \tfrac{1}{2}O_2 \rightarrow NiO, \qquad (8)$$
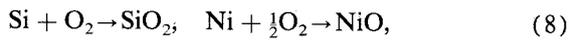
$$\mu_{Si} + \mu_{O_2} = \mu_{SiO_2}, \quad \mu_{Ni} + \tfrac{1}{2}\mu_{O_2} = \mu_{NiO}. \qquad (9)$$

Combining Eqs. (6) and (9),

$$J_{Ni} = \frac{-C_{Ni}D_{Ni}}{RT}\left(\frac{\partial\mu_{NiO}}{\partial x} - \frac{1}{2}\frac{\partial\mu_{O_2}}{\partial x}\right). \qquad (10)$$

Similarly for the flux of silicon,

$$J_{Si} = \frac{-C_{Si}D_{Si}}{RT}\left(\frac{\partial\mu_{SiO_2}}{\partial x} - \frac{\partial\mu_{O_2}}{\partial x}\right). \qquad (11)$$

When steady state is attained, there is no further decomposition of the silicate and all components move with the same steady-state velocity v_s. At steady state

$$J_{Ni}/C_{Ni} = J_{Si}/C_{Si}. \qquad (12)$$

Substituting for fluxes using Eqs. (10) and (11), one finds that

$$D_{Ni}\left(\frac{\partial\mu_{NiO}}{\partial x} - \frac{1}{2}\frac{\partial\mu_{O_2}}{\partial x}\right) = D_{Si}\left(\frac{\partial\mu_{SiO_2}}{\partial x} - \frac{\partial\mu_{O_2}}{\partial x}\right). \qquad (13)$$

Rearranging yields

$$D_{Ni}\left(\frac{\partial\mu_{NiO}}{\partial x}\right) = \frac{\partial\mu_{O_2}}{\partial x}\left(\frac{D_{Ni}}{2} - D_{Si}\right) + D_{Si}\left(\frac{\partial\mu_{SiO_2}}{\partial x}\right). \qquad (14)$$

The Gibbs–Duhem equation for the binary NiO–SiO_2 system is

$$N_{NiO}\,d\mu_{NiO} + N_{SiO_2}\,d\mu_{SiO_2} = 0. \qquad (15)$$

Mass balance requires that $N_{NiO} = 2N_{SiO_2}$ in stoichiometric Ni_2SiO_4. Therefore

$$\frac{\partial\mu_{SiO_2}}{\partial x} = -2\frac{\partial\mu_{NiO}}{\partial x}. \qquad (16)$$

Combination of Eqs. (14) and (16), and rearrangement, leads to

$$\frac{\partial\mu_{NiO}}{\partial x}\,(D_{Ni} + 2D_{Si}) = \frac{\partial\mu_{O_2}}{\partial x}\left(\frac{D_{Ni}}{2} - D_{Si}\right). \qquad (17)$$

Integrating between $x = x'$ and $x = x''$ defined in Fig. 4,

$$\Delta\mu_{NiO}\,(D_{Ni} + 2D_{Si}) = \Delta\mu_{O_2}\left(\frac{D_{Ni}}{2} - D_{Si}\right), \qquad (18)$$

where $\Delta\mu_{NiO}$ and $\Delta\mu_{O_2}$ are the differences in the respective chemical potentials of NiO and O_2 at the extremities of Ni_2SiO_4. The maximum value for $\Delta\mu_{NiO}$ is given by

$$\Delta\mu_{NiO}^{max} = -\Delta G_2^0/2, \qquad (19)$$

since mutual solid solubility between NiO and SiO_2 is negligible. Therefore the minimum oxygen potential difference required to affect decomposition of Ni_2SiO_4 is

$$\Delta\mu_{O_2}^{min} = RT\ln\left(\frac{P_{O_2'}}{P_{O_2''}}\right) = -\left(\frac{\beta+2}{\beta-2}\right)\Delta G_2^0, \qquad (20)$$

where $\beta = D_{Ni}/D_{Si}$ and ΔG_2^0 is the Gibbs' energy of formation of Ni_2SiO_4 from component oxides according to reaction (2). The greater the value of β, the smaller is the oxygen potential difference required to initiate decomposition. As β tends to infinity,

$$\Delta\mu_{O_2}^{min} = -\Delta G_2^0. \qquad (21)$$

When nickel in the ternary oxide is much more mobile than silicon ($\beta \rightarrow \infty$), the minimum oxygen potential gradient required for decomposition is directly related to the stability of the compound relative to the binary oxides. When the value of $\beta = 2$, decomposition due to the kinetic reasons is not possible and the oxygen potential difference required for decomposition tends to infinity. The variation of $\mu_{O_2}^{min}$ with β is shown in Fig. 5 for Ni_2SiO_4 at 1373 K, where β is taken as a variable. The value for the free energy of formation of Ni_2SiO_4 is from a recent study due to Jacob et al.[8] In the region above the curve in Fig. 5 kinetic decomposition is feasible, while in the region below kinetic decomposition is impossible.

The values of β for Ni_2SiO_4 can be calculated from the results obtained in this study, ΔG_2^0 and Eq. (20). The values are 67.3 from series A experiments, and 8.0 from series B. The difference is clearly beyond the range of experimental error. The reason for the difference probably lies in the assumptions on which Eq. (20) is based, especially the constancy of diffusion coefficients. Nickel ions probably move through Ni_2SiO_4 via vacancies so that D_{Ni} may be proportional to $P_{O_2}^{1/6}$. The dominant defect on the silicon sublattice is likely to be interstitial and D_{Si} may therefore decrease with increasing P_{O_2}. The increase in the value of β with increasing average oxygen potential over the Ni_2SiO_4 sample observed experimentally is in accord with these speculations. A more exact formulation must await a detailed study of point defects in Ni_2SiO_4. There appears to be no published work on diffusion coefficients in Ni_2SiO_4 to verify the computed values for β. Tracer diffusion studies in air at 1418 K indicate values of β equal to ~ 110 for Co_2SiO_4 and ~ 30 for Mg_2SiO_4.[7]

On imposing an oxygen potential difference larger than the minimum value specified by Eq. (20) on
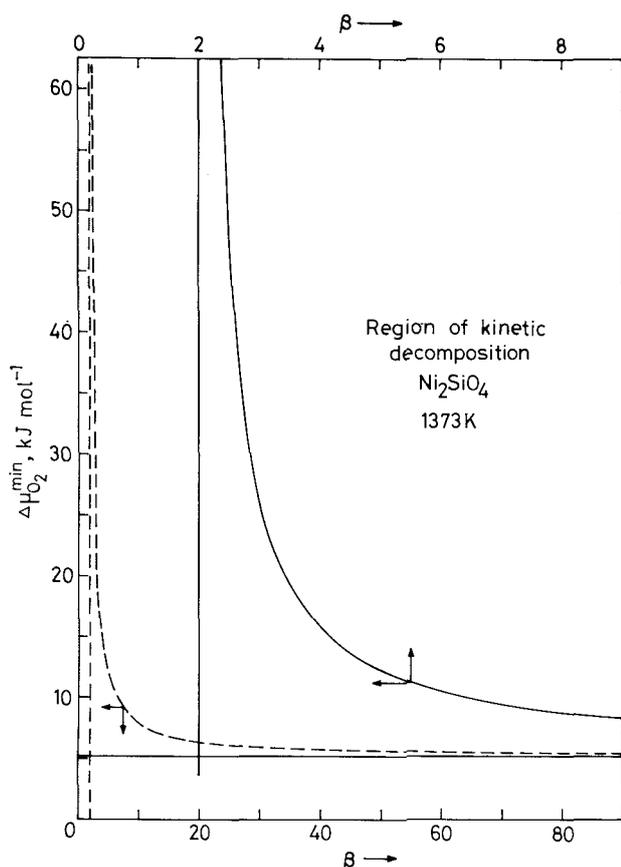
FIG. 5. Graphical representation of the minimum oxygen potential difference required for kinetic decomposition of Ni_2SiO_4 at 1373 K as a function of the ratio of average diffusivities $\beta(= D_{Ni}/D_{Si})$. The solid curve corresponds to the magnified scale for β and the dotted curve corresponds to the contracted scale for β.

Ni_2SiO_4, it will decompose into NiO and SiO_2 until steady state is reached. At steady state no further decomposition occurs and the oxygen potential difference across the undecomposed Ni_2SiO_4 is equal to $\Delta\mu_{O_2}^{min}$ given by Eq. (20). The difference between $\Delta\mu_{O_2}$ imposed by the gas mixtures and $\Delta\mu_{O_2}^{min}$ is dissipated across the NiO and SiO_2 layers. Since the SiO_2 layer was found to be fissured, the oxygen potential gradient across it is likely to be small. Most of the difference between $\Delta\mu_{O_2}$ imposed by the gas mixture and $\Delta\mu_{O_2}^{min}$ would be across the NiO layer. It is therefore reasonable to expect the thickness of the NiO layer (and consequently the SiO_2 layer) to increase with the difference in the chemical potential oxygen established by the gas mixtures, in agreement with experimental observation.

When the imposed oxygen potential difference is less than $\Delta\mu_{O_2}^{min}$, there is no decomposition of Ni_2SiO_4. However, there will be a flux of nickel and silicon ions from the low oxygen potential side to the high oxygen potential surface. As nickel and silicon ions move to the high oxygen potential surface, they release oxygen to the

low potential gas phase. The nickel and silicon ions that arrive at the high oxygen potential surface combine with oxygen to extend the silicate lattice. The net effect is the movement of the crystal with respect to a fixed frame in the direction of increasing oxygen potential. The steady-state velocity of movement of Ni_2SiO_4 is given by

$$v_s = J_{Ni}/C_{Ni} = J_{Si}/C_{Si}, \qquad (22)$$

where J_{Ni} is defined by Eq. (6). Combination of Eqs. (9) and (17) gives

$$\frac{\partial\mu_{Ni}}{\partial x} = \left(\frac{D_{Ni} - 2D_{Si}}{D_{Ni} + 2D_{Si}} - 1\right)\frac{1}{2}\frac{\partial\mu_{O_2}}{\partial x}. \qquad (23)$$

Combining Eqs. (6), (22), and (23) and integrating the resulting equation, one obtains

$$v_s = \frac{2\beta D_{Si}\Delta\mu_{O_2}}{RT(\beta + 2)\Delta x}. \qquad (24)$$

This equation permits the evaluation of D_{Si} from information on the movement of Ni_2SiO_4 with respect to inert markers at the high oxygen potential side using values of β obtained from Eq. (20) as discussed earlier. However, an accurate value for v_s could not be obtained in this study. In experiment A4, where a Ni_2SiO_4 disk of 3.36 mm thickness was used, the movement of bulk Ni_2SiO_4 relative to platinum markers was found to be approximately 1 μm in 600 ks at 1373 K. With a value of $\beta = 67.3$ from series A experiments, the average value of D_{Si} is approximately 9×10^{-12} cm² s⁻¹. This value should only be taken as an order of magnitude estimate since the time required for the establishment of steady-state conditions in experiment A4 cannot be easily estimated. Tracer-diffusion studies on olivine structures indicate diffusion coefficients between 10^{-14} and 10^{-15} cm² s⁻¹ in air at comparative temperature. The present estimate is much higher and may be indicative of a grain boundary diffusion process rather than bulk diffusion. Experiments with single crystals of Ni_2SiO_4 can resolve this point.

The porosity and fissures observed at the lower oxygen potential side of the sample (SiO_2 layer) is partly due to the removal of nickel during the decomposition stage and partly due to the shift of the bulk Ni_2SiO_4 toward the higher oxygen potential under steady-state conditions. The bulk movement occurs by diffusion of nickel and silicon away from the lower oxygen potential side and simultaneous release of oxygen to the gas phase. Martin and Schmalzried[9] have suggested that the velocity of pore migration is approximately three times the steady-state velocity of crystal movement in the case of pure CoO. Pores can therefore be expected to penetrate the entire crystal given sufficient time.

After completion of this article, we noticed a recent review article by Schmalzried[10] on decomposition of semiconducting oxides and a paper by Wolfenstine et al.[11] on the decomposition of Ni_2SiO_4 at 1609 K. Unlike

the present study, Wolfenstine *et al.*[11] have not determined the critical oxygen partial pressure ratio required to initiate kinetic decomposition, and their observations are confined to a single ratio of oxygen partial pressures $(P'_{O_2}/P''_{O_2} = 677)$. Wolfenstine *et al.*[11] did not observe a continuous layer of NiO at the high oxygen pressure side of Ni_2SiO_4: instead, NiO was found to be dispersed along the pores and grain boundaries in Ni_2SiO_4.[10] In our opinion their morphology is a direct consequence of the low density of Ni_2SiO_4 pellets (86% of theoretical) used in their experiments: the oxygen potential gradient was ill defined in their porous sample and critical conditions for decomposition were probably satisfied at multiple sites inside the Ni_2SiO_4 sample. Further, the value for the Gibbs' energy of formation used by Wolfenstine *et al.*[11] is different from that used in this study,[8] and their estimation of the oxygen partial pressure ratio required for decomposition in the limit $\beta \to \infty$ is erroneous.

V. SUMMARY

The critical oxygen potential difference required for kinetic decomposition of Ni_2SiO_4 has been determined by experiment at 1373 K. The critical oxygen potential difference is a function of the average chemical potential over the sample. The decomposition is due to unequal rates of migration of cations towards the higher oxygen potential side, as revealed by the position of inert makers. A layer of nickel oxide was formed at the higher oxygen potential side and a porous and fissured layer of SiO_2 appeared at the lower oxygen potential boundary. A theoretical analysis of the decomposition process indicates that the maximum ratio of oxygen partial pressures that the olivine-type compounds can withstand without decomposing to component oxides, depends on kinetic (diffusivities) as well as thermodynamic (standard Gibbs' energy of formation of Ni_2SiO_4 from component oxides) parameters. The ratio of average diffusion coefficient of nickel to that of silicon derived from the critical oxygen partial pressure ratio for decomposition was found to increase with average oxygen potential of the sample from 8–67.3.

When steady state is achieved the cations move with the same velocity, causing bulk movement of Ni_2SiO_4 sample toward the higher oxygen potential. An approximate value for the average diffusion coefficient of silicon has been estimated as 9×10^{-12} cm^2 s^{-1} from the displacement of Ni_2SiO_4 relative to platinum markers. Kinetic decomposition is considered to be an important factor in the use of multicomponent ceramics as high-temperature structural and support materials.

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