STUDY OF DIFFUSION OF OXYGEN IN DILUTE VANADIUM ALLOYS USING

SOLID ELECTROLYTIC CELLS

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The bulk diffusivity of oxygen has been measured as a function of temperature in dilute vanadium alloys. The emf vs time is measured on the electrolytic cell: $Pt/Nb+NbO/ThO_2-7\%Y_2O_3/V-alloy/Zr/Pt$. The oxygen content, which is initially uniform in the vanadium-based alloy, drains into the zirconium sink as a function of annealing time. After a short transient, the rate of cell emf change is directly proportional to the diffusivity of oxygen in the alloy. Substitutional solutes in vanadium have been chosen on the basis of their atomic sizes in vanadium and the heats of formation of their oxides. Oxygen diffusion results have been obtained for nickel, chromium, niobium, tantalum, titanium, zirconium and hafnium as binary solute additions of up to 4 at.%. The oxygen diffusivity results are compared with those for niobium-based alloys. Interpretations of the results are made using two models for the thermodynamics and kinetics of trapping of interstitial atoms by substitutional solute atoms.

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Introduction

Interstitial atoms, such as H, C, O and N, have an important influence on most physical and mechanical properties and processes in metals. However, their influence depends strongly on their interaction with other defects also present in the metal. In particular, small concentrations of substitutional atoms can cause profound modifications in the behavior of these interstitials. This study is concerned with the effect of substitutional atoms on the oxygen diffusion in vanadium. It is part of a larger effort directed to the understanding of solute-solute interactions in BCC metals. We have used the solid electrolytic cell technique which was brilliantly introduced and explored by Carl Wagner, on both experimental and theoretical bases (1).

Experimental

The electrolytic cell technique allows the determination of kinetic data through the monitoring of either its current during transient or steady-state conditions (2), or its emf during transient conditions (3,4). The present work uses the latter method proposed by Kirchheim et al (3). The cell geometry is shown in Fig. 1. The oxygen is initially uniform in concentration in the specimen, but drains into a sink during the diffusion
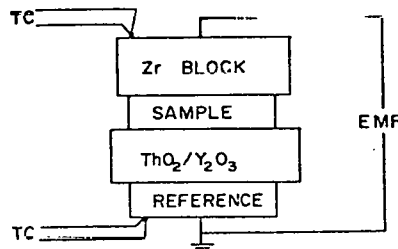
Fig.1 - Electrolytic cell configuration for oxygen diffusion measurements.

run. The sink must be a material with high oxygen mobility, high solubility for oxygen and negligible interdiffusion with the sample (5). A zirconium block has been used with excellent results for Nb, V (4) and Ta (3). The reference electrode in the kinetic study was either a Nb+O (2 phase) or a V+O (1 phase) binary alloy. It was placed on the bottom, Fig. 1, and was not disturbed for several consecutive runs. The temperature was held at 450 K for approximately 14 hours and then brought to 1173 K within two hours. The emf was recorded as a function of time until the curve showed a distinct straight-line portion, with a slope given by a solution of Fick's law with the appropriate boundary conditions (3,6)

$$\frac{dE}{dt} = - \frac{R\ T\ \pi^2\ D}{8\ F\ L^2} \qquad (1)$$

where L is the thickness of the electrode and E is the cell emf. This slope was calculated by a linear regression of at least eight experimental points. After the slope was established at one temperature, the temperature was changed and a new curve of emf versus time obtained. The diffusion coefficient was then calculated from the above equation for each temperature of interest. Measurements were made from 873 to 1423 K. The relative error of a measurement of D is estimated at less than ± 7%. This error arises chiefly from nonuniformity of the electrode thickness and contact, with smaller contributions from emf slope determination, temperature measurements and temperature gradient. This technique enables the determination of D at several temperatures on a single specimen and is limited only by the onset of electronic conduction in the electrolyte, i.e., the electrolyte is outside its essentially ionic conductivity range due to the extremely low oxygen partial pressure associated with the oxygen concentration at the electrolyte/sample interface (7).

The cell was supported on Lucalox tubes in a thoriated tungsten wound furnace placed inside the bell jar of an ion-pumped UHV system. The cell compartment was separated from the heating element by a cylindrical niobium sheet, which provided electrical shielding and a getter for impurities. Six concentric radiation shields around the entire assembly reduced the heat loss and helped maintain a uniform cell temperature. The temperature difference between the upper and lower electrodes was typically less than 5 K. The total pressure was usually 10^{-4} to 10^{-6} Pa during the measurements. The cell was carefully isolated electrically to assure low

leakage and thus more accurate emf measurements.

Dilute binary alloys containing Ti, Cr, Ni, Zr, Nb, Hf or Ta (Table 1) were prepared by arc melting in an argon atmosphere furnace with a water cooled copper hearth and tungsten electrode. The furnace was purged twice with argon and then a zirconium button was melted in a separate compartment of the hearth before melting the alloy. Each alloy was melted four times. Both zirconium and alloy ingots were etched to remove any oxide layer picked up during cooling, and they were turned over between melts. Total metallic impurity amounts were typically less than 150 at.ppm after melting. After swaging and rolling, metal strips were alloyed with measured amounts of oxygen in a high vacuum Sieverts' apparatus described elsewhere (8). The strips were annealed for approximately 3 hours at temperatures from 1350

Table I

Oxygen Diffusivity in Vanadium-based Alloys

$$D = D_0 \exp\left(- Q/RT\right)$$

Alloy*	LnD_0 (m^2/s)	Activation Energy, Q (kJ/mole)
V-1.2Ti-2.1 O	-14.19	118.0
V-0.95Cr-2.2 O	-12.53	129.8
V-0.95Cr-0.88 O	-12.95	129.1
V-0.96Ni-2.0 O	-13.00	126.5
V-1.0Nb-1.4 O	-12.12	135.1
V-3.5Nb-0.93 O	-12.73	134.5
V-3.6Ta-2.4 O	-12.38	131.9
V-3.6Ta-0.87 O	-10.91	152.0
Pure V (0.6 & 1.5 O)	-13.42	123.7

*Alloy compositions in atomic per cent

to 1600 K and pressures from 10^{-4} to 10^{-5} Pa. At about 1600 K the pumps were valved off for 40 minutes while oxygen was leaked in. This was done slowly to prevent the formation of an oxide layer on the surface of the strip and to insure complete absorption. After doping, a homogenization anneal was carried out in vacuum with the specimens held at approximately 1550 K for about 1.5 hours. The specimens contained 0.7 to 2.5 at% oxygen. The final oxygen concentrations were determined by a vacuum fusion technique. The strips were cut into segments 13 x 6 x 0.5 mm, and the surfaces were ground through 600 grit SiC and attack polished with 0.05 m) alumina in a chromic acid slurry.

Results

The diffusivities of oxygen in pure vanadium and in substitutional alloys are presented in Figs. 2 through 5. Activation energies and pre-exponential values determined from a least-squares fitting of the Arrhenius equation for all the experimental data are given in Table 1. The straight line in Figs. 3-5 is for oxygen diffusion in pure vanadium (Fig. 2). Two
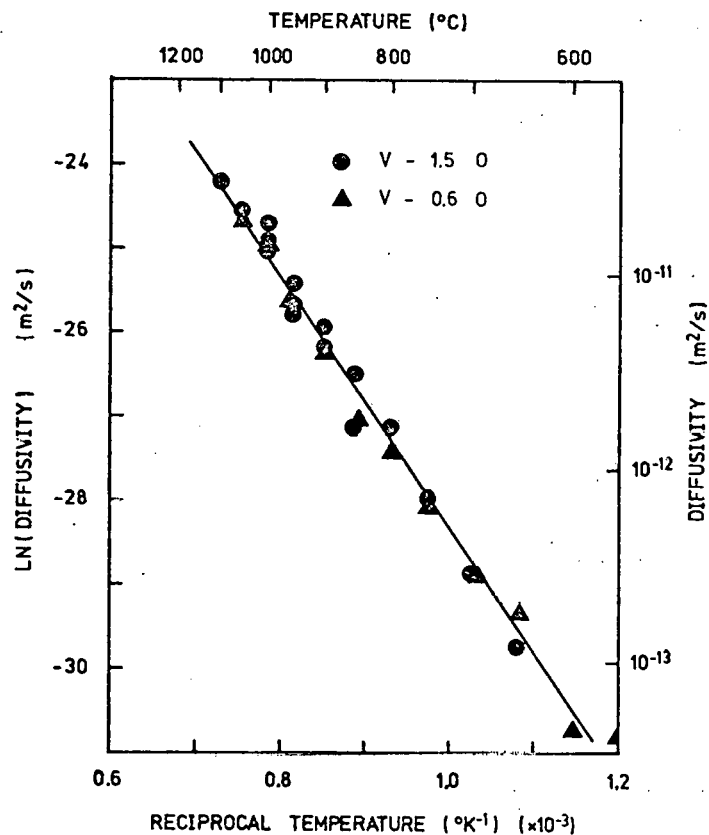

Fig. 2 - Arrhenius plot for oxygen diffusion in V-0.6 O and V-1.5 O binary alloys. The line is the best fit through the data points.

different oxygen concentrations were used for the binary V-O alloy (Fig. 2) and the V-Cr alloy (Fig. 3).

The activation energy for oxygen diffusion was usually greater in the substitutional alloys than in pure V, except for the oxygen diffusivity in the V-1.2Ti and V-0.96Ni alloys, which coincided with pure V within the experimental error. No evidence for oxygen diffusion with traps was found for any of the more dilute alloys (1 at%). Both V-3.5Nb (Fig. 4) and V-3.6Ta (Fig. 5) alloys presented oxygen diffusivities below the pure V line. This is characteristic of diffusion in the presence of traps (4,9,10). The diffusion coefficients could not be determined by the above techniques for the V-1Hf-0.8 O, V-4Ti-1. O, V-4.4Ti-1.7 O, V-1Zr-0.7 O and V-1Zr-2.1 O alloys. The cell emf in these samples did not show the linear region predicted by Eq. (1). Nonetheless, the cell emf did decrease with
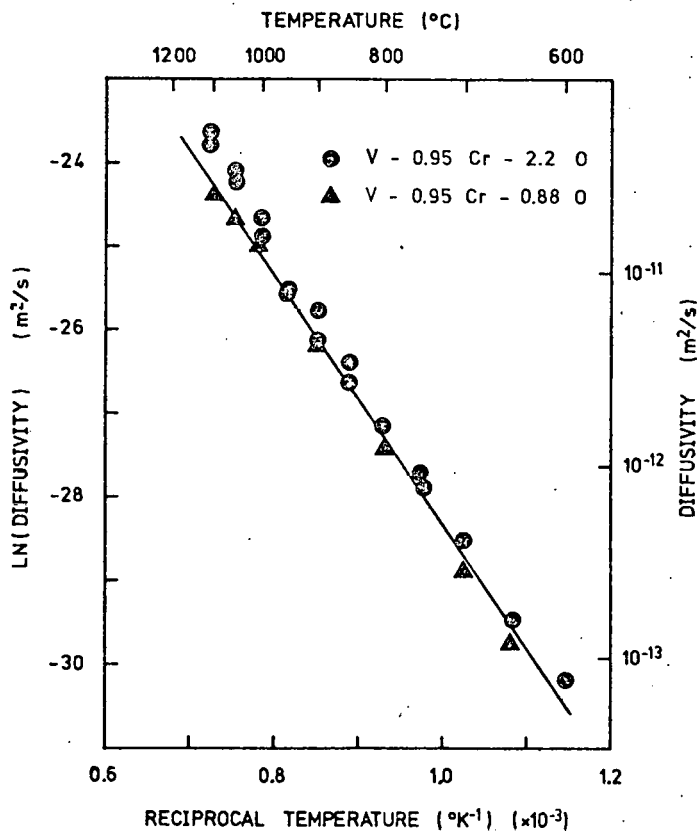

Fig. 3 - Arrhenius plot for oxygen diffusion in V-0.95 Cr alloy (points) compared to oxygen diffusion in pure vanadium (line).

time, indicating a continuous depletion of the oxygen content in these
samples. Some equilibrium measurements made with these samples proved that
there was no electronic conduction in the electrolyte, since the cell emf
eventually reached a constant value for each temperature. The existence of
a local oxygen precipitation process in the alloy is a possible explanation
for this behavior, since second phases were found in these vanadium
alloys. In particular, Zr- and Hf-rich precipitates may drain the oxygen
from the matrix thereby decreasing the cell emf as a function of time.
These precipitates then play the same role as the zirconium sink in the cell
configured for diffusion measurements (Fig. 1), except that the boundary
conditions for diffusion are entirely different and thus yield a different
solution to Fick's law. These results will be treated in a separate
paper. Similar precipitation problems have been encountered in a study of
hydrogen diffusion in vanadium alloyed with Ti and Zr (11).
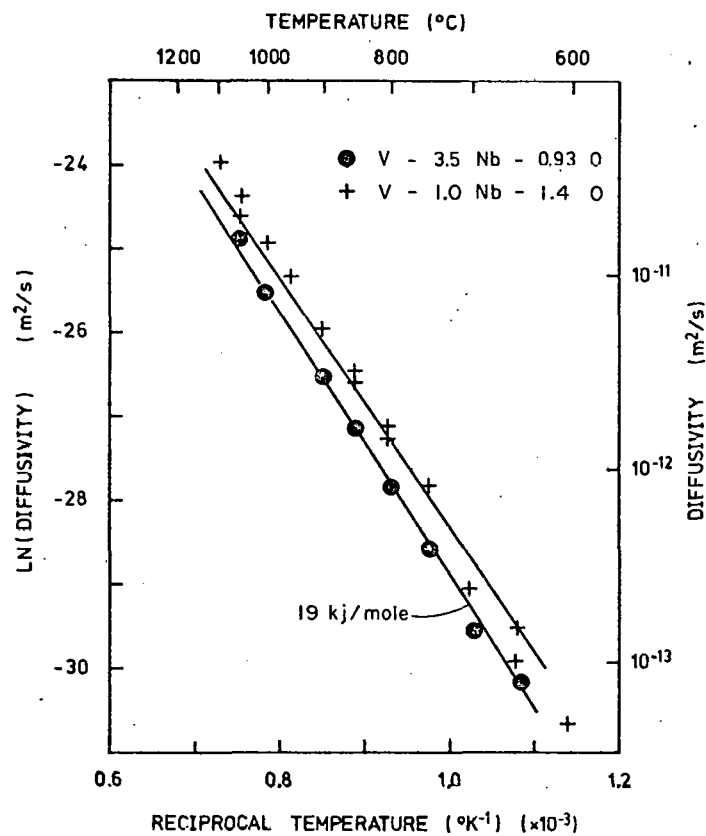

Fig. 4 - Arrhenius plot for oxygen diffusion in two V-Nb alloys (points)
         compared to oxygen diffusion in pure vanadium (upper line). The
         lower line is the prediction of Oriani's trapping model (9) for the
         V-3.5Nb-0.93 0 alloy.

Discussion

The excellent agreement of the oxygen diffusivities for vanadium doped with 1.5% and 0.6% of oxygen, Fig. 2, supports the equilibrium results that Henry's law is obeyed in V-O binary alloys up to 3% O (12). Moreover, the high temperature diffusivity measurements in this study and that of Lauf and Altstetter (4) agree very well with the diffusivity data, based mostly on low temperature internal friction measurements, compiled by Boratto and Reed-Hill (13). Their statistical calculations (14) yielded 124.7 ± 0.8 kJ/mole and -12.84 ± 0.20 for the activation energy and the natural logarithm of the pre-exponential factor ($\ln D_0$), respectively, which may be compared with the present values in Table I. The agreement is remarkably good -- within 0.8% for the activation energy and 4.5% for D_0! The oxygen diffusivities in the alloys with 1 at% Ti, Cr, Ni, Nb and Ta showed only small deviations from the Arrhenius line for oxygen diffusion in pure V, suggesting that oxygen is
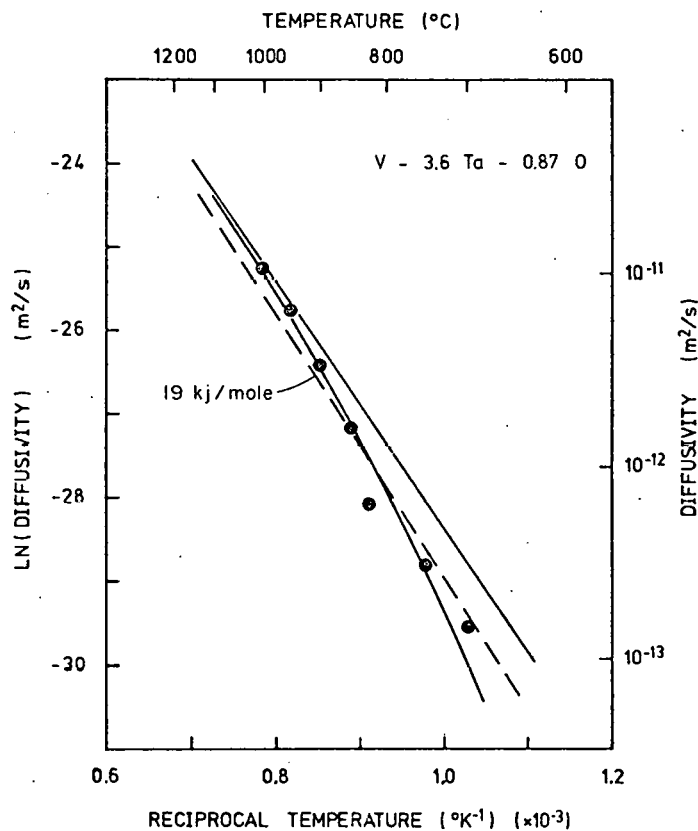

Fig. 5 - Arrhenius plot for oxygen diffusion in V-3.6Ta-0.89 O alloy (points) compared to oxygen diffusion in pure vanadium (upper line). The dashed line is the prediction of Oriani's trapping model (9) using a 19 kj/mole binding energy. The curved line assumes a temperature dependent binding energy.

not strongly trapped by these substitutional solutes in vanadium. However, the absence of an observable effect on oxygen diffusivity in these dilute alloys could also be due to a fractional occupancy of trap sites close to one, that is, trap saturation due to very strong binding. The oxygen content relative to substitutional solute content in most samples would suggest that if the trapping energy were high, possibly only one or two trap sites exist per substitutional solute atom, or else there is a binding energy less than 28 kJ/mole, if six trap sites per substitutional solute atom is assumed. Three different approaches may be attempted to handle the case of a small binding energy: extend the measurements to lower temperatures, decrease the oxygen content in the samples or increase the substitutional solute content. The lower temperature measurements are restricted by sample and electrolyte thickness, and by the electrolyte's low ionic conductivity. The lowest temperature was 873 K, due to exceedingly long time intervals required below this temperature. This was not low enough to resolve any possible trapping effects in these samples.

Two different oxygen concentrations were used with the V-.95Cr alloy, 2.2 and 0.88 at%O. The main effect, though small, was to decrease the diffusivities in the alloy with lower oxygen content providing a better agreement with the diffusivities in pure V (Fig. 3). This effect is most prominent for higher temperatures, where the changes are greater than the associated errors. Since these temperatures were the first to be measured, the oxygen concentration was very large, and the experimental diffusivities were possibly composition dependent, i.e. they were chemical diffusion coefficients. The same effect seems to be present for the V-1.0Nb alloy and for the V-0.96Ta and V-0.96Ni alloys at higher temperatures. The chemical diffusion coefficient arises whenever the activity coefficient depends on the concentration of the diffusing species. It can be related to the diffusion coefficient for an infinitely dilute solution of oxygen D_∞, by the expression (15)

$$D = D_\infty \left(1 + \frac{\delta \ln \gamma}{\delta \ln N}\right) \tag{2}$$

where γ is the activity coefficient and N the mole fraction of oxygen in solution. If the activity coefficient is given by Wagner's approximation (16), Eq. (3), the diffusivity in the ternary alloy is

$$D = D_\infty \left(1 + N\varepsilon_i^{(i)}\right) \tag{3}$$

which can be approximated by an exponential function if $|N\varepsilon_i^{(i)}| << 1$

$$D = \bar{D}_\infty \exp N\varepsilon_i^{(i)} , \qquad (4)$$

where the oxygen-oxygen interaction coefficient $\varepsilon_i^{(i)}$ may be expressed as a function of temperature by Eq. (5).

$$\varepsilon_i^{(i)} = \frac{n_i^{(i)}}{RT} - \frac{\sigma_i^{(i)}}{R} \qquad (5)$$

where n and σ are enthalpy and entropy terms, respectively (17). Thus Eqs. (4) and (5) predict a change of both activation energy and preexponential factor for oxygen diffusion in the alloys whenever the oxygen solution is non-Henrian. Furthermore, the change depends on the oxygen concentration, and the diffusivity for an infinitely dilute solution is obtained whenever the concentration is low enough to satisfy Henry's law. This effect seems to be present in the two V-Cr alloys doped with different oxygen concentrations. Here the positive changes found for the alloy doped with more oxygen correspond to a positive interaction coefficient, which is probably due to repulsive oxygen-oxygen interactions (18). Although another sample with lower oxygen content was not prepared for the V-Ni alloy, it is expected that it would behave similarly to the V-Cr alloy, since equilibrium data measured on these alloys proved that these solutes have similar effects on the activity coefficient of oxygen (6). Hence, the oxygen diffusion and the equilibrium data for the Cr and Ni solute in vanadium suggest that substitutional-interstitial solute interactions are either repulsive or non-existent.

Although the oxygen diffusivities in the two dilute V-based alloys containing Nb and Ta do not present characteristics of diffusion with traps, the other two, more concentrated, Nb and Ta alloys clearly show diffusivities below the Arrhenius line for pure V, Figs. 4 and 5. Oriani's (9) and McLellan's (10) models for diffusion in the presence of traps were employed to fit the experimental diffusivities for these alloys. Both models assume no change of the saddle point energy, hence an interstitial atom has the same probability to make any jump until it is trapped. However, McLellan's model takes into account the different chemical environments for the interstitial in a pure and an alloy matrix. Both

models assume equilibrium between trapping and normal sites.

Table II

Binding Energies (kJ/mole) of Oxygen to Nb and Ta dissolved in V
(Assuming Six Trap Sites per Substitutional Solute Atom)

	Oriani Model (9)	McLellan Model (10)
Nb	18.9 ± 0.9	14.3 ± 0.6
Ta	19.4 ± 2.6	15.1 ± 1.8

Table II shows the binding energies obtained by using a nonlinear least-squares program to fit the data. Both models gave essentially the same fitting, while McLellan's model yielded smaller binding energies. Figures 4 and 5 show Arrhenius plots for oxygen diffusion in V-3.5Nb and V-3.6Ta, respectively, where one line represents the diffusivity according to Oriani's model for six trap sites per substitutional atom and the other line is for oxygen diffusion in pure V. The poor fitting for the V-3.6Ta alloy was improved (Fig. 5) by using a binding energy linearly dependent on the temperature, as proposed by Lauf and Altstetter (4). A temperature-dependent binding energy is certainly a possibility, however its absence in most Nb-based alloys except Nb-4.1Ta, and in the V-3.6Ta alloy suggests that it may be characteristic of Ta or possibly due to the higher substitutional solute content. A smaller number of trap sites per substitutional solute or a large fractional occupancy of the trap sites are also possible explanations for the observed oxygen diffusivities in the V-3.6Ta alloy. However, both assumptions would require less than 1 trap site/substitutional solute atom, which means that the substitutional solutes are not equivalent in their interaction with oxygen atoms. This seems to be inconsistent with the V-3.6Ta-0.87 O alloy, unless an interstitial superlattice is formed (ordering reaction), which would also lead to increasing activation energies and decreasing diffusivities, without being necessarily a diffusion with traps. Therefore, a simple model for diffusion with traps may not be valid for the V-3.6Ta or Nb-4.1Ta alloys.

The indication of only weak trapping of oxygen in the V-3.5Nb and V-3.6Ta alloys is in accord with expectations based on simple concepts of

atomic size and position in the same group of the periodic table. The fact
that trapping was not observed in the more dilute alloys with Nb and Ta is
also, then, to be expected. Trapping at metal solute pairs or higher order
clusters is an alternative explanation of the substitutional solute
dependence (11). Measurements over a broader compositional range would be
desirable to resolve this question. Equilibrium activity measurements are
being made in the same alloy systems at several oxygen and several Nb or Ta
concentrations. Preliminary indications are that the deviations from
Henry's law are slight. In the V-O binary system Henry's law is obeyed for
compositions up to 3.at% oxygen (12).

The present diffusion results in vanadium-based ternary alloys are in
sharp contrast to related results in niobium-based ternary alloys with some
of the same substitutional solutes (4). There strong oxygen trapping
(binding energies between 50 and 70 kj/mole) was observed for Ti, V and Zr
in niobium. The greater solubility of oxygen and significantly lower oxygen
chemical potential in vanadium compared to niobium is probably an important
factor and may be due to the same fundamental cause. Comparison of solute
behavior in Nb and V based on concepts of atomic size and electronic
structure will be discussed in a separate paper. Measurements on Ta-based
alloys are presently under way.

Conclusions

1. Wagner's solid state electrolytic cell technique provides a powerful
   tool for studying not only equilibrium but also kinetic behavior.

2. Oxygen diffusion in vanadium was not significantly modified by small
   additions of Ti, Cr, Ni, Nb and Ta.

3. The small increase in the activation energy for oxygen diffusion in the
   V-based alloys containing Cr, Ni, Nb and Ta probably reflects the effect
   of these substitutional solutes on the activity coefficient of oxygen.

4. Additions of several percent of Nb or Ta give indications of trapping
   with a binding energy of approximately 20 kj/mole, using either the
   Oriani or McLellan models of trapping.

Acknowledgements

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