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The self diffusion of Ni in undoped and Al-doped NiO single crystals

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Résumé. — Nous avons constaté le coefficient d'autodiffusion de ^{63}Ni dans des monocristaux purs de NiO et aussi dans des monocristaux contenant 0,17 % pds Al. Les mesures ont été effectuées sous une pression d'oxygène de 1 atm et dans le domaine de température de 755-1 700 °C. En plus, nous avons fait des mesures en fonction de la pression partielle d'oxygène dans le domaine 10^{-4} -1 atm à 1 460 °C.

Aux températures inférieures à 1 200 °C la majorité de l'Al se précipite en forme de NiAl_2O_4 et il en résulte que la concentration d'Al se représente par la solubilité d'Al dans NiO. On ne peut pas comprendre les résultats tirés des mesures aux températures supérieures à 1 200 °C à partir de l'un ou l'autre des deux modèles proposés, soit que toutes les lacunes cationiques n'apportent qu'une seule charge, soit que quelques-unes d'entre elles apportent une charge, les autres deux charges. Il semble nécessaire, afin d'expliquer les résultats à proposer qu'il y existe des agglomérats Al-lacune cationique, qui affectent une mobilité inférieure à la mobilité des lacunes libres. En se servant de paramètres vraisemblables pour décrire la solubilité d'Al dans NiO, on peut rendre compte, pour toutes les températures, des données sur les cristaux contenant Al, en admettant que chaque lacune apporte une seule charge et s'associe avec un atome d'Al, grâce à une énergie de liaison de 1,2 eV.

Abstract. — The ^{63}Ni tracer diffusion coefficient for diffusion in undoped NiO single crystals and crystals doped with 0.17 % Al has been measured, at an oxygen pressure of 1 atm., in the temperature range 755-1 700 °C. It has also been measured at 1 460 °C as a function of oxygen pressure in the range 10^{-4} -1 atm.

At temperatures below 1 200 °C some of the Al dopant was precipitated as NiAl_2O_4 and the degree of doping was determined by the saturation solubility of Al in NiO. At temperatures above 1 200 °C defect models assuming either only singly charged Ni vacancies, or both singly and doubly charged vacancies, were incapable of a satisfactory interpretation of the data. It is suggested that this is due to the formation of Ni vacancy-Al complexes having lower mobility than the unassociated Ni vacancies. A model in which singly charged vacancies form associates with Al dopant with a binding energy of 1.2 eV is shown to fit the diffusion data in Al-doped NiO over the whole temperature range, using reasonable parameters to describe the solubility of Al in NiO.

1. Introduction. — The defect structure and transport properties of NiO have been studied extensively in the past, but there is much disagreement between early investigations of the defect-dependent properties of NiO [1] because of the influence of impurities on the defect structure of the samples used. As higher purity single crystals of NiO have become available some of the earlier discrepancies are being resolved and there is general agreement that the majority of lattice defects are Ni vacancies compensated by electronic holes which give p-type electrical conductivity.

Although the electrical properties of NiO doped with Li have been widely studied there have been no direct measurements of the effects of deliberate aliovalent doping on either the deviation from stoichiometry or the self-diffusion of Ni. The purpose of the work reported here was to test the applicability of a simple defect model to the diffusion of Ni in doped NiO. Al was chosen as a trivalent dopant, because it will replace Ni substitutionally in NiO, and Li as a monovalent dopant because of the data already available on electrical conductivity.

2. Experimental. — The diffusion specimens were supplied by Cristal Tec Ltd. (Grenoble, France) in the form of discs 10 mm in diameter and 3 mm in thickness, cut from single crystal boules grown by the Verneuil method. Three types of crystal were employed, differing in their nominal doping levels. The first were nominally pure (series P), the second doped with 0.1 mole % Al_2O_3 (series A) and the third doped with 0.1 mole % Li_2O (series L). Chemical analysis of samples of the three types showed that series L specimens had not been doped significantly with Li; this was presumably because of the high volatility of Li_2O at the growth temperature of the crystals. The series A specimens were found to contain 0.17 % Al.

A detailed description of the preparation of crystal surfaces, preannealing, application of ^{63}Ni tracer, diffusion anneal and sectioning by grinding has been given elsewhere [2]. Oxygen pressures below 1 atm. were established using Ar/O_2 mixtures and were measured using an electrochemical oxygen cell having a CaO-stabilised ZrO_2 electrolyte at 800 °C and air as a reference. Diffusion anneal times ranged from ~ 1 h at 1 700 °C to 9 days at 755 °C and sectioning depths from 370 μm at 1 700 °C to 7 μm at 755 °C.

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3. **Results.** — The Ni-diffusion coefficients determined in this way are shown on an Arrhenius plot in figure 1. The data for the series P specimens are described by [2]

$$D_{\text{Ni}}^*(P_{\text{O}_2} = 1 \text{ atm.}) = 1.5 \times 10^{-2} \times \exp(-2.51 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1}. \quad (1)$$

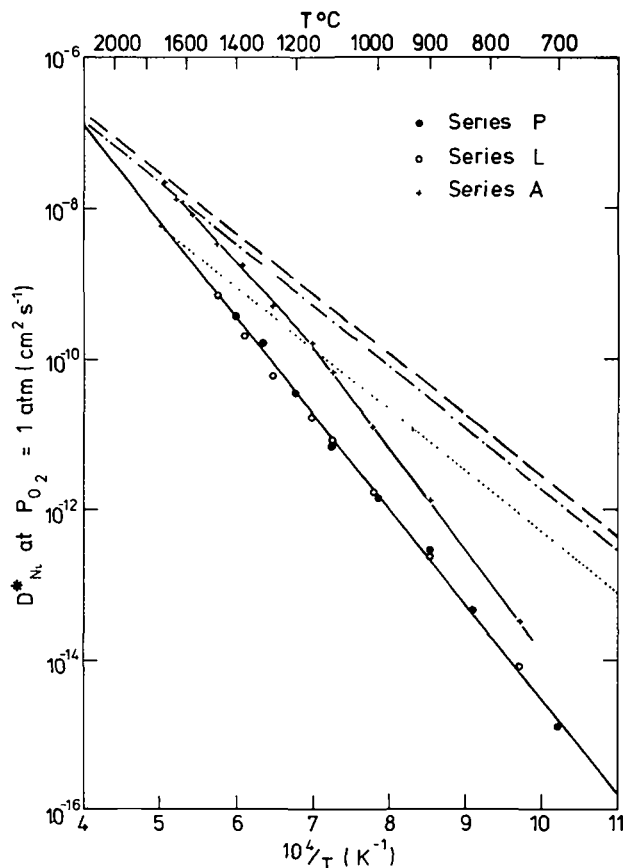


Fig. 1 — Arrhenius plot of the diffusion data at $P_{\text{O}_2} = 1$ atm. showing the predicted behaviour in Al-doped samples according to an « isolated » vacancy defect model : ———, using equation (5); —.—.—, using equation (6), using equation (7).

The data for the series L specimens are also in agreement with equation (1) as expected from the chemical analysis. The Arrhenius plot of the diffusion coefficients in the Series A crystals shows two straight line regions with a break at $\sim 1200^\circ\text{C}$.

The dependence of D_{Ni}^* on P_{O_2} at 1460°C in the three series of samples is shown in figure 2. In the series A samples D_{Ni}^* is nearly independent of P_{O_2} indicating that at this temperature the defect structure is mainly controlled by the Al doping and not by reaction with the ambient atmosphere whereas in the series P samples D_{Ni}^* is proportional to $P_{\text{O}_2}^{1/8}$ and in the series L to $P_{\text{O}_2}^{1/5.4}$.

4. **Discussion.** — 4.1 PREDICTED BEHAVIOUR USING A SIMPLE DEFECT MODEL. — An attempt will first be

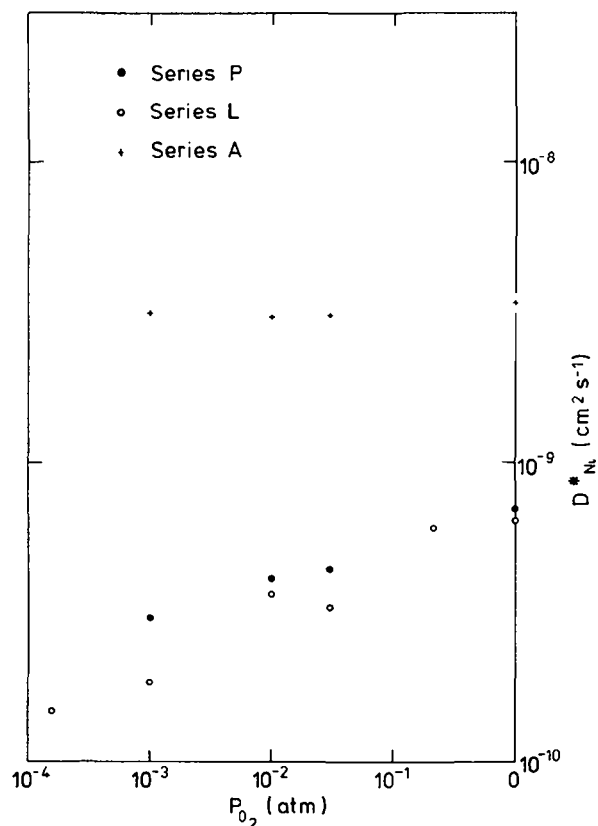


Fig. 2. — Dependence of D_{Ni}^* on oxygen pressure at 1460°C .

made to interpret the results using a simple model for the defect structure of NiO in which only one type of vacancy will be assumed to exist under all experimental conditions. Most recent studies of the dependence of electrical conductivity of undoped NiO on P_{O_2} in the temperature range 1000 – 1400°C come to the common conclusion that singly charged vacancies are predominant at $P_{\text{O}_2} \sim 1$ atm. For the purpose of the simple model it will therefore be assumed that all vacancies are singly charged. The tracer diffusion coefficient can then be written

$$D_{\text{Ni}}^* = f D_{\text{V}} [V_{\text{Ni}}] \quad (2)$$

where f is the correlation factor (equal to 0.78) and D_{V} is the diffusion coefficient of the singly charged vacancy.

In the extrinsic region of the Al-doped crystals the electroneutrality condition can be approximated by

$$[V_{\text{Ni}}] = [\text{Al}_{\text{Ni}}] = 4.7 \times 10^{-3} \text{ per ion pair}. \quad (3)$$

Therefore if D_{V} is known D_{Ni}^* can be estimated from equation (2). There are two ways in which D_{V} can be determined from experimental data on undoped NiO.

The first is using measurements of the chemical diffusion coefficient, D_{chem} , in which case [1]

$$D_{\text{chem}} = 2 D_{\text{V}}. \quad (4)$$

From the published data available, the best estimate of $D_{V'}$ was considered to be

$$D_{V'} = 8.5 \times 10^{-2} \exp(-1.68 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1} \quad (5)$$

When this is combined with equations (2) and (3), D_{Ni}^* in the Al doped samples is predicted by the broken line in figure 1. The alternative way of estimating $D_{V'}$ is by combining the results of tracer diffusion and deviation from stoichiometry measurements in undoped NiO. There have been several determinations of the total vacancy concentration $[V_T]$ in NiO. The data divide into two sets in which those based on thermogravimetry are lower by a factor of 4 than those from other methods. The thermogravimetric data when combined with equations (1) and (2) give

$$D_{V'} = 6.9 \times 10^{-2} \exp(-1.60 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1} \quad (6)$$

in good agreement with equation (5). On the other hand the density and coulometric measurements give

$$D_{V'} = 1.83 \times 10^{-2} \exp(-1.60 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1} \quad (7)$$

The values of D_{Ni}^* in Al-doped samples predicted from equations (6) and (7) are also shown in figure 1.

The simple model also predicts that D_{Ni}^* should be proportional to $P_{\text{O}_2}^{1/4}$ in undoped samples and independent of P_{O_2} below $\sim 1600^\circ\text{C}$ in Al-doped samples.

The details of the disagreement between the predicted and actual behaviour of D_{Ni}^* depend upon which expression for $D_{V'}$ is considered to be the most reliable. However, all the predictions are at variance with actual behaviour in the following respects :

- (i) The measured dependence of D_{Ni}^* on P_{O_2} in undoped samples is weaker than predicted.
- (ii) The measured activation energy of D_{Ni}^* in Al-doped samples is greater than predicted in both the high and low temperature regions.

The reasons for the latter disagreement are discussed in the following sections.

4.2 Al-DOPED SAMPLES BELOW 1200°C . — In the low temperature region one possible reason for the measured D_{Ni}^* falling below that predicted is that most of the Al-dopant was not in solid solution, but was precipitated as a second phase. The NiO- Al_2O_3 phase diagram suggests that the spinel NiAl_2O_4 may be precipitating at low temperatures; even at the low concentration of dopant in these experiments.

To test this possibility, thin foils suitable for transmission electron microscopy were prepared from a series A crystal which had been annealed in 1 atm. of oxygen at 800°C for $5 \times 10^5 \text{ s}$ (i.e. similar to the pre-diffusion anneal at this temperature). Electron diffraction patterns showed extra reflections which could be indexed as coming from NiAl_2O_4 which

is coherent with the NiO matrix. Dark-field imaging (Fig. 3) using these extra reflections revealed the

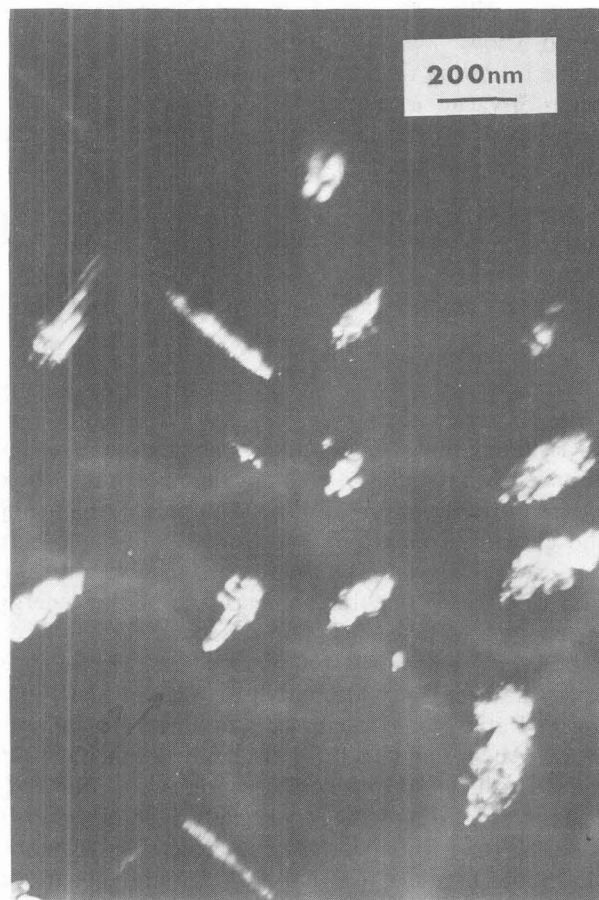


Fig. 3. — Dark field transmission electron micrograph of Al-doped NiO foil annealed at 800°C imaged using a precipitate reflection. Beam direction $[011]$.

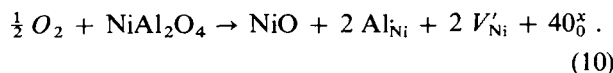
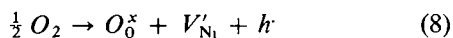
presence of plate shaped spinel precipitates (average dimensions $0.23 \mu\text{m}$ side $\times 0.04 \mu\text{m}$ thickness) lying along $\{100\}$ planes.

It can therefore be concluded that in the low temperature region the concentration of Ni vacancies in the series A crystals was determined by the saturation solubility of Al_2O_3 in NiO, the excess dopant being precipitated as NiAl_2O_4 .

4.3 VACANCY-DOPANT ASSOCIATION. — The simple defect model is incapable of explaining the large activation energy of D_{Ni}^* in Al-doped samples and the P_{O_2} dependence of D_{Ni}^* in undoped samples. Consequently it is necessary to consider the possible contributions of neutral vacancies, V_{Ni}^{\bullet} , and doubly charged vacancies, $V_{\text{Ni}}^{\bullet\bullet}$, to the diffusion coefficient. A complete analysis is not possible at present, but we have estimated the influence of doubly charged vacancies using the model of Koel and Gellings [3]. It was concluded that extending the model to include doubly charged vacancies only resulted in a slight improvement in agreement with the experimental measurements.

It appears that the high activation energy can only be accounted for by the partial association of Al_{Ni} and vacancies into more complex defects having lower mobility than unassociated vacancies as described below.

The following defect reactions describing the generation of vacancies by reaction with external oxygen, association of vacancies with Al dopant and the solution/precipitation of NiAl_2O_4 have been considered :



By assuming that V_{Ni}' is the defect which dominates the diffusion behaviour, D_{Ni}^* was calculated over the whole temperature range for Al-doped samples. The entropy and enthalpy changes for reactions (9) and (10) were chosen so as to optimise the fit with the experimental data (Fig. 4). From this analysis the binding energy of the Ni vacancy-Al dopant associate was deduced to be 1.2 eV, which is a reasonable value. The analysis also enabled the solubility of Al in NiO (at $P_{\text{O}_2} = 1$ atm.) to be calculated as a function of temperature. According to Iida [4] this lies between 5×10^{-3} and 2.5×10^{-2} Al ions per NiO molecule at 1 650 °C. The corresponding solubility predicted by our analysis is 4.6×10^{-2} ions per NiO molecule. Furthermore, the model predicts that NiAl_2O_4 should precipitate from the series A crystals at temperatures below 1 135 °C which is in good agreement with the temperature of the « break » (~ 1 200 °C) in the Arrhenius plot of the diffusion data.

A similar analysis in which the diffusing defects were assumed to be doubly charged Ni vacancies was not capable of a reasonable fit to the diffusion data.

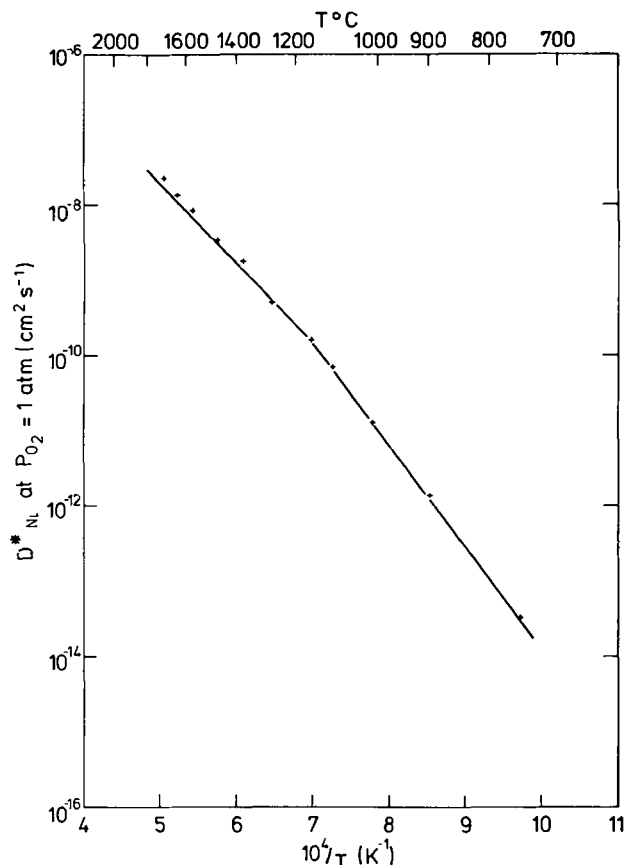


Fig. 4 — Arrhenius plot of D_{Ni}^* in series A specimens. The solid line is predicted using a model which takes account of both precipitation of NiAl_2O_4 and vacancy-dopant association.

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DISCUSSION

Question. — J. PHILIBERT.

I wonder if some surface segregation of the dopant would not cause you some trouble at temperatures where penetration is low ?

Reply. — A. ATKINSON.

At the lowest temperature the sectioning depth was 7 μm which should be much deeper than any surface segregation.

Question. — R. A. MCKEE.

For the vacancy diffusion coefficient in D^* you

have used the chemical diffusion coefficient even though there is a strong interaction with the aluminium dopant. Is this correct ?

Reply. — A. ATKINSON.

The final model assumes that the associated vacancies are much less mobile than the unassociated vacancies and therefore it seems reasonable to use the chemical diffusion coefficient measured in undoped NiO to calculate the diffusion coefficient of the unassociated vacancies.

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