Cation Transport Phenomena in NiO*

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The cation tracer diffusion coefficient D and the electric conductivity σ in NiO were measured as a function of temperature and oxygen partial pressure P_{O_2} . Polycrystalline NiO sample was prepared by oxidation of zone refined nickel platelets in an oxygen stream. For conductivity measurement single crystal was also used. It was found that σ was proportional to $P_{O_2}^{1/4 \sim 1/5}$, regardless of the method of sample preparation. This suggests strongly the superiority in concentration of the singly ionized vacancy V' . On the other hand, D depended very slightly on P_{O_2} , much less than the $1/4$ power. This discrepancy of the P_{O_2} dependence of σ and D can be successfully explained by the following assumption: The cation diffusion takes place in a dual manner, through singly ionized vacancies V' and through doubly ionized vacancies V'' . The contribution of V' to the diffusion is predominant in the higher P_{O_2} region because of its high concentration, whereas that of V'' is more important in the lower P_{O_2} region because of its large mobility.

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I. Introduction

The studies of cation diffusion^{(1)~(8)} and electric conductivity^{(9)~(14)} in NiO have been made by a considerable number of investigators. Their conclusions about the correlation between the defect nature and transport properties are not always in agreement. According to Mitoff⁽⁹⁾, Pizzini et al.⁽¹⁰⁾ and Meier et al.⁽¹¹⁾, the electric conductivity of NiO varied in proportion to the $1/6$ power of oxygen partial pressure, $P_{O_2}^{1/6}$. Their observation leads to the model that cation defects dissociate completely from electron holes. On the other hand, Bransky et al.⁽¹²⁾, Eror et al.⁽¹³⁾, Uno⁽¹⁴⁾ and Koel et al.⁽¹⁵⁾ concluded, from their observation that the conductivity depended on $P_{O_2}^{1/4}$, that a cation vacancy is associated with an electron hole to form a complex. Fueki et al.⁽⁵⁾ measured the oxidation rate of Ni and calculated the cation diffusion coefficient D in NiO as a function of P_{O_2} and temperature, using oxidation parabolic constants observed. Their calculation showed the $P_{O_2}^{1/6}$ dependence of D in the lower temperature region and $P_{O_2}^{1/4}$ dependence in the higher temperature region. By contrast, in the lower P_{O_2} region D was found to be nearly independent of P_{O_2} at any temperatures investigated. They suggested from their results that the cation defect would be doubly ionized in the lower temperature region and singly ionized in the higher temperature region, and that NiO was almost stoichiometric in the lower P_{O_2} region. Baur et al.⁽¹⁶⁾ also found in their measurements of the oxidation rate

of Ni at different oxygen partial pressures and high temperatures, that the parabolic constant k_p was nearly proportional to $P_{O_2}^{1/5}$.

The work by Volpe et al.⁽⁷⁾⁽⁸⁾ on the P_{O_2} dependence of both cation diffusion coefficient and electric conductivity in NiO showed that these two quantities were proportional to $P_{O_2}^\beta$, where β lay between $1/4$ and $1/6$ for the diffusion coefficient and was nearly equal to $1/5$ for the electric conductivity. They concluded that the two kinds of vacancies, singly ionized and doubly ionized, contributed to the cation diffusion in NiO.

In the present experiment the P_{O_2} dependence of the diffusion coefficient and the electric conductivity in NiO was measured, and thereafter an attempt was made to give consistent interpretation of the transport behavior in NiO.

II. Experimental

NiO specimens were prepared by oxidation of platelets of zone-refined Ni in oxygen stream at 1370°C . These polycrystalline specimens, about 0.5 cm^2 in area and about 1 mm thick, consisting of dense outer layers and a less dense inner layer, were used for measurements of diffusion and conductivity. Electric conductivity measurements were made on a single crystal also.

The diffusion coefficient was measured by a radio-tracer technique. Each NiO specimen was pre-annealed at the same temperature and pressure as in the following diffusion run, in order to establish the equilibrium defect concentration. After pre-annealing, non-active nickel was evaporated onto the surface of specimen in vacuum, followed by electroplating of radioactive nickel ^{63}Ni from NiCl_2 solution. After the oxidation of this nickel deposit at $500\sim 600^\circ\text{C}$ in the air, the diffusion anneal was carried out in the temperature range of 850 to 1170°C in a stream of the atmosphere of oxygen, air or nitrogen. The oxygen partial pressure in this nitrogen ($3 \times 10^{-3}\text{ atm}$) was determined with an oxymeter⁽¹⁷⁾, which is based on the measurement of a change in the electric resistance of CoO wire as a function of oxygen partial pressure.

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Radioisotope penetration was measured by a sectioning method. When a specimen of d in thickness and w in weight is ground, the removed thickness Δd is expressed as $\Delta d = \Delta w(d/w)$, where Δw denotes the weight change by sectioning. The sectioning was restricted within the dense outer layer. Residual activity was counted on every section in a windowless gas-flow counter. Prior to the counting, the sides of the specimens were ground away slightly to reduce the effects due to the surface diffusion. The sample holders with a hole fitting to dimensions of the specimen assured the same geometry in the counter for each counting procedure. The diffusion coefficient was calculated from the penetration profile by Gruzin's method⁽¹⁸⁾.

The electric conductivity measurements were carried out in the apparatus designed by Desmarescaux et al.⁽¹⁹⁾ or in a modified one. In them a NiO platelet was pressed between two Pt electrodes by means of a spring and a wheatstone bridge method was employed. Pt was in advance evaporated onto the ends of NiO specimen to give a close electric contact between the specimen and these Pt electrodes. The conditions of temperature and atmosphere were similar to those of the diffusion experiment.

III. Results

Some typical penetration plots of ^{63}Ni into NiO are represented in Fig. 1. The slope of these plots and the time of diffusion anneal give the diffusion coefficient D through Gruzin's method⁽¹⁸⁾. Choi et al.⁽³⁾ corrected their penetration plots using the absorption coefficient μ for β ray of ^{63}Ni ($1.18 \times 10^4 \text{ cm}^{-1}$). Our penetration plots were also corrected by using both the same absorption coefficient as in Ref. (3) and that obtained from Ref. (1) ($2.18 \times 10^4 \text{ cm}^{-1}$), in the case of the diffusion in air at 1050°C . This correction, however, makes practically no change in D value.

Fig. 1 Typical penetration plots (residual activity vs square of the penetration depth x^2).

- (1) In $\text{N}_2(P_{\text{O}_2}=3 \times 10^{-3} \text{ atm})$ at 1000°C for 142.3 hr.
- (2) In air at 1050°C for 72 hr.
- (3) In O_2 at 1000°C for 126 hr.
- (4) In air at 1000°C for 100.7 hr.
- (5) In air at 900°C for 167 hr.

Thus other D values were calculated without the correction.

Figure 2 shows Arrhenius plots of the self-diffusion coefficient D . The temperature dependence of the diffusion coefficient is expressed as follows:

$$D = 1.85 \times 10^{-3} \exp(-48.1 \times 10^3/RT) \text{ cm}^2/\text{sec in } \text{O}_2,$$

$$D = 1.01 \times 10^{-3} \exp(-47.2 \times 10^3/RT) \text{ cm}^2/\text{sec in air},$$

$$D = 2.91 \times 10^{-4} \exp(-44.8 \times 10^3/RT) \text{ cm}^2/\text{sec in } \text{N}_2$$

$$(P_{\text{O}_2} = 3 \times 10^{-3} \text{ atm}).$$

D depends only slightly on oxygen partial pressure. If D were proportional to $P_{\text{O}_2}^{1/4}$, its values obtained in $\text{N}_2(P_{\text{O}_2} = 3 \times 10^{-3} \text{ atm})$ should fall on the dotted line,

Fig. 2 Self-diffusion coefficient of Ni in NiO. The broken or dotted line should result for N_2 if $D \propto P_{\text{O}_2}^{1/6}$ or $P_{\text{O}_2}^{1/4}$, respectively, the line for O_2 being taken as a reference.

Fig. 3 Arrhenius plots for electric conductivity of NiO.

- (1) Single crystal in air.
- (2) Polycrystal in O_2 .
- (3) Polycrystal in air.
- (4) Polycrystal in N_2 ($P_{\text{O}_2} = 2 \times 10^{-2} \text{ atm}$).

Fig. 4 Electric conductivity of NiO as a function of P_{O_2} . The slopes are between $1/4$ and $1/5$.

the line for pure O_2 being taken as a reference, and if proportional to $P_{O_2}^{1/6}$, on the broken line.

Results on electric conductivity σ are summarized in Figs. 3 and 4. The Arrhenius plots give the following equations for polycrystalline specimens (Fig. 3).

$$\begin{aligned}\sigma &= 2.93 \times 10^2 \exp(-19.9 \times 10^3/RT) \text{ ohm}^{-1} \text{ cm}^{-1} \\ &\text{in } O_2 \\ \sigma &= 3.02 \times 10^2 \exp(-20.8 \times 10^3/RT) \text{ ohm}^{-1} \text{ cm}^{-1} \\ &\text{in air} \\ \sigma &= 1.51 \times 10^2 \exp(-20.3 \times 10^3/RT) \text{ ohm}^{-1} \text{ cm}^{-1} \\ &\text{in } N_2(P_{O_2} = 2 \times 10^{-2} \text{ atm})\end{aligned}$$

As seen in Fig. 4, σ of single crystal NiO as well as the polycrystal has proved to be proportional to $P_{O_2}^{1/5} \sim P_{O_2}^{1/4}$.

IV. Discussion

It is well known that the cation vacancies play a prominent role in the transport phenomena in NiO. The creation of one cation vacancy (V) must be accompanied by the formation of two electron holes ($h\cdot$) in order to maintain electroneutrality. The vacancies are classified into three types according to their degree of association with electron holes. If the cation vacancies are doubly ionized, i.e. not associated with electron hole, the concentration of vacancy and hole should be proportional to $P_{O_2}^{1/6}$ as shown below.

For the reaction

the equilibrium constant K'' is expressed by an equation

$$K'' = [V'']p^2/P_{O_2}^{1/2},$$

where $h\cdot$ and p denote the positive hole and its concentration, respectively. Substitution of a relation $2[V''] = p$ into the above equation leads to the following

equations:

$$[V''] = (K''/4)^{1/3} P_{O_2}^{1/6}, \quad p = (2K'')^{1/3} P_{O_2}^{1/6}.$$

The vacancy model requires that the cation diffusion coefficient D and the electric conductivity σ should be proportional to $[V'']$ and p , respectively. Therefore, both D and σ also should be proportional to $P_{O_2}^{1/6}$.

If the vacancies are singly ionized, i.e. associated with one electron hole, the $P_{O_2}^{1/4}$ dependence of D and σ should result. In this case the equilibrium is expressed as

and the following equations are obtained:

$$[V'] = K'^{1/2} P_{O_2}^{1/4}, \quad p = K'^{1/2} P_{O_2}^{1/4}.$$

Thus D and σ should be proportional to $P_{O_2}^{1/4}$.

Another type of vacancies is a neutral one, i.e. the vacancy associated with two electron holes. This results in the $P_{O_2}^{1/2}$ dependence.

Hence D should be proportional to $P_{O_2}^{1/2}$. As there is no free electron hole in NiO crystal in this case, the conductivity should be only ionic. The conductivity would therefore be negligibly small compared to that in the former cases and would have the same P_{O_2} dependence as D has.

The present result on conductivity in Fig. 4 ($P_{O_2}^{1/4} \sim P_{O_2}^{1/5}$ dependence) suggests that the singly ionized vacancy V' may be of a dominant type. Consequently the $P_{O_2}^{1/4} \sim P_{O_2}^{1/5}$ dependence of D also would be expected by the simple vacancy model mentioned above. In practice, however, a slight P_{O_2} dependence of D which was observed in our experiments (Fig. 2) rejects this model.

Volpe et al.⁽⁷⁾ found that the P_{O_2} dependence of D is not always equal to that of σ and proposed some possible mechanisms to explain their results. But they restrained themselves from drawing a definite conclusion on the transport mechanism.

Our results, similar to those of Volpe et al., can be successfully explained by means of the following defect model: the coexistence of the singly ionized vacancy higher in concentration but lower in mobility, and of the doubly ionized vacancy lower in concentration but higher in mobility. As will be shown later in Fig. 5, $[V'']$ depends very slightly on P_{O_2} under the condition that V' is the predominant defect species. Consequently, the slight P_{O_2} dependence of D observed in the present study may be reasonably accounted for, by assuming that V'' has a considerable contribution to the cation diffusion. This contribution can be realized by virtue of the high mobility of V'' which will be justified by being completely free from electron holes. In contrast with it, V' , being accompanied by an electron hole, will be less mobile than V'' , and consequently V' will contribute to the diffusion to a limited extent in spite of its high concentration.

If the neutral vacancy predominates in NiO, both D and σ should depend on $P_{O_2}^{1/2}$. The observed P_{O_2}

dependence of D and σ , however, was quite different from the $1/2$ power. In addition, V , associated with 2 electron holes, will be the least mobile. Consequently, the contribution of V to transport phenomena is probably negligible. Some quantitative consideration will be given to this problem.

The following equilibria will be established in NiO.

From eqs. (1), (2) and (3), and the electroneutrality condition $[V'] + 2[V''] = p$, the following equations are obtained:

$$p^3 - K_1 \cdot K_2 \cdot P_{\text{O}_2}^{1/2} \cdot p - 2K_1 \cdot K_2 \cdot K_3 \cdot P_{\text{O}_2}^{1/2} = 0, \quad (4)$$

$$[V']^3 + \frac{K_1 \cdot K_2}{2K_3} \cdot P_{\text{O}_2}^{1/2} \cdot [V']^2 - \frac{(K_1 \cdot K_2)^2}{2K_3} P_{\text{O}_2} = 0, \quad (5)$$

$$[V'']^3 - \frac{K_1 \cdot K_2}{4K_3} \cdot P_{\text{O}_2}^{1/2} \cdot [V'']^2 + \frac{K_1 \cdot K_2}{2} \cdot P_{\text{O}_2}^{1/2} \cdot [V''] - \frac{K_1 \cdot K_2 \cdot K_3}{4} \cdot P_{\text{O}_2}^{1/2} = 0. \quad (6)$$

We will now try to estimate the p , $[V']$ and $[V'']$ values. The conductivity results suggest strongly that the singly ionized vacancy is dominant, i.e. $[V'] \gg [V'']$. In other words, K_2 must be much greater than K_3 . So K_2 was assumed to be 10^4 times greater than K_3 , and then K_1 , K_2 and K_3 were adjusted in such a way that the total vacancy concentration agrees with that determined by Mitoff⁽⁹⁾ from weight change. In this way we found reasonable values 5×10^{-7} , 5×10^{-3} , 5×10^{-7} for K_1 , K_2 and K_3 , respectively. By using these values, eqs. (4), (5) and (6) were solved for p , $[V']$ and $[V'']$ as a function of P_{O_2} . The result is shown in Fig. 5. The slope of p is found to be between $1/4$ and $1/5$, which is similar to the observed slope of σ (Fig. 4). On the other hand, $[V'']$, the concentration of the most mobile vacancy, depends on P_{O_2} very

weakly, which may correspond to a slight P_{O_2} dependence of the diffusion coefficient. This suggests that our model mentioned above is reasonable although K_1 , K_2 and K_3 values are somewhat arbitrary.

We consider now a mobility difference between V' and V'' . When two types of vacancies contribute to the diffusion simultaneously, Fick's second law is expressed as follows,

$$\frac{\partial c}{\partial t} = (D' + D'') \frac{\partial^2 c}{\partial x^2} \quad (7)$$

where c denotes an isotope concentration. Its solution in the case of tracer experiments as ours,

$$c = \frac{Q}{\sqrt{\pi(D' + D'') \cdot t}} \exp \left(-\frac{x^2}{4(D' + D'')t} \right).$$

Then, observed diffusion coefficient D is a sum of D' and D'' , the diffusion coefficient through V' and that through V'' , respectively. Q is an amount of radioisotope deposited on a specimen surface. Other notations are in general use.

A diffusion coefficient in the case of vacancy mechanism is expressed as the product of a vacancy concentration and a mobility D_m ,

$$D' = [V'] \cdot D'_m, \quad D'' = [V''] \cdot D''_m \quad (8)$$

It is assumed that V'' is more mobile than V' , that is, D''_m is greater than D'_m and that the mobilities are independent of P_{O_2} . On the other hand, $[V']$ is larger than $[V'']$ and increases with P_{O_2} whereas $[V'']$ increases very slightly with P_{O_2} as shown in Fig. 5. Consequently, it is expected that D' is greater than D'' in the higher P_{O_2} region and that D' is smaller than D'' in the lower P_{O_2} region. Baur et al.⁽¹⁶⁾ studied high temperature oxidation of Ni as a function of P_{O_2} . Though they concluded that the parabolic constant k_p was dependent on $P_{\text{O}_2}^{1/5}$, the slopes of $\log k_p$ vs $\log P_{\text{O}_2}$ plots appear to change in the range of $1 \sim 10^{-1}$ atm. The P_{O_2} dependence of k_p is somewhat greater in the higher P_{O_2} region than in the lower. This seems to show that the diffusion through V' is predominant in the higher P_{O_2} region and that the diffusion through V'' is so in the lower P_{O_2} region. One might, therefore, consider that D' is comparable to D'' in the range of $1 \sim 10^{-1}$ atm. We assumed that D' is equal to D'' at an oxygen partial pressure of 10^{-1} atm. The $[V']$ and $[V'']$ values at $P_{\text{O}_2} = 10^{-1}$ atm are obtained from Fig. 5. Substituting these values into eq. (8) and equating D' to D'' , one obtains a relation,

$$D''_m = 55D'_m, \quad (9)$$

that is, V'' is about 50 times greater in mobility than V' . Since D is a sum of D' and D'' , it is expressed by using eqs. (8) and (9) as follows;

$$D = D'_m([V'] + 55[V'']) \quad (10)$$

The $[V']$ and $[V'']$ values are obtained from Fig. 5 as a function of P_{O_2} and accordingly one can estimate the P_{O_2} dependence of D from these values and eq. (10), leaving aside the mobility term D_m . The curve of $\log D$ vs $\log P_{\text{O}_2}$ is compared with the experimental $\log D$ values in Fig. 6, where the values of D at 1000°C

Fig. 5 Concentrations of vacancies and positive hole as a function of P_{O_2} . Calculated on the assumption that the singly ionized vacancy is dominant in NiO, considering the total vacancy concentration determined by Mitoff⁽⁹⁾.

Fig. 6 Diffusion coefficient at 1000°C as a function of P_{O_2} . Comparison between results observed (○) and calculated (—).

obtained from the lines in Fig. 1 is represented as an example. D'_m was assumed to be 1.5×10^{-7} cm²/sec. The agreement is very satisfactory.

This D'_m value is arbitrary but will be shown to be reasonable. The tracer self-diffusion coefficient D is related to the vacancy diffusion coefficient D_v by the equation

$$D = f \cdot D_v \cdot [V] \quad (11)$$

where f is the correlation factor which is 0.78 for the *fcc* crystals. Thus one sees that D_m in eq. (8) is equal to $f \cdot D_v$ in eq. (11) and accordingly D_m can be estimated if D_v is known. Morlotti⁽⁶⁾ obtained the vacancy diffusion coefficient in a unique fashion. Sintered NiO pellet was equilibrated with an oxygen partial pressure. After changing P_{O_2} , transient electric resistance was measured until a new equilibrium was attained. The time dependence of resistance may give the vacancy diffusion coefficient with the aid of Jost's equation⁽²⁰⁾

$$\frac{R_i}{R_t} \cdot \frac{R_t - R_f}{R_i - R_f} = \frac{C_t - C_f}{C_i - C_f} = \frac{4}{2.405} \exp(-t/\tau) \quad (12)^\dagger$$

where $\tau = r^2 / (2.405)^2 D_v$.

Here C is the vacancy concentration and R is the electric resistance. The subscripts t , i and f designate $t = t$, 0 and ∞ respectively, and r the sample radius. He obtained in this way vacancy diffusion coefficient $1.9 \sim 4.7 \times 10^{-5}$ cm²/sec at 1005°C. This value is two orders of magnitude greater than the value assumed above, 1.5×10^{-7} cm²/sec. This discrepancy may be due to open pores which remained probably in his sintered pellets with a density of about 92% of the theoretical. The time required for his pellet to attain a new equilibrium was only two hours, whereas our single crystal sample smaller in size than his pellet required two days. This suggests that his pellet contained unnegligibly open pores and that its effective radius r was smaller than the apparent one (6 mm).

Thus we calculated the vacancy diffusion coefficient

[†] Morlotti⁽⁶⁾ utilized the equation

$$\frac{R_t - R_f}{R_i - R_f} = \frac{C_t - C_f}{C_i - C_f} = \frac{4}{2.405} \exp(-t/\tau).$$

But the diffusion equation is expressed more correctly as eq. (12), for σ is proportional to C .

$$\frac{C_t - C_f}{C_i - C_f} = \frac{\sigma_t - \sigma_f}{\sigma_i - \sigma_f} = \frac{1/R_t - 1/R_f}{1/R_i - 1/R_f} = \frac{R_i}{R_t} \cdot \frac{R_t - R_f}{R_i - R_t}$$

Fig. 7 Time dependence of electric resistance when P_{O_2} was changed from 2×10^{-1} to 2×10^{-2} atm at 1000°C.

using our conductivity data on the single crystal. In Fig. 7 $\log [(R_i/R_t)(R_f - R_i)/(R_i - R_t)]$ vs t plots are represented. The slope gives $D_v = 2.9 \sim 1.1 \times 10^{-7}$ cm²/sec and so $D_m = 2.26 \sim 0.86 \times 10^{-7}$ cm²/sec, which is in good agreement with the assumed D'_m value 1.5×10^{-7} cm²/sec. The sample had the shape of a parallelepiped instead of a cylinder, whose section had dimensions 0.262×0.323 cm². As eq. (12) is the solution for a cylinder, our D_v values are only approximate. They will be, nevertheless, in correct order of magnitude because of the high density of the single crystal sample. The P_{O_2} variation will produce a much greater concentration gradient for V' than for V'' in the NiO as expected from Fig. 5 and therefore the flux of V' is most probably to be greater than that of V'' . Thus one may consider that D_v obtained from the transient resistance measurement corresponds to D'_m .

The transient electric resistance has been recently measured by using a single crystal NiO cylinder. It was confirmed that D_v is of the order of 1×10^{-7} cm²/sec at 1000°C. The details of this work will be published elsewhere.

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