The self-diffusion of Ni in NiO and its relevance to the oxidation of Ni

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The tracer self-diffusion coefficient of Ni in single crystals of NiO, at atmospheric pressure of oxygen, has been measured by sectioning in the temperature range 700 to 1400° C and is given by

$$D_{Ni}^* = (1.5 \pm 0.8) \times 10^{-2} \exp\{-58 \pm 1 \ (kcal)/RT\} \ cm^2 \ sec^{-1}.$$

Hence it is argued that the breakdown in the application of Wagner's theory to the oxidation of Ni at intermediate temperatures is not an impurity effect, but a result of short-circuit diffusion. Diffusion of Ni along grain boundaries in NiO at 600° C has been observed using autoradiography and the product $D_{GB}^* \delta$ estimated to be $3 \times 10^{-19} \ cm^3 \ sec^{-1}$. This value is reasonably consistent with estimates from oxidation kinetics, but it is not yet established that grain boundary diffusion of Ni will account completely for the kinetics of nickel oxidation at this temperature.

1. Introduction
When metals or alloys are employed in high-temperature oxidizing environments they are protected by the oxide scale which forms *in situ* and acts as a partial barrier to continuing attack by the environment. The requirements for good protection over long periods are that the transport of reactants through the scale should be sufficiently slow and that the scale should not crack or spall to re-expose the underlying metal. In spite of the importance of these phenomena, present understanding of the mechanisms involved is poor. In the case of technologically important alloys this is mainly because of the complexity of both the alloys themselves and the environments in which they are required for use. However, even in simple model systems (i.e. pure metal in oxygen) many important aspects of the oxidation mechanism remain unresolved. This contribution concerns the inadequacy of the basic oxidation theory in describing the oxidation of Ni at "intermediate" temperatures (400 to 1000° C).

The oxidation of transition metals has been reviewed recently by Smeltzer and Young [1] in which they summarized the application of Wagner's theory [2] to the oxidation of Ni. Wagner's theory relates the parabolic rate constant, for oxidation of the metal, to the diffusion coefficients of mobile species in the oxide scale. In the case of NiO only the nickel diffusion coefficient, D_{Ni}, need be considered at high temperatures, since the oxygen diffusion coefficient is small in comparison [3]. Previous determinations of D_{Ni} in NiO have been summarized by Kofstad [3]. Only Choi and Moore [4] and Volpe and Reddy [5] employed a sectioning method on single crystals, and these two determinations differ by an order of magnitude at 1200° C. However, the data of Volpe and Reddy are considered the more reliable since their crystals contained less Cr and were preannealed under the diffusion conditions. Therefore diffusion data and oxidation data are only available for comparison over a limited temperature range (1200 to 1400° C), the lower limit being the lowest temperature in the diffusion study [5]. In this range the data can be correlated satisfactorily using Wagner's theory and, by extrapolating the diffusion coefficients to lower temperatures, this is apparently true down to ~900° C [1]. Below 900° C, however, this agreement deteriorates and
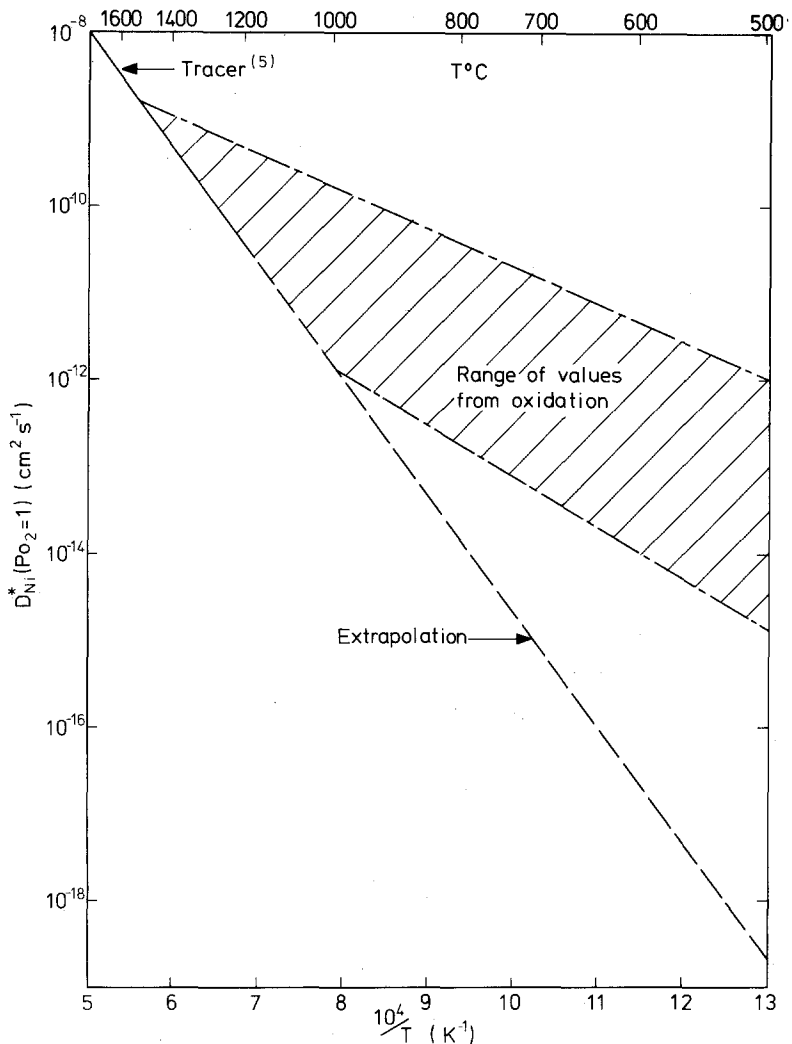
Figure 1 Tracer diffusion coefficient of Ni in NiO compared with that deduced from oxidation kinetics using Wagner's theory.

eventually reaches a discrepancy of 5 to 7 orders of magnitude at 500° C. The situation is depicted in Fig. 1, where the nickel self-diffusion coefficient, calculated from the parabolic rate-constant measured in oxidation experiments, is compared with an extrapolation of the bulk diffusion data [5].

There appear to be three possible explanations to account for the anomaly:

(1) The intermediate temperature (500 to 1000° C) defect structure of NiO may be dominated by impurity effects [6]. For example, trivalent impurities may lead to an increased concentration of Ni vacancies.

(2) Transport of oxygen may occur along grain boundaries in NiO [7].

(3) Transport of Ni may occur along grain boundaries in NiO [1]. Explanations (2) or (3) are more likely than (1) since they can account for differences in the oxidation kinetics of different crystal faces of Ni [1]; a point which is inconsistent with Wagner's theory and with mechanism (1). However, there are no direct observations of impurity dominated diffusion or grain boundary diffusion in NiO to support any of these possibilities.

Consequently, the first objective of this study was to extend the diffusion data for lattice diffusion of Ni in NiO to lower temperatures in order to determine whether the defect structure, and hence bulk diffusion coefficient, is influenced by trace impurities in single crystals. The second
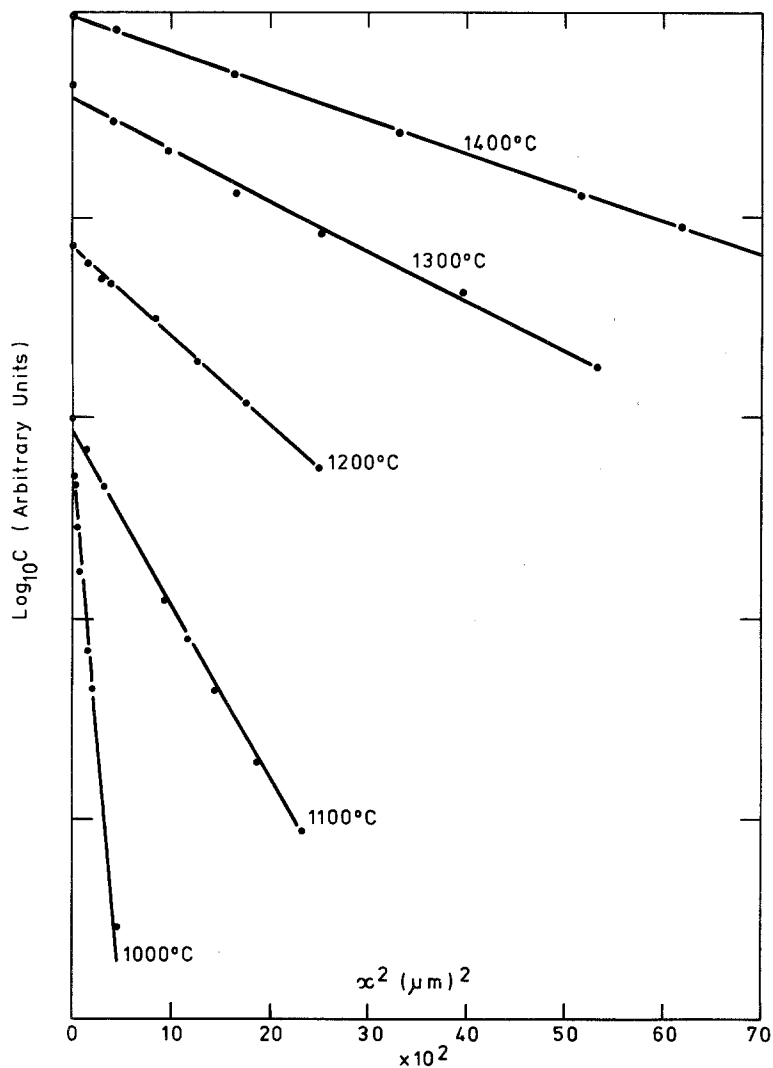
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Figure 2 Penetration profiles of ^{63}Ni in NiO (1000° C to 1400° C).

objective was to attempt to observe grain boundary diffusion in bicrystals of NiO to assess the plausibility of explanation (3) above.
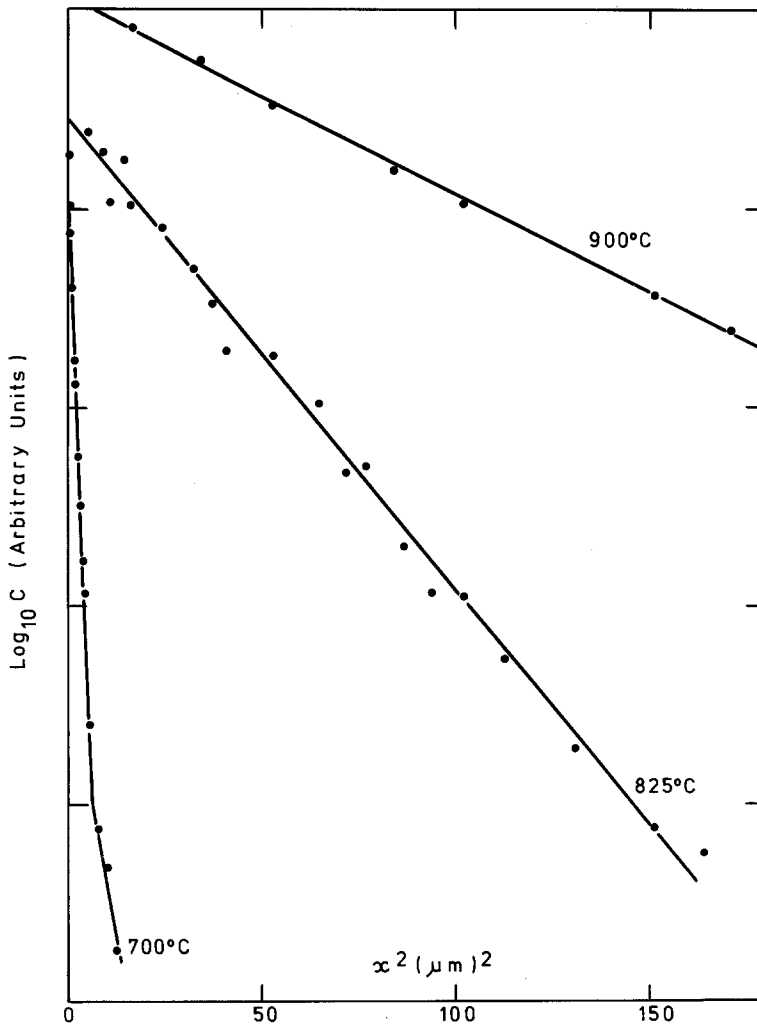
2. Experimental

NiO single crystals and bicrystals (Cristal Tec Ltd., Grenoble) were cut to a suitable size for diffusion samples (approximately 1 cm^2 surface area and 3 mm thickness). The samples were annealed in oxygen at 1300° C for 24 h to remove any damage introduced during the initial preparation and then polished using successively finer diamond abrasive to a scratch-free surface finish and flatness better than ± 0.2 μm, using a precision polishing jig (Metals Research Ltd.). Examination of the polished (1 1 1) face of the crystal by X-ray

diffraction indicated a variation in lattice parameter of ± 30 ppm over the surface and the presence of some low angle subgrain boundaries (~0.2° misorientation). Spectrographic analysis for 32 possible metallic contaminants detected 100 wpm Si and 75 wpm Fe, the remainder being below the detection limit. Each crystal was given a prediffusion anneal under the conditions (temperature, oxygen pressure and time) of the planned diffusion anneal to establish the equilibrium defect structure over a depth greater than the tracer penetration.

Specimens were coated on one face with a thin layer of ^{63}NiO tracer (~1 nm), by evaporation and oxidation, and then given a diffusion anneal at atmospheric pressure of oxygen. After the anneal

429

about 200 μm of oxide was ground from the back and edges of the specimen, to eliminate errors from side effects, and then the specimens were sectioned using the precision polishing jig. The Gruzin technique (i.e. measurement of surface activity after each section) was employed for annealing temperatures $\geqslant 900°$ C, correcting for self-absorption of the 67 keV β radiation as described by Volpe and Reddy [5]. At the lower temperatures paper discs impregnated with 6 μm diamond paste were used to remove sections $\gtrsim 0.2\,\mu$m and collect the grindings. The thickness of each section was determined from the weight lost.

The penetration profiles are shown in Figs. 2 and 3, plotted according to the appropriate solution for the diffusion geometry and boundary conditions:

$$C = A (\pi D^* t)^{-1/2} \exp(-x^2/4D^* t) \qquad (1)$$

where C is the tracer concentration at penetration x and A the initial area concentration at the surface. Values of the tracer diffusion coefficient, D^*, deduced from these profiles are presented in Table I, together with details of diffusion anneals and sectioning method. The same results are compared with those of Volpe and Reddy on an Arrhenius plot (Fig. 4) and are described by:

$$D_{Ni}^*(PO_2 = 1) = (1.5 \pm 0.8) \times 10^{-2}$$

$$\exp \{-58 \pm 1 \,(kcal)/RT\}\,cm^2\,sec^{-1}$$

in the temperature range 700 to 1400° C.

3. Discussion
3.1 Lattice diffusion of Ni in NiO
The activation energy and pre-exponential factor, for [63]Ni tracer diffusion in NiO determined here, differ slightly from those published by Volpe and

TABLE I Tracer self diffusion coefficient of ^{63}Ni in NiO at atmospheric pressure of oxygen

$T(^\circ C)$	$D_{Ni}^{*}(cm^2\, sec^{-1})$	Anneal time (sec)	Sectioning method
1400	3.65×10^{-10}	$1.8\ \times 10^4$	Gruzin
1300	1.63×10^{-10}	2.63×10^4	Gruzin
1200	3.40×10^{-11}	$7.2\ \times 10^4$	Gruzin
1100	$7.3\ \times 10^{-12}$	1.73×10^5	Gruzin
1000	1.34×10^{-12}	1.73×10^5	Gruzin
900	2.69×10^{-13}	$4.1\ \times 10^5$	Gruzin
825	4.55×10^{-14}	9.52×10^5	Section counting
700	1.25×10^{-15}	1.80×10^6	Section counting

Reddy [5]. However, the agreement, in the temperature range common to both studies (1200 to 1400°C), is good (see Fig. 4) and supports the view that these data are more representative of the true diffusion coefficient than those previously published. The data also show that the defect structure of these NiO crystals is not dominated by impurity effects even at 700°C. Our extrapolation of the defect concentration [8] in NiO suggests that approximately 50 apm of aliovalent metallic impurity would be required to influence D_{Ni}^{*} significantly at 700°C. Since the concentrations of Fe and Si in the crystals were greater than 50 apm (Section 2) it is perhaps surprising that they do not make themselves felt more strongly. It must be assumed that they are either not dissolved in the NiO lattice or that they do not disturb the intrinsic defect structure in the simple way expected, e.g. they may form bound impurity—vacancy complexes. The impurity levels in the nickel single crystals used in studies of oxidation kinetics at intermediate temperatures [1], from which the lower bound of the hatched area of Fig. 1 was deduced, were lower than those of the NiO crystals used in this study. It is therefore
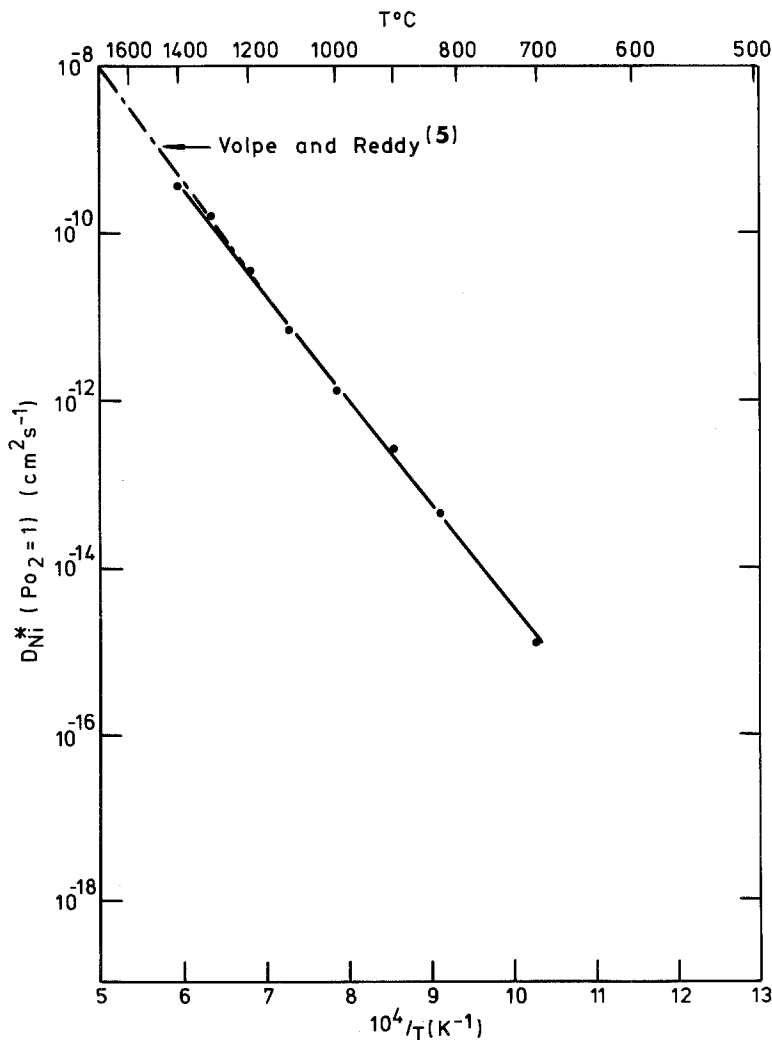

Figure 4 Arrhenius plot of tracer diffusion coefficient of ^{63}Ni in NiO.

confirmed that the application of Wagner's theory to the oxidation of Ni at temperatures below 1000° C is invalid in that bulk diffusion of Ni predicts an oxidation rate which, at 700° C, is slower by a factor of ~100 than the slowest experimental oxidation rate. The discrepancy between theory and experiment is not explicable in terms of impurity effects.

3.2 Short-circuit diffusion in NiO

These experiments support the widely held view that short-circuit diffusion is the dominant transport mechanism in the oxidation of Ni at intermediate temperatures. However, the question remains as to whether oxygen or nickel is the diffusing species along short circuit paths. The penetration profile at 700° C (Fig. 3) exhibits a "tail" (more evident on an expanded scale) which may be due to short-circuit diffusion of Ni along dislocations even in single crystals.

The possibility of grain boundary diffusion was investigated, in a preliminary way, using a high angle grain boundary in a NiO bicrystal. The bicrystal was prepared in the manner previously described for single crystals and given a diffusion anneal of 2.07×10^6 sec at 600° C and atmospheric pressure of oxygen. The specimen was then bevelled at a shallow angle ($\sim 10^{-2}$ rad) and the

tracer distribution determined by autoradiography using Kodak AR10 stripping emulsion. The autoradiograph (Fig. 5) shows the preferential migration of tracer along the grain boundary. The concentration of tracer at the grain boundary was estimated by microdensitometry and the data analysed using Whipple's [9] solution of the grain boundary diffusion problem. Hence the product of the grain boundary diffusion coefficient, D_{GB}^*, and the grain boundary width, δ, was estimated to be

$$D_{GB}^* \delta = 3 \times 10^{-19} \, cm^3 \, sec^{-1}.$$

Values of $D_{GB}^* \delta$ deduced by Perrow et al. [10] and Khoi et al. [11] from oxidation experiments at 600° C span a wide range from 2×10^{-22} to $6 \times 10^{-17} \, cm^3 \, sec^{-1}$, the more reliable values [11] being at the top of this range. Hence, although enhanced diffusion of Ni along NiO grain boundaries has been demonstrated to occur, the quantitative correlation between grain boundary diffusion parameters and Ni oxidation kinetics requires more detailed study. Diffusion in single crystals of NiO in the intermediate temperature range is presently being studied more thoroughly to separate bulk and short-circuit (dislocation-pipe) contributions.

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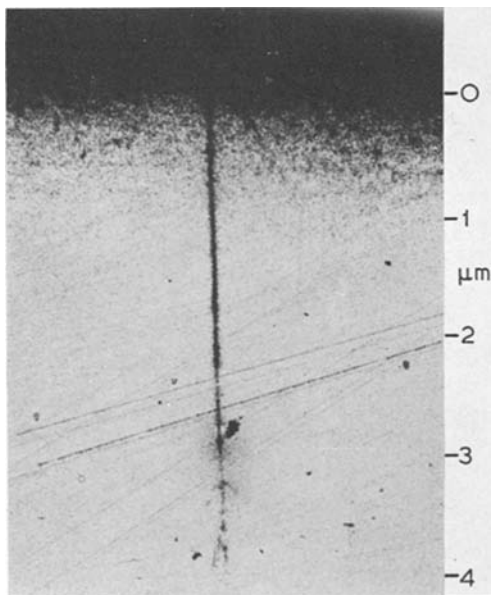
Figure 5 Autoradiograph showing grain-boundary diffusion of ^{63}Ni in NiO bicrystal (2.07×10^6 sec at 600° C, magnification × 200 reduced by 30% for reproduction). Scale gives depth of tracer penetration.