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Diffusion of ^{57}Co Along Grain Boundaries in NiO

A. Atkinson and R.I. Taylor

Abstract

The characteristic parameter $\alpha D'\delta$, which is the product of the segregation coefficient, the boundary diffusion coefficient and the boundary width, has been measured for the diffusion of ^{57}Co along both high-angle and low-angle grain boundaries in high purity polycrystalline NiO. The measurements were made at an oxygen pressure of 1 atm. at temperatures in the range 500-800°C, and at an oxygen pressure of 10^{-11} atm. at 700°C. The results show that the close similarity between the diffusion of Co and Ni in the NiO lattice is also true of the diffusion of Co and Ni along NiO grain boundaries.

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1. Introduction

The diffusion of solutes in solid-state solvents has been studied in many systems, both for technological reasons and also to obtain fundamental information about the interaction between the solute and other lattice defects. When the solvent is an oxide, such information is essential for understanding the influence of impurities on the properties of oxides at high temperatures e.g. in sintering, creep or the oxidation of alloys. NiO has proved to be a suitable model oxide for studies of the relationships between these macroscopic phenomena and the atomistic defect structure of the matrix because the concentration of lattice defects in undoped NiO is normally large enough to be insensitive to uncontrollable trace impurities, but yet small enough for the formation of complex defects to be ignored to a good approximation. The defect structure of undoped NiO is known to be controlled by reaction with the oxygen in the gas phase to produce non-stoichiometric (Ni-deficient) NiO in which the point defects are Ni vacancies and electronic holes (p-type semiconductor). The reaction can be expressed as

$$\tfrac{1}{2}O_2 \rightleftharpoons O_o^{x} + V_{Ni}'' + 2h^{\cdot}. \qquad \ldots\ldots (1)$$

Since the 'intrinsic' lattice defects are on the cation sublattice studies of solute effects in NiO have concentrated on cation solutes and their influence classified according to their valency relative to that of nickel. Consequently a solute with the same valency and similar ionic radius to nickel represents the simplest solute for study; and cobalt satisfies both these criteria.

Volpe and Reddy (1970) and Atkinson and Taylor (1979) have both studied the tracer diffusion of nickel in NiO single crystals at $P_{O_2} = 1$ atm. In the temperature range 1182-1762°C Volpe and Reddy found that

$$D_{Ni} = 4.8 \times 10^{-2} \exp\left\{-2.64(\mathrm{eV})/kT\right\} \mathrm{cm}^2\mathrm{s}^{-1}, \qquad \ldots\ldots (2)$$

and Atkinson and Taylor found in the temperature range 522-1400°C

$$D_{Ni} = 2.2 \times 10^{-2} \exp\left\{-2.56(\text{eV})/kT\right\} \text{cm}^2\text{s}^{-1}. \qquad \ldots\ldots (3)$$

The diffusion of ^{55}Co and ^{60}Co tracers in NiO crystals has been studied in air (P_{O_2} = 0.2 atm.) in the temperature range 1179-1649°C by Chen and Peterson (1972). They found the cobalt diffusivity to be given by

$$D_{Co} = 9.1 \times 10^{-3} \exp\left\{-2.35(\text{eV})/kT\right\} \text{cm}^2\text{s}^{-1}. \qquad \ldots\ldots (4)$$

The diffusion of non-radioactive cobalt in NiO crystals (at cobalt concentrations typically less than 1%) has been studied by Tabet (1980) in air in the temperature range 800-1700°C. He found that above 1100°C the cobalt diffusivity was given by

$$D_{Co} = 3.5 \times 10^{-2} \exp\left\{-2.52(\text{eV})/kT\right\} \text{cm}^2\text{s}^{-1} \qquad \ldots\ldots (5)$$

but at lower temperatures D_{Co} was greater than given by equation (5), perhaps due to contributions from dislocation diffusion or trace impurities. The measurements by these various workers are summarised graphically in Fig. 1. Although there are small, but significant, differences between different workers' results, it can be concluded that the diffusivity of cobalt in the NiO lattice is slightly greater than that of nickel for all temperatures studied (i.e. above 800°C). This similarity between the diffusivities is to be expected since cobalt should dissolve in NiO as a doubly charged ion which is of similar size to the Ni^{2+} ion.

However, evidence has been accumulating to indicate that for temperatures below about two-thirds of the absolute melting temperature of the lattice, transport of material in crystalline solids is mainly by diffusion along grain boundaries and dislocations and not through the bulk of the crystal lattice. For example, in the case of NiO it has been demonstrated that the diffusion of nickel along NiO grain boundaries controls the rate of oxidation of nickel metal at temperatures below about 1100°C (Atkinson, Taylor and Hughes, 1981). Atkinson and Taylor (1981) (abbreviated in the remainder of the text as AT 1981) have measured the parameters describing the diffusion of nickel along high- angle grain boundaries and low-angle sub-grain boundaries (dislocation arrays) in NiO. By treating a grain boundary as a high diffusivity slab, these experiments yielded the product of the width of the slab, δ , and the diffusion coefficient within it, D'. This product is shown as a function of temperature in Fig. 2. The measurements also showed that the boundary width is of the order of 10 Å and that $D'\delta$ increases as P_{O_2} increases. This latter observation strongly suggests that grain boundary diffusion in NiO, just like lattice diffusion, takes place by a vacancy mechanism, but with a lower activation energy; the P_{O_2} dependence arising from a reaction such as equation (1) injecting vacancies into the boundary 'slab' as well as into the lattice. From this similarity between the mechanisms of lattice and grain boundary diffusion of nickel in NiO and the established similarity between lattice diffusion of cobalt and nickel in NiO one would not expect large differences between the grain boundary diffusion parameters for cobalt and nickel in NiO.

Chen and Peterson (1980) have studied the diffusion of cobalt along grain boundaries in bicrystals and large grain-size (>500 μm) polycrystalline NiO. For solute diffusion along a grain boundary it can be shown that tracer diffusion experiments yield the product $\alpha D'\delta$, where α is the partition coefficient (segregation coefficient) of the solute between the boundary and the lattice ($\alpha = 1$ for self diffusion). These measurements are also shown in Fig. 2. Although the temperature ranges of the cobalt and nickel diffusion measurements are different it is clear that the expected similarity was not observed in the following respects. First, at the temperature common to both sets of data (800°C), the cobalt diffusion parameter is approximately thirty times greater than for nickel. Secondly, the activation energy for $\alpha D'\delta$ for cobalt diffusion measured by Chen and Peterson is approximately the same as for lattice diffusion ($\sim$2.5 eV per atom) whereas $D'\delta$ for nickel diffusion has a significantly lower activation energy (1.78 eV per atom; AT 1981). Chen and Peterson suggest that this high activation energy may result from a negative binding enthalpy between the cobalt and the grain boundary (i.e. $\alpha < 1$). However, such a rejection of solute from the boundary would be difficult to reconcile with values of $\alpha D'\delta$ being so much greater for cobalt than for nickel diffusion. Furthermore, Chen and Peterson found $\alpha D'\delta$ for cobalt diffusion to be independent of P_{O_2} at 857°C, whereas $D'\delta$ for nickel diffusion was found to increase with increasing P_{O_2} (AT 1981).

The purpose of the work described here was to determine whether this surprising qualitative divergence in the grain boundary diffusion behaviour of cobalt and nickel could be confirmed by measurements of cobalt diffusion in polycrystalline NiO samples similar to those used in the nickel diffusion experiments.

2. Experimental methods

High purity polycrystalline NiO diffusion specimens were prepared by oxidising nickel foil in contact with substrates (16 x 16 x 2 mm) of cold-pressed and sintered NiO as described in earlier work (AT 1981). These polycrystalline specimens contained high-angle boundaries having a mean grain-size of 8.5 μm and also dislocation arrays of a similar effective subgrain-size.

Pre-diffusion anneals, tracer application and diffusion anneals were carried out in the temperature range 500-800°C at $P_{O_2} = 1$ atm. as described previously for the nickel diffusion experiments. The tracer used in the current experiments was ^{57}Co (obtained from the Radiochemical Centre, Amersham, U.K., as a solution of $CoCl_2$) which has a half-life of 270 days and decays by K-capture. At 700°C a diffusion experiment was carried out at an oxygen pressure of 10^{-11} atm. by annealing in a flowing mixture of CO_2 with 10 vpm CO.

After the diffusion anneals the specimens were sectioned using the radio-frequency sputtering technique (Atkinson and Taylor, 1977) and the activity of each section measured using a gas-filled proportional counter to detect the Fe characteristic X-ray (energy 6.404 keV) emitted by the tracer.

3. Results

Some selected tracer penetration profiles are shown in Figs. 3 and 4. $\bar{C}$ is the average activity of tracer per unit volume at depth y below the original surface of the specimen and K is the activity per unit surface area at t = 0. The profiles in Fig. 3 were chosen to illustrate the effect on the profile of changing the anneal time (at constant T and P_{O_2}) and those in Fig. 4 the effect of changing P_{O_2} (at constant T and t). The profiles were analysed in an analogous manner to that applied previously to ^{63}Ni profiles in similar NiO specimens (AT 1981). In the analysis each profile was divided into three parts: the near-surface region which was attributed to lattice diffusion, the low activity 'tail' (diffusion along high-angle boundaries) and an intermediate region (diffusion along dislocation arrays).

Values of the lattice diffusion coefficient, D, deduced from the near-surface region of profiles are plotted in Fig. 1. It should be borne in mind that these experiments were specifically designed to study grain boundary diffusion and therefore the values of D are not very precise. Indeed, at 500°C the lattice diffusion penetration was so shallow ($\lesssim$100 Å) as to preclude any worthwhile estimate of D. However, the results shown in Fig. 1 are sufficiently accurate to confirm that D measured in these specimens is compatible with the results of other workers obtained at temperatures above 800°C. The dotted line in Fig. 1 was calculated from the geometric mean of equations (4) and (5) corrected to P_{O_2} = 1 atm. and is given by

$$D_{Co} = 2.5 \times 10^{-2} \exp\left\{-2.43(\text{eV})/kT\right\} \text{cm}^2\text{s}^{-1}. \qquad \ldots\ldots (6)$$

The characteristic parameter for diffusion along high-angle boundaries was calculated from the slope of the 'tail' on each profile using the expression

$$\alpha D'\delta = 0.66 \left(- \frac{d \ln \bar{C}}{dy^{6/5}} \right)^{-5/3} \left(\frac{4D}{t} \right)^{\frac{1}{2}} . \qquad \ldots\ldots (7)$$

The values of D required by equation (7) were calculated from equation (6) except for the profile obtained at $P_{O_2} = 10^{-11}$ atm. for which the directly measured value had to be used. The characteristic parameter for diffusion along dislocation arrays $(\alpha D'\delta)_s$ was deduced by applying the same analysis to the intermediate portion of each penetration profile. The solid curves in Fig. 4 are best fits to the experimental data when all three contributions to the penetration profile are summed; the lattice diffusion coefficient being taken from equation (6). Details of the diffusion anneals and diffusion parameters obtained from them are summarised in the Table.

Since measurements of grain boundary diffusion rely on analysing low activity 'tails' in the penetration profiles it is important to demonstrate that the 'tails' do not arise from some spurious source of penetration such as microfissures or pores. This is best done by autoradiography, as demonstrated for the diffusion of ^{63}Ni in similar NiO specimens (AT 1981). Unfortunately there are no cobalt isotopes which are suitable for high resolution autoradiography and therefore we must rely on less direct methods. One method is to observe the penetration profiles for different anneal times at the same temperature. Such data as those in Fig. 3 show that the 'tails' result from a diffusive process and not from the deposition of tracer directly into microfissures or open porosity. A second method is to compare the activity in the 'tail' with that calculated from Suzuoka's (1964) theoretical solution using values of $\alpha D'\delta$ (calculated from the slope of the 'tail') and the grain-size of the specimen (see AT 1981). The broken lines in Figs. 3 and 4 are the theoretical 'tail' profiles calculated in this way. It can be seen that for three of the profiles the agreement between theory and experiment is within a factor of 2. The divergence between theory and experiment at low temperatures and short times was reported earlier for nickel diffusion (AT 1981) and is caused by the boundary condition at the specimen surface assumed in Suzuoka's theory not being fulfilled. It can be concluded that there is strong evidence for interpreting the 'tails' as being a result of grain boundary diffusion.

4. Discussion

The measured values of $\alpha D'\delta$ for cobalt diffusion along both high-angle boundaries and dislocation arrays in NiO are compared in Fig. 2 with the corresponding earlier data for nickel diffusion. It can be seen that the cobalt diffusivities measured here are not compatible with the measurements of Chen and Peterson (1980) made at higher temperatures. In fact the present results are in accord with the simple arguments given in the introduction in that the diffusivity of cobalt in the boundaries is observed to be somewhat faster than that of nickel (by approximately a factor of three) and the activation energies for cobalt and nickel diffusion are the same to within experimental error and less than the activation energies for lattice diffusion. Furthermore, Chen and Peterson (1980) reported that they found no dependence of $\alpha D'\delta$ on P_{O_2} at 850°C whereas in the present study a dependence on P_{O_2} was observed at 700°C. These data are shown in Fig. 5 together with all our earlier measurements of the effects of P_{O_2} on diffusivity in NiO at 700°C. (The broken lines are merely to link together measurements of the same parameter and are not meant to imply linear relationships). It is clear from Fig. 5 that the parameters for both cobalt and nickel diffusion in both grain boundaries and the lattice all depend on P_{O_2} in a qualitatively similar way. This dependence also indicates that the diffusion is not controlled by trace impurities at 700°C and $P_{O_2} = 1$ atm. It can therefore be concluded that the measurements of cobalt diffusivity presented here are completely compatible with earlier measurements of nickel grain boundary diffusivity (AT 1981) and the lattice diffusivities of cobalt and nickel in NiO. The reason for the disagreement between the present measurements and those of Chen and Peterson (1980) remains to be clarified but may reside in the very different methods used to prepare the diffusion specimens in the two studies.

Acknowledgement

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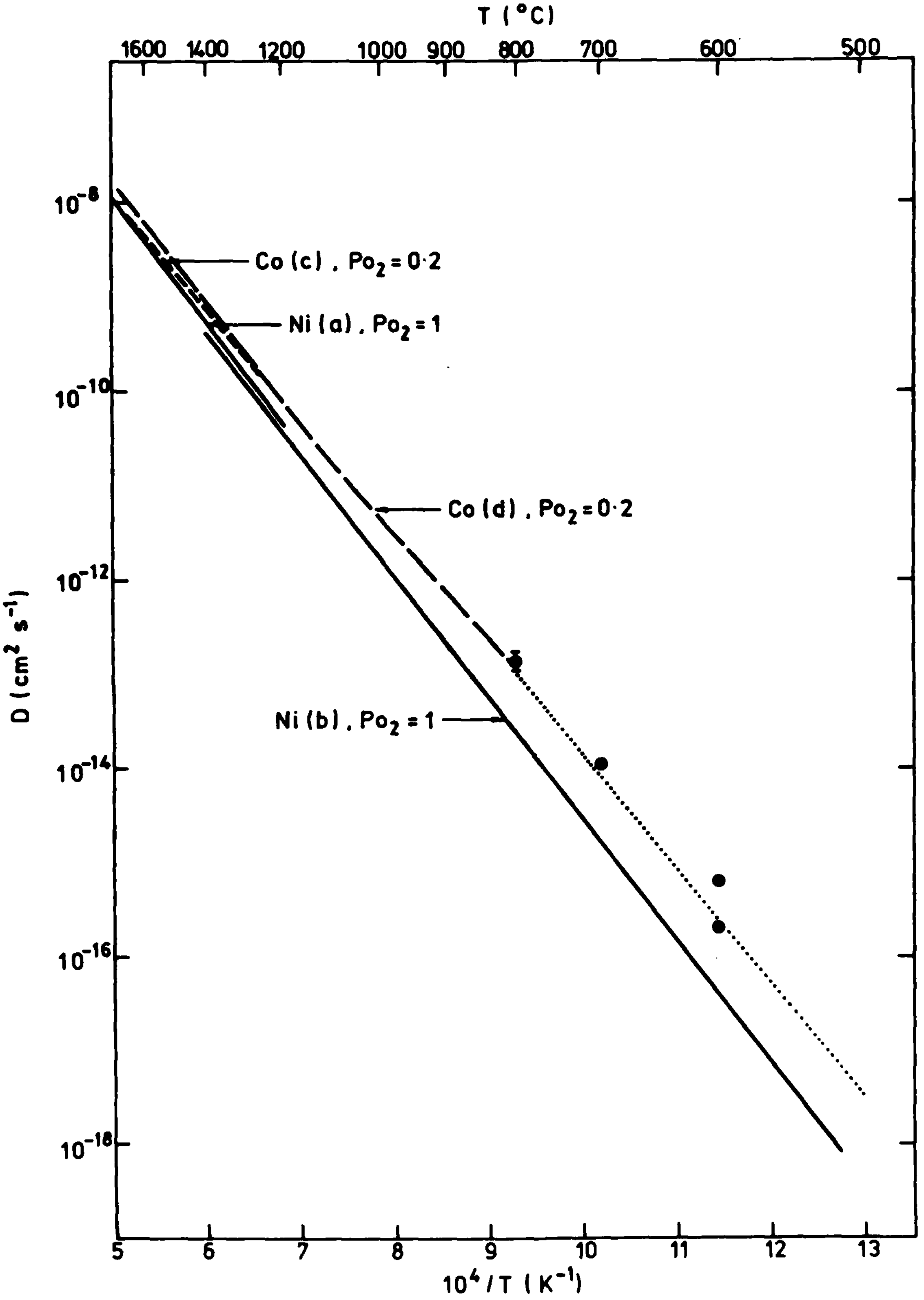
Table

Details of diffusion anneals and diffusion parameters

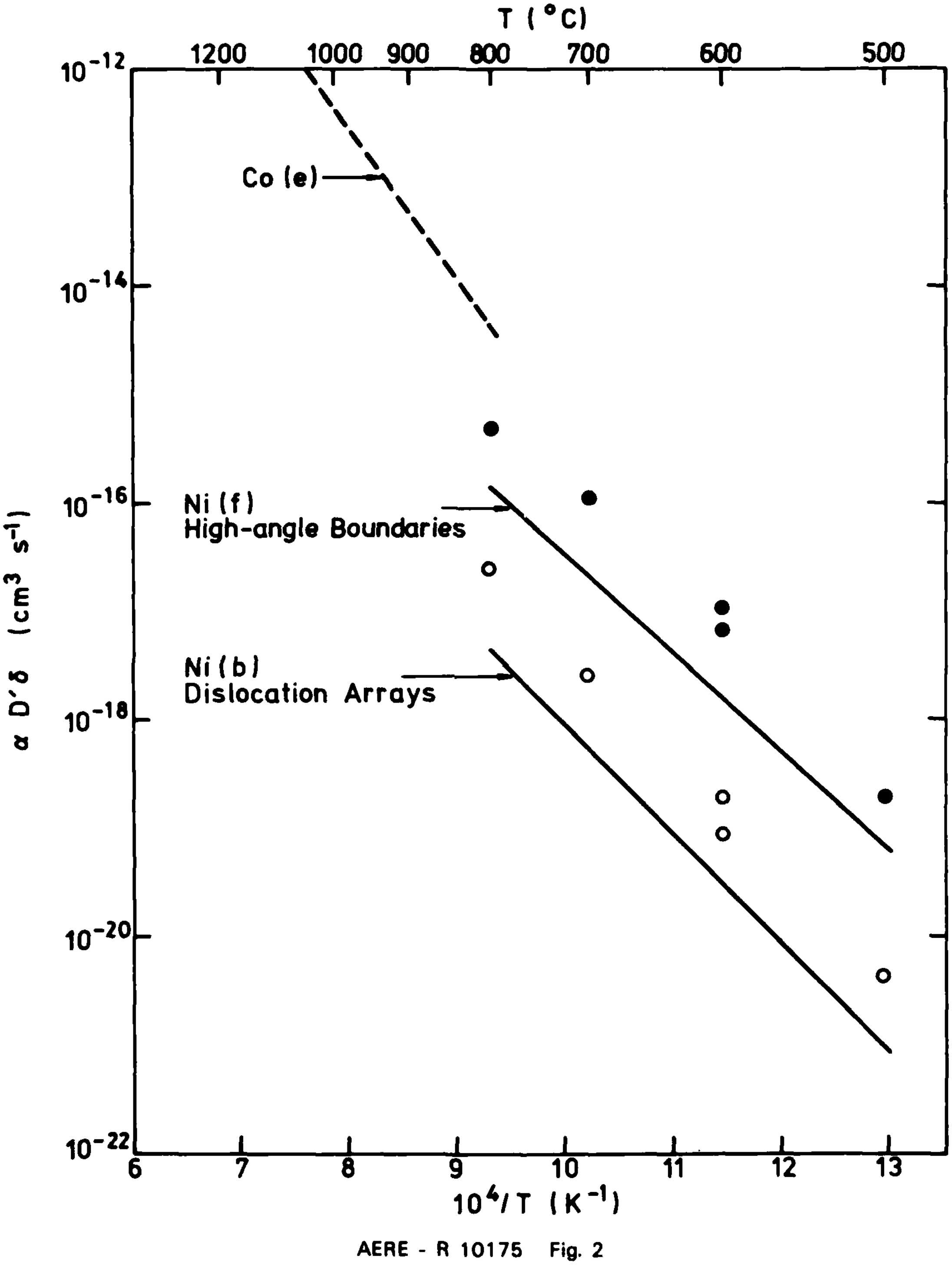
Run No.	Temperature (°C)	Anneal time (s)	D (eq. 6) ($cm^2\ s^{-1}$)	$(Dt)^{\frac{1}{2}}$ (cm)	$\alpha D'\delta$ ($cm^3\ S^{-1}$)	$(\alpha D'\delta)_s$ ($cm^3\ s^{-1}$)	y_{max} (μm)
1	800	1.8×10^3	9.7×10^{-14}	1.3×10^{-5}	4.8×10^{-16}	2.6×10^{-17}	6.1
2	700	7.2×10^3	6.6×10^{-15}	6.9×10^{-6}	1.1×10^{-16}	2.5×10^{-18}	4.9
3	700 ($P_{O_2} = 10^{-11}$ atm)	7.2×10^3	$9.5^* \times 10^{-16}$	2.6×10^{-6}	1.2×10^{-18}	1.5×10^{-20}	1.5
4	600	7.2×10^3	2.4×10^{-16}	1.3×10^{-6}	6.8×10^{-18}	8.9×10^{-20}	3.5
5	600	5.76×10^4	2.4×10^{-16}	3.7×10^{-6}	1.05×10^{-17}	1.9×10^{-19}	6.5
6	500	8.65×10^4	3.6×10^{-18}	5.6×10^{-7}	2.0×10^{-19}	4.3×10^{-21}	4.2

*Measured value in Run 3.



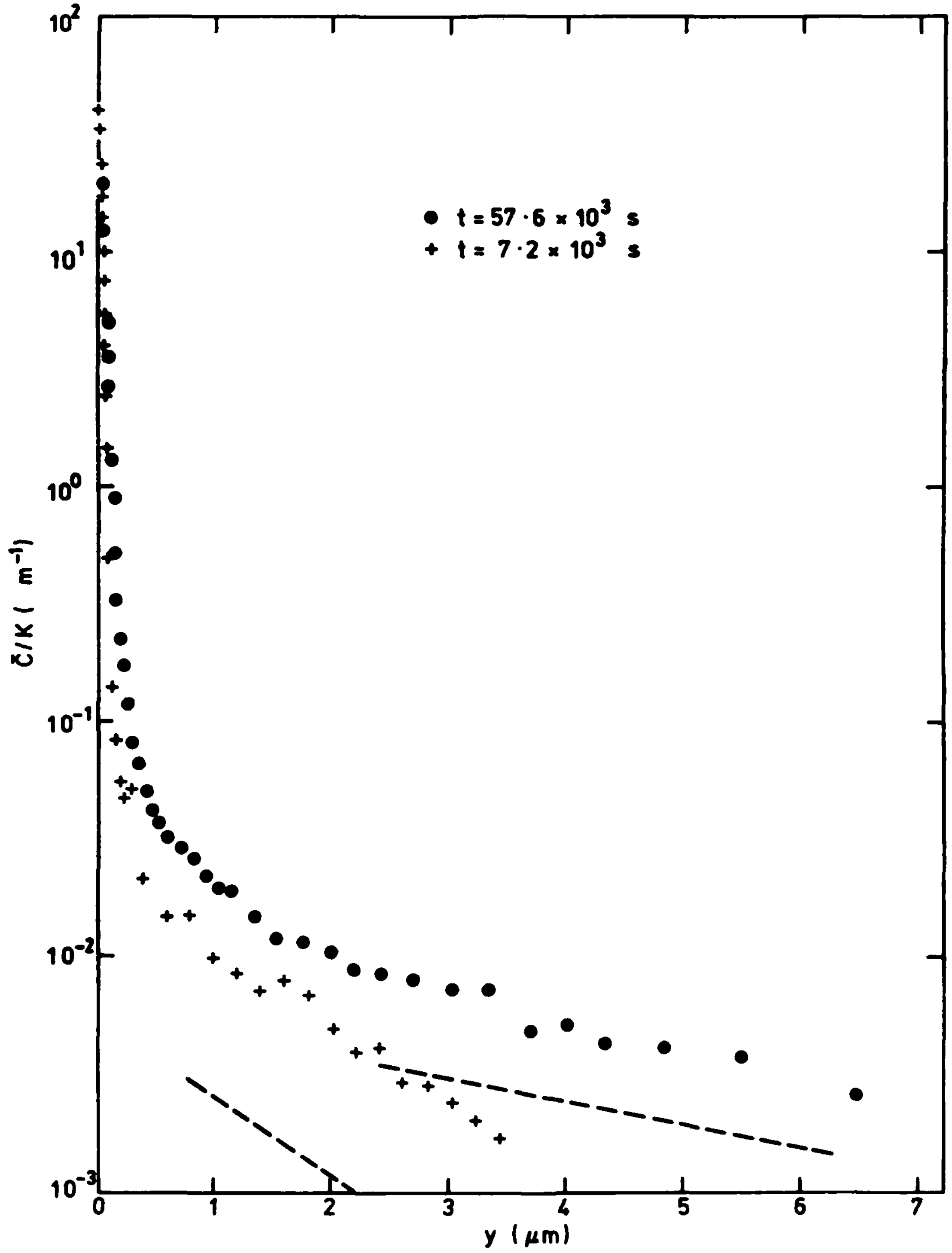
AERE - R 10175 Fig. 1

A comparison between the lattice diffusion coefficients for cobalt and nickel in NiO. The data points are for cobalt from this study. Ref. (a) Volpe and Reddy (1970); ref. (b) Atkinson and Taylor (1979); ref. (c) Chen and Peterson (1972); ref. (d) Tabet (1980); for dotted line see text.



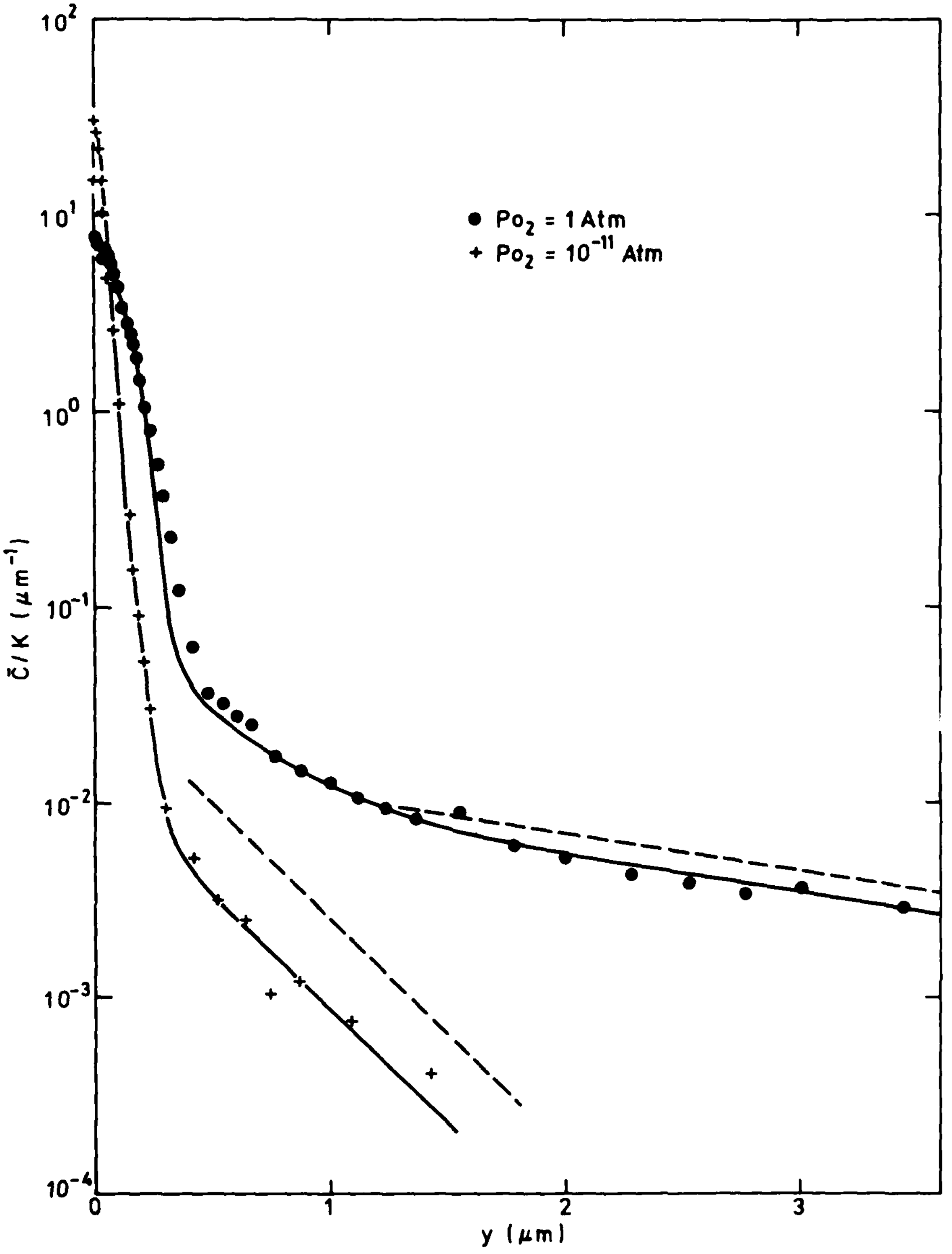
AERE - R 10175 Fig. 2

A comparison between the grain boundary diffusion parameters for cobalt and nickel in NiO. The data points (solid for high-angle boundaries, open for dislocation arrays) are for cobalt from this study. Ref. (e) Chen and Peterson (1980); ref. (f) Atkinson and Taylor (1980).



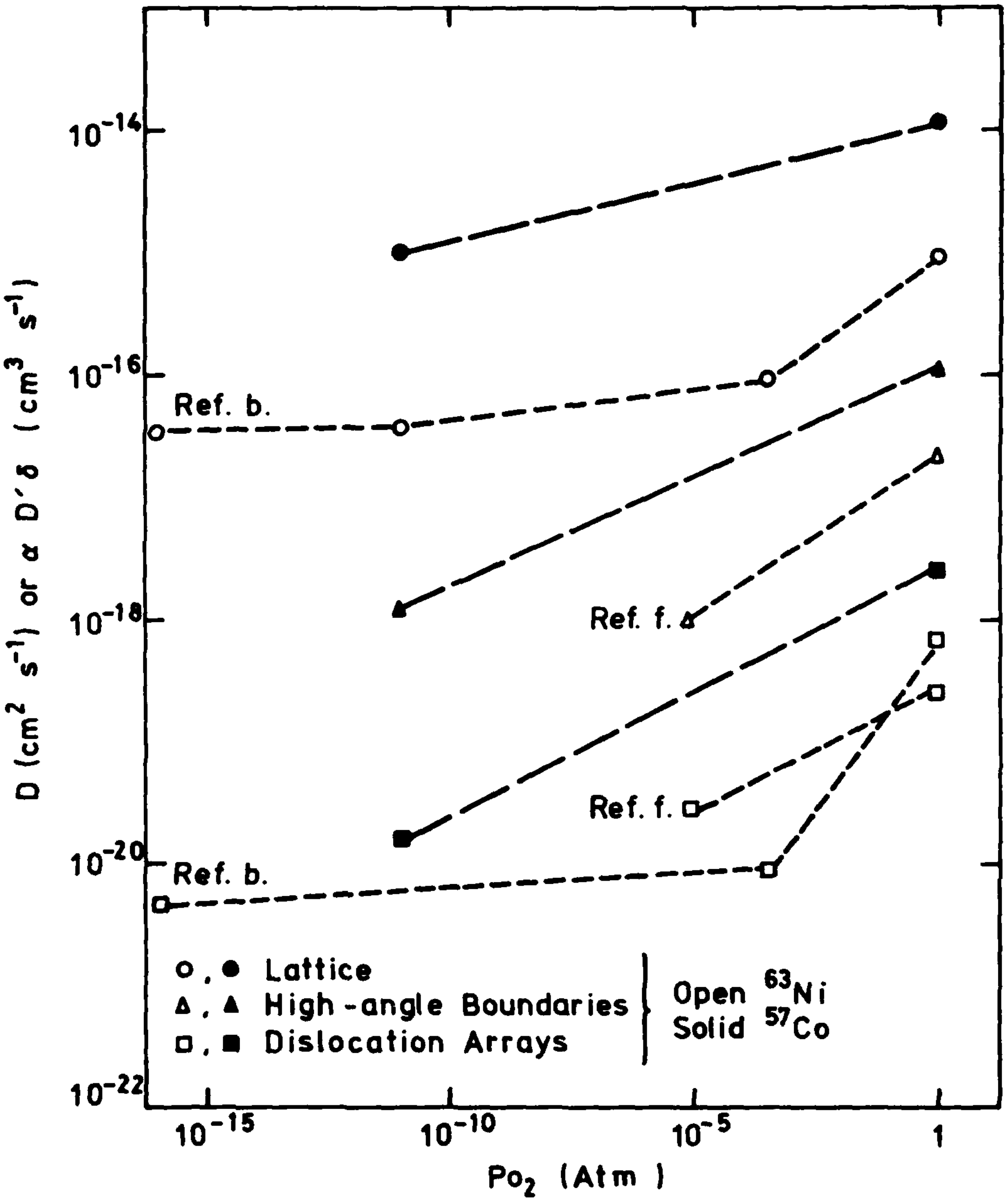
AERE - R 10175 Fig. 3

Penetration profiles of ^{57}Co in polycrystalline NiO after annealing for two different times at 600°C and P_{O_2} = 1 atm. (Runs 4 and 5). The dashed lines are calculated using Suzuoka's (1964) theoretical solution.



AERE - R 10175 Fig. 4

Penetration profiles of ^{57}Co in polycrystalline NiO after annealing for the same time under two different oxygen pressures at 700°C (Runs 2 and 3). The dashed lines are calculated using Suzuoka's (1964) theoretical solution.



AERE - R 10175 Fig. 5

The effect of P_{O_2} on the diffusivity of cobalt in NiO at 700°C observed in this work compared with earlier results for nickel diffusion (n.b. at 690°C from ref. (b)).