Determination of Diffusion Coefficient of Cation Vacancies in Nickel Oxide

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Polycrystalline NiO samples were equilibrated with different oxygen partial pressures from 10^{-3} to 1 Atm in the temperature range 750 °C — 1000 °C.

Transient electrical conductivity was measured until a new equilibrium was attained after changing the oxygen partial pressure. By the time dependence of the electrical conductivity in isothermal conditions the diffusion coefficient of nickel vacancies was determined.

Using the pertinent value for the vacancies equilibrium concentration, the self-diffusion coefficient of nickel in nickel oxide was obtained in good agreement with literature data.

At elevated temperatures the reaction between NiO and oxygen is known to promote essentially the formation of cation vacancies and electron holes [1–8]. As diffusional contributions, due to the oxygen ion, are known to be negligible in NiO [9], the time dependence of the electrical conductivity (after varying the oxygen partial pressure in isothermal conditions) could be used to measure the diffusion coefficient of nickel vacancies. In fact, if we consider that the electrical conductivity is proportional to the concentration of cation vacancies and that any modification of the equilibrium conditions between the gas phase and the bulk of the oxide establishes a defect concentration gradient within the solid [10], the time dependence of the electrical conductivity is a measure of the migration rate of the defects in the oxide.

When the use of cylindrical samples with flat platinized ends is possible, we may utilize the diffusion equation proposed by JOST [11]:

$$\frac{\lambda_t-\lambda_\mathrm{f}}{\lambda_\mathrm{i}-\lambda_\mathrm{f}}=\frac{C_t-C_\mathrm{f}}{C_\mathrm{i}-C_\mathrm{f}}=\frac{4}{2{,}405}\exp(-t/\tau) \qquad (1)$$

where

$$\tau=r_0^2/(2{,}405)^2\,D_\mathrm{v}\,.$$

In this expression C_t, C_i, C_f are the vacancies concentration at time t, at time 0 (initial) and at time ∞ (final) respectively, and λ_t, λ_i, λ_f are the corresponding electrical resistance values, t is the time, r_0 the radius of the specimen and D_v the diffusion constant of nickel vacancies.

The right handside of Eq. (1) is the first term of a series, and it is a good approximation for a sufficiently large time [11, 12].

Eq. (1) has been recently employed to obtain the defects diffusion coefficients in Nb_2O_5 [13, 14], while solutions for parallelepipedic forms were used in the case of $SrTiO_3$ [15].

Experimental

The dc. electrical resistance has been measured with a two electrodes system on sintered cylindrical samples with a thickness of about 2 mm and about 12 mm of diameter. The density was about 92% of the theoretical one. The flat faces of the pellets were platinized by sputtering under vacuum. For other experimental details and samples preparation see [1].

Before every change of equilibrium conditions with the gas phase the sample was annealed at 1000 °C in

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purified Argon ($P_{O_2} = 10^{-6}$ Atm) for about one hour, then, maintaining the inert gas atmosphere, the selected temperature was fixed and, at last, the new oxygen partial pressure was established in the cell at zero time.

Results and Discussion

Fig. 1 shows representative transient electrical resistances. The decrease with the oxygen partial pressure is in agreement with the semi-conducting properties of NiO [1–8]. The initial horizontal portion of the curves refers to the sample in equilibrium with the P_{O_2} of the inert gas at the considered temperature. At time zero a step in the P_{O_2} was introduced and the equilibrium time recorded.

Fig. 2 shows as an example, the plot of $\log\{(\lambda_t - \lambda_f)/(\lambda_i - \lambda_f)\}$ vs time for an oxygen partial pressure of 1 Atm.

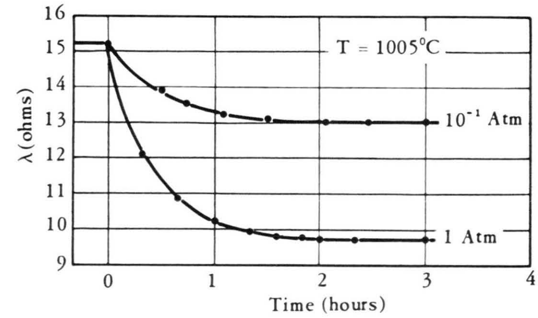

Fig. 1. Plots of the electrical resistance versus time when the sample is equilibrated at 1 atm. and 0.1 atm. of oxygen respectively, at the specified temperature.

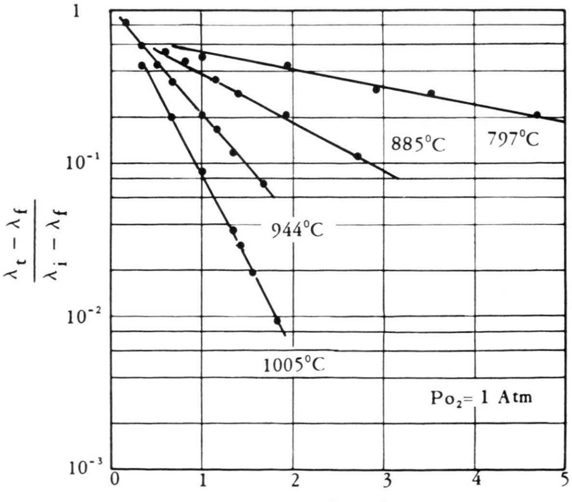

Fig. 2. Plot of $\log\{(\lambda_t - \lambda_f)/(\lambda_i - \lambda_f)\}$ values versus time.

In Table 1 are reported the diffusion coefficient values obtained from the slopes at different temperatures and oxygen partial pressures.

The Arrhenius plot of the experimental D_V values reported in Fig. 3 fits the empirical relationship:

$$D_V = 14 \exp\left(-\frac{31\,000}{R\,T}\right) \text{cm}^2 \cdot \text{sec}^{-1}. \qquad (2)$$

The insensitiveness of D_V on the oxygen partial pressure is apparent.

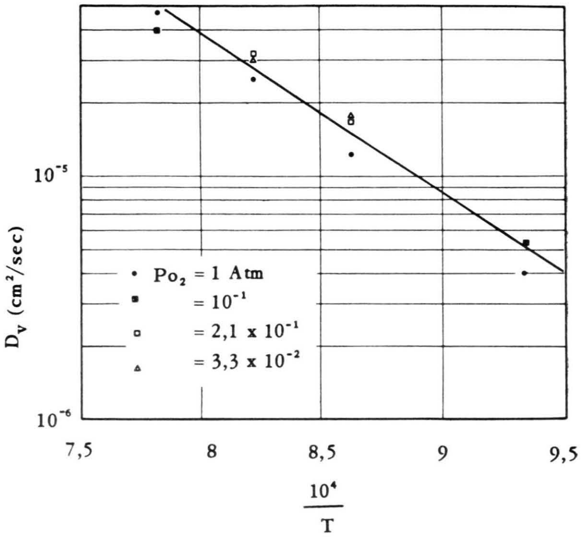

Fig. 3. Arrhenius plot of the experimental D_V values.

Temperature [°C]	P_{O_2} [Atm]	D_V [cm²/sec]
1005	10^{-3}	$1{,}9 \times 10^{-5}$
	10^{-2}	$2{,}5 \times 10^{-5}$
	10^{-1}	$3{,}9 \times 10^{-5}$
	1	$4{,}7 \times 10^{-5}$
944	$3{,}3 \times 10^{-2}$	$3{,}0 \times 10^{-5}$
	$2{,}1 \times 10^{-1}$	$3{,}2 \times 10^{-5}$
	1	$2{,}5 \times 10^{-5}$
885	$3{,}3 \times 10^{-2}$	$1{,}7 \times 10^{-5}$
	$2{,}1 \times 10^{-1}$	$1{,}7 \times 10^{-5}$
	1	$1{,}2 \times 10^{-5}$
797	10^{-1}	$5{,}3 \times 10^{-6}$
	1	$4{,}0 \times 10^{-6}$

Table 1.

To compare this result with other literature data, we observe at first that for a crystal with cubic symmetry and lattice parameter a_0 the diffusion coefficient of vacancies, D_V may be expressed as [10, 16, 17]

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$$D_v = \alpha\, a_0^2\, \varkappa\, \nu \exp(-\Delta G\, m/R\,T)$$
$$= \alpha\, a_0^2\, \varkappa\, \nu \exp \frac{\Delta S\, m}{R} \exp\left(-\frac{\Delta H\, m}{R\,T}\right) \qquad (3)$$

where α is a geometric constant, $\varkappa$ represents the probability that an atom, which sufficient energy to make a jump, actually will complete the jump, ν is a frequency factor, $\Delta G\, m$, $\Delta S\, m$, $\Delta H\, m$ represent the free energy, the entropy and the enthalpy change of the thermally activated process. Eq. (3) shows that the temperature dependence of D_v is determined by the migration enthalpy only.

The value of 31 000 cal/mol, given in Eq. (2) is in good agreement with the value of 28 500 cal/mol, suggested by KOFSTAD[10] and of 27 600 cal/mol given by CHOI and MOORE[18]. The agreement is good also with the $\Delta H\, m$ values for CoO and FeO, of 30 000 cal/mol in both cases[10], which supports the well recognized analogy of the diffusion mechanism in these oxides.

The present results could moreover also be compared with the tracer self-diffusion coefficient of Ni in NiO, measured by different authors with radiotracer technique. The tracer self-diffusion coefficient of nickel D^*_{Ni} is related in fact to the diffusion coefficient of vacancies by the expression[10, 19–21]

$$D^*_{\mathrm{Ni}} = f\, D_v\, N_v \qquad (4)$$

where f is the correlation factor which is 0.78 for a vacancy mechanism[21] and N_v the molar fraction of vacancies etxpressed by the equation:

$$N_v = K_0'\, P_{O_2}^{1/n} \exp\left(-\frac{\Delta H_f}{n\,R\,T/2}\right) \qquad (5)$$

in which the term K_0' contains the entropy factor $\Delta S_f/R$.

A valuable equation for the equilibrium vacancy concentration N_v is given by MITOFF[4]:

$$N_v = 0.11\, P_{O_2}^{1/6} \exp(-17\,800/R\,T) \qquad (6)$$

where P_{O_2} is in atmospheres and the vacancy concentration is expressed as vacancies per ion pair.

By means of Eqs. (6) and (2), we obtain the experimental expression of Eq. (4), in air:

$$D^*_{\mathrm{Ni}} = 6.5 \times 10^{-2} \exp(-48\,800/R\,T). \qquad (7)$$

In Table 2 the present result is compared with selected literature values[22].

Conclusions

The cation vacancy diffusion coefficient has been determined to be

$$D_v = 14 \exp\left(-\frac{31\,000}{R\,T}\right) \mathrm{cm^2/sec}\,.$$

Using pertinent data for the vacancy equilibrium concentration, the self-diffusion coefficient of Nickel was calculated, in reasonable accordance with literature values, as given by the equation:

$$D^*_{\mathrm{Ni}} = 6.5 \times 10^{-2} \exp\left(-\frac{48\,800}{R\,T}\right) \mathrm{cm^2/sec}\,.$$

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Ref.	D_0 [cm²/sec]	Q [kcal/mole]	Temperature range [°C]	Method (S) single crystal (P) polycrystalline
23	4,1 × 10^{-2}	55	900–1000	(P) Ni^{63} radiotracer
24	5 × 10^{-4}	44,2 ± 3	1000–1400	(P) Ni^{63} radiotracer
	3,9 × 10^{-4}	44,2 ± 3	1000–1400	(S)
25	1,7 × 10^{-2}	56 ± 1,3	700–1400	(S) Ni^{63} radiotracer
18	1,83 × 10^{-3}	45,6	1000–1400	(S) Ni^{63} radiotracer
26	4,8 × 10^{-4}	48,4 ± 2	1190–1400	(S) Ni^{63} radiotracer during oxidation
27	1,1 × 10^{-3}	50,3	900–1400	parabolic oxidation const.
this work	6,5 × 10^{-2}	48,8	750–1000	(P) transient electrical conductivity

Table 2.

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