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OXYGEN DIFFUSION IN VANADIUM-BASED ALLOYS

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THESIS

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OXYGEN DIFFUSION IN VANADIUM-BASED ALLOYS

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The experimental study of transport and equilibrium properties of oxygen in vanadium-based alloys was made by EMF measurements on solid electrolytic cells over the temperature range of 873-1423°K. The oxygen diffusion in vanadium was not significantly modified by small additions of Ti, Cr, Ni, Nb and Ta. The 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. The oxygen activity was increased by the addition of 1 at% of Cr, Ni and Nb, and decreased by the addition of Ti and Ta. However, the effects in the alloys containing Nb and Ta are very small.

Approximate values for the first order elastic interaction energy between a substitutional solute and oxygen interstitial were computed and compared with the oxygen binding energies to substitutional solutes in niobium. These comparisons together with the present results for the vanadium system suggest that the main contribution to the interactions between substitutional-interstitial solutes arises from chemical effects.

The EMF technique was shown capable of monitoring the kinetics of a precipitation process. The oxygen precipitation in vanadium alloys containing Ti, Zr and Hf certainly suggests attractive interactions between oxygen and these solutes.

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1. 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 will be concerned with the theoretical and experimental evaluation of substitutional-interstitial (S-I) interactions and the diffusion of interstitials under the influence of trapping centers.

The technique of Kirchheim et al.^[1] and Lauf^[2] was used for making oxygen diffusion measurements in vanadium and its dilute substitutional alloys. This technique utilizes EMF measurements on solid electrolytic cells incorporating a zirconium sink, which drains the oxygen from one of the electrodes, resulting in a time-dependent EMF. This can be used to calculate the diffusivity of oxygen. Equilibrium cell measurements were made by eliminating the zirconium sink.

1.1 Theory of Substitutional-Interstitial Interactions

The continuum elastic theory proposed by Eshelby^[3] was one of the first to account for the elastic interaction of point defects. He considered a body containing two systems of internal stresses. If the sources of one system of internal

stress S lie entirely within the surface Σ , and the sources of the other system T lie entirely outside Σ , a fictitious distribution of body forces F^S inside Σ can be defined such that it produces the same stress on and outside Σ as does the actual source of internal stress S within Σ . The elastic interaction energy, ΔE_{el} , is given by a volume integral taken over the interior of Σ ,

$$\Delta E_{el}(S,T) = - \int \underline{F}^S \cdot \underline{u}^T dr \quad (1)$$

where $\underline{u}^T$ is the displacement field produced by the system T . However, continuum elasticity clearly breaks down at atomic distances and, therefore, can not be used to compute the displacement field and distribution of forces around a solute atom or other point defect.

Savino^[4] extended Eq. (1) to include the discrete nature of the lattice through a proper calculation of $\underline{F}^S$ and $\underline{u}^T$, and replacing the integral by a summation over lattice points. He assumed the core of a point defect S to be enclosed by a surface Σ , far enough to satisfy approximately the equation

$$\underline{u}^S = \epsilon^S \underline{x}^0 \quad (2)$$

in the absence of other strain sources in the crystal, where ϵ^S is a homogeneous strain field and $\underline{x}^0$ the perfect lattice position. Furthermore, if an equivalent expression for the displacements arising from the interacting defect or source of internal stress T is assumed valid on and within Σ

$$\underline{u}^T = \epsilon^T \underline{X}^O. \quad (3)$$

Then the atomic configuration of a block Σ , containing the defect S , must be solved with boundary conditions

$$\underline{u}^\Sigma = \underline{u}^S + \underline{u}^T = (\epsilon^S + \epsilon^T) \underline{X}^O. \quad (4)$$

Once the displacements $\underline{u}^S$ are calculated, the forces $\underline{F}^S$ (Eq. (1)) correspond to the Kanzaki forces^[5] defined as:

$$\underline{F}^S = \phi^O \underline{u}^S \quad (5)$$

ϕ^O being the perfect lattice force constant matrix.

In order to determine the forces $\underline{F}^S$, the effect of the boundary displacements (Eq. (4)) can be introduced through a change in these forces

$$\delta \underline{F} = - \underline{t} \cdot \underline{u}^\Sigma \quad (6)$$

where the matrix $\underline{t}$ describes the changes induced on the perfect lattice coupling forces by the defect S .^[6] Hence, the Kanzaki forces are

$$\begin{aligned} \underline{F}^S &= \underline{F}^{OS} + \delta \underline{F} \\ &= \underline{F}^{OS} - \underline{t}(\epsilon^S + \epsilon^T) \underline{X}^O \\ &= \underline{F}^{OS} - \underline{t} \epsilon^T \underline{X}^O \end{aligned} \quad (7)$$

where $\underline{F}^{OS}$ corresponds to a set of Kanzaki forces obtained if the boundary atoms had remained at the perfect lattice position, and the forces $\underline{F}^{OS}$ are the Kanzaki forces corresponding to a

single defect S in an infinite crystal. Substituting Eqs. (3) and (7) in Eq. (1), the interaction energy is

$$\begin{aligned}\Delta E_{el}(S,T) &= - \sum (\underline{F}^S - \underline{t} \underline{u}^T) \underline{u}^T \\ &= - \sum \underline{F}^S \underline{u}^T + \sum \underline{t} \underline{u}^T \underline{u}^T .\end{aligned}\quad (8)$$

The first term in Eq. (8) corresponds to the first order size interaction energy. The second term arises because the lattice response to an applied stress in the vicinity of the point defect differs from the response in the defect-free matrix. However, the interaction energy given by Eq. (8) is a crude approximation for close point defects when it may be impossible to define the surface Σ properly, i.e., the two point defects can not be distinguished.

Another way to determine the elastic interaction energy between two point defects S and T is to subtract the total elastic energy stored in the crystal when each defect is present alone, E_S and E_T , from the total elastic energy due to the interacting defects S and T , E_{ST} ,

$$\Delta E_{el}(S,T) = E_{ST} - E_S - E_T . \quad (9)$$

Both Eqs. (8) and (9) require the knowledge of the forces and displacements produced by the defects. This can be reached through different approaches such as pair potential,^[7] Kanzaki forces,^[5,8] and Green's function.^[9] The Green's function formalism for lattice statics^[9] will be employed to study the defect configurations. However, its limitations must be kept in mind.

The lattice is described by the Born-von Kármán model, in which any attempt to displace an atom from its equilibrium position is resisted by a harmonic restoring force directed towards the equilibrium site and proportional to the atomic displacement. The other two main assumptions are the adiabatic approximation and the cyclic boundary conditions. The first assumes that the electrons follow the motion of the nuclei adiabatically, hence the nuclei motions can be treated independently of the electrons in so far as the effect of the electrons are included in terms of the interactions between the nuclei. The last assumption implies that the whole crystal can be divided into identical super-cells with a large but finite number of atoms. So it avoids complications due to surface effects. Furthermore, from symmetry considerations, there is no net force $\underline{F}(\underline{I})$ on each atom at site $\underline{I}$ of a perfect lattice.

The introduction of a point defect in an otherwise perfect lattice modifies it in two ways. It will exert forces on the host atoms so that $\underline{F}(\underline{I})$ does not vanish, and the force constants will be modified and thus change the Green's functions of the lattice. If the potential energy is minimized with respect to the atomic displacements, the lattice distortion $\underline{u}$ is given by the following matrix equation:

$$\underline{u} = \underline{G}^* \underline{F} \quad (10)$$

or

$$u_{\alpha}(\underline{I}) = \sum_{\beta \underline{I}'} G_{\alpha\beta}^*(\underline{I}, \underline{I}') F_{\beta}(\underline{I}') \quad (11)$$

where $\underline{G}^*$ is the defect Green's function and $\underline{F}$ is the applied force at the lattice sites. The above formalism is equivalent to the Kanzaki method^[5] with the displacements given by

$$\underline{u} = \underline{G} \underline{F}^* \quad (12)$$

where $\underline{G}$ is the Green's function for the perfect lattice, and $\underline{F}^*$ can be interpreted as the force due to the defect on the host atoms at their relaxed positions, i.e., the Kanzaki forces. Hence, the relaxation energy of the defect, defined as the change in the elastic energy of the lattice due to the point defect, is:

$$E_{el} = - \frac{1}{2} \sum \underline{F}^*(\underline{I}) \underline{u}(\underline{I}) \quad (13)$$

where the summation is to be performed over all the sites $\underline{I}$.

The interaction energy calculated by Eqs. (8) or (9) can not, however, account for the "chemical" interaction except, perhaps, through an indirect way in the calculation of the Kanzaki forces. A point defect in an otherwise perfect lattice will definitely alter the surrounding electronic distribution of the matrix. Therefore, the modified electronic structure around two point defects must result in a chemical interaction between them. Blandin and Deplanté^[10,11] showed that the chemical interaction would be proportional to the product of the charge difference between the impurities and the matrix atoms. They got reasonable agreement between theory and experimental data for transition metal impurities in normal

metals. Friedel^[12] discussed the electronic structure of hydrogen in metals using a screened potential approach similar to Blandin and Deplanté. He concluded that hydrogen should be attracted at very short range by substitutional impurities with a lower valency than the matrix but repelled by impurities with a higher valency than the matrix, when hydrogen forms a dilute solid solution in a matrix of either normal or transition metals.

Masuda and Mori^[13] investigated the electronic interaction between two interstitial atoms (I-I interactions) and substitutional-interstitial atoms (S-I interactions) in transition metals. They represented the d bands in transition metals by a single band (tight-binding approximation) and neglected the sp band. As further simplifications, they used a single-site potential in the Wannier representation for the substitutional atom, assumed the interstitial solute atom to have a single energy level, and considered only nearest-neighbor interactions in a simple cubic or body-centered cubic lattice. Their conclusions based on computer calculations parallel those reached by Friedel^[12] in his simple description of hydrogen in metals.

Demangeat, Gautier and Parlebas^[14,15] developed a more general description of the electronic structure of an interstitial atom in a ferromagnetic transition metal. Again, the tight-binding approximation was used for the host metal which was characterized by a single hybridized d and sp band. Moreover, they considered only interactions between the host "d"

band and the interstitial "p" orbitals. Their results for the binding energy of a pair of carbon atoms in α -iron give the same strong anisotropy found by elastic calculations, but it seems the elastic interaction dominates. They also determined the S-I interactions in bcc transition metals, where they assumed the d orbitals of the impurity substitutional atom were localized on the impurity site. They proved that, as a first approximation, the electronic (chemical) interaction energy is proportional to the difference of charge ΔZ between the substitutional impurity and the matrix ionic cores

$$\Delta E_{\text{chem}} \sim \Delta Z \quad (14)$$

which is in qualitative accord with the results described in the previous paragraphs, although Eq. (14) is only valid for $|\Delta Z| < 1$.

McLellan^[16-18] has analyzed a variety of liquid and solid ternary solutions containing H, O, N and C. He calculated the difference between interstitial-substitutional, E_{IS} , and interstitial-matrix, E_{IM} , nearest-neighbor bond energies

$$\Delta E = E_{\text{IS}} - E_{\text{IM}} \quad (15)$$

and plotted it against the function

$$f = (X_{\text{S}} - X_{\text{I}})^2 - (X_{\text{M}} - X_{\text{I}})^2 \quad (16)$$

where X_{S} , X_{M} , and X_{I} are the Allred-Rochow^[19] electronegativities of the various atomic species. The degree of

correlation was excellent for both solid and liquid solutions. Furthermore, the sign of the binding energy for all solutions involving transition metal impurities agrees with Eq. (14), as shown in Table I for a few ternary solid solutions.

The most striking correlation obtained from the data in Table I is, perhaps, that the binding energies and the size factors present the same trends as ΔZ , both in sign and magnitude, for substitutional solutes belonging to the same period as the solvent. This semiquantitative agreement is valid even for $|\Delta Z| > 1$ when the approximations leading to Eq. (14) are no longer valid. Hence, it suggests that the S-I binding energies depend on the electronic structure of the substitutional solute and solvent atoms. This correlation, however, fails when the substitutional atom belongs to the same group as the solvent and $\Delta Z = 0$, e.g., Ta and V in Nb. Since Eq. (14) was derived for $|\Delta Z| < 1$, the failure seems to indicate that not all valence electrons participate in the S-I interaction.

It is worthwhile to emphasize the connection between the elastic and electronic models of a point defect. As it has already been mentioned, the introduction of a point defect exerts forces $\underline{F}(\underline{I})$ on the surrounding atoms of the initially perfect lattice. Hardy^[20] established the link between this local property and the dilation volume of the crystal caused by the defect, a macroscopic property. Tewary^[9] generalized Hardy's argument for those defect configurations which have

Table I

Substitutional-Interstitial Interaction Energies in Transition Metal Alloys

Solvent	Interstitial	Substitutional	ΔE kJ/mole	Size Factor* $\Omega\%$	ΔZ (ds bands)
Fe ^[16]	C	Cu	+6.36	-2.0	1
		Al	-0.33	13.6	—
		Mn	-3.89	8.0	-1
		Cr	-12.52	0.6	-2
V ^[17]	H	Ti	-3.05	9.3	-1
		Cr	+3.53	-4.4	+1
		Fe	+6.72	-4.9	+3
		Co	+8.80	-6.6	+4

Table I continued

Solvent	Interstitial	Substitutional	ΔE kJ/mole	Size Factor* $\Omega\%$	ΔZ (ds bands)
Nb [2,64]	O	V	-52.8	-7.9	0
		Ta	-28.8	-0.3	0
		Ti	-67.2	-0.8	-1
		Zr	-67.2	9.6	-1

* Calculated from the atomic volumes of substitutional solute, Ω_s , and solvent, Ω_m , atoms according to

$$\Omega = \frac{1}{3} \frac{\Omega_s - \Omega_m}{\Omega_m} .$$

at least the operators $\bar{x}yz$, $x\bar{y}z$, and $xy\bar{z}$ in their point groups (the overhead bar denotes the minus sign), whence the dipole or double force tensor

$$P_{\alpha\beta} = \sum_I F_{\alpha}^*(I) R_{\beta}(I), \quad (17)$$

where $F^*(I)$ is the Kanzaki force (cf. Eq. (12)) on the atom I and $R(I)$ is the radius vector for the site I , will be given by its diagonal elements, $P_{\alpha\alpha}$. Provided the above condition is satisfied, the change in the total volume of the crystal due to the introduction of a point defect is

$$\Delta V = \frac{\text{Trace } P}{3K} \quad (18)$$

K being the bulk modulus of the solid (for a cubic crystal $K = (C_{11} + 2C_{12})/3$, where C_{11} and C_{12} are the elastic constants). The force $F^*(I)$ can be interpreted as the force due to the point defect on the host atoms at their relaxed positions:

$$F^*(I) = - \left. \frac{\partial V(r)}{\partial \underline{r}} \right|_{\underline{r}=\underline{r}(I)+\underline{u}(I)} \quad (19)$$

where $V(r)$ gives the pair potential for the defect-host interaction.

Schober and Ingle^[21] have pointed out that Eq. (19) is only an approximation since it does not take into account the anharmonic terms present in the crystal. Hence, any computed values based on Eq. (19), e.g., Eqs. (8), (12) and (17) must be regarded as approximations. However, Eq. (19) together

with Eqs. (17) and (18) provide a link between the elastic and electronic models, and experimental data reported in the literature for the change of volume of a crystal. Although the pair potential for the defect-host interaction is usually determined from empirical or semiempirical potentials,^[7] it can be evaluated from the basic electronic structure of the defect and host atoms. Moraitis and Gautier^[22] performed a simple calculation of the band-structure contribution to the dipole tensor of dilute transition metal solutions within the tight-binding formalism (cf. earlier paragraphs and references therein). Their most important approximation is in the calculation of the Kanzaki forces $\underline{F}^*(\underline{I})$, where they substituted the derivative of the pair potential $V(\underline{r})$ for the variation of the total energy of the system due to the displacement $\underline{u}(\underline{I})$ of the atom at site $\underline{I}$, but evaluated it in the unrelaxed configuration. In spite of their approximations, their results have good qualitative and even semiquantitative agreement with experimental data which suggests that the evolution of the dipole tensor P along the transition series is mainly given by the electronic structure. However, as they emphasized, a detailed calculation of the repulsive term must be done to confirm this conclusion.

The band structure calculations of binding energies between interstitial and substitutional atoms, and of the dipole tensor for substitutional impurities, together with the correlations between binding energies and electronegativities suggest that both the lattice distortion due to point defects and the

interaction energies between them are dependent on the electronic structure of point defect and matrix. This is not a very surprising result; nonetheless it means that it may be misleading to try to separate the interaction energy between two point defects into strain and electronic, or chemical, components.

1.2 Lattice Distortion and Interaction Energies

The Green's function method will be used to estimate the lattice distortion around a point defect in an "infinite" bcc lattice. Expressions for lattice distortion around a substitutional and an interstitial atom will be provided together with an approximate value for their elastic interaction energy. Numerical values will be provided for oxygen interstitial and V, Ta, Ti, Zr and Hf substitutional solutes in niobium.

Since G in Eq. (12) denotes the perfect lattice Green's function, its matrix elements $G_{\alpha\beta}(\underline{I}, \underline{I}')$ will depend on the positions $\underline{I}$ and $\underline{I}'$ only through their difference:

$$G_{\alpha\beta}(\underline{I}, \underline{I}') = G_{\alpha\beta}(\underline{I} - \underline{I}') \quad (20)$$

Further, in a cubic lattice $G_{\alpha\beta}(\underline{I} - \underline{I}')$ is symmetric in α and β , so the two Cartesian indices can be replaced by Voigt's notation, where the single index i goes from 1 to 6. The following notation will be used for the Green's function matrix elements

$$G_{\alpha\beta}(\underline{I}) = \Gamma_i^n \quad (I \neq 0) \quad (21)$$

and

$$G_{\alpha\beta}(\underline{I} = 0) = \Gamma^0 \delta_{\alpha\beta} \quad (22)$$

where n is a label for the invariant subspace of $\underline{I}$ and $\delta_{\alpha\beta}$ is the Kronecker delta. The perfect lattice Green's function for niobium was taken from Schober et al. [27]

The lattice distortions for an atom in an octahedral interstice were derived assuming that this atom interacts with only its two nearest lattice atom neighbors and its four next-nearest neighbors. If the interstitial atom is at the origin, it causes forces $(0,0,\pm F_1)$ on its nearest neighbor atoms in positions $(0,0,\pm 1)^*$, and forces $(\pm F_2, \pm F_2, 0)$ on its next-nearest neighbor atoms in positions $(\pm 1, \pm 1, 0)$. The displacements of the surrounding atoms due to these forces are shown in Tables II and III. The displacements on other neighbors can be determined from the configuration symmetry. The forces exerted by the interstitial atom on its neighbors can not be calculated from Eq. (17) alone, and the difference between the dipole tensor elements P_{zz} and $P_{xx} = P_{yy}$ is obtained from internal friction measurements. [24] This problem has been solved for hydrogen, oxygen and nitrogen interstitials in niobium, tantalum and vanadium, [25,26] which provided $F_1 = 3.573 \text{ eV/\AA}$ and $F_2 = 0.740 \text{ eV/\AA}$ for oxygen interstitial in niobium. [25] Numerical values for the displacements caused by an oxygen interstitial in niobium are also shown in Table III.

* One-half cubic dimensions are used throughout.

Table II

Forces and Displacements Induced by an Interstitial Atom in an Octahedral Site of a
bcc Lattice on its Nearest Neighbors

Neighbor Shell	Lattice Site [*]	Displacements	Kanzaki Forces
1	001	0 0 U_1	0 0 F_1
2	110	U_2 U_2 0	F_2 F_2 0
3	021	0 U_3^2 U_3^1	_____
4	112	U_4^1 U_4^1 U_4^2	_____
5	221	U_5^2 U_5^2 U_5^1	_____
5	003	0 0 U_5^3	_____
6	130	U_6^1 U_6^3 0	_____

*The interstitial is at the origin 000.

Table III

Theoretical Expressions and Numerical Values for the Displacements Induced by an
Oxygen Interstitial in Niobium

Displacement	Expression	U/a*
U_1	$(\Gamma_o - \Gamma_1^2)F_1 - 8\Gamma_6^1F_2$	0.282
U_2	$-2\Gamma_6^1F_1 + (\Gamma_o - \Gamma_1^2 + \Gamma_2^2 - \Gamma_1^3 - \Gamma_6^3)F_2$	0.012
U_3^1	$-\Gamma_6^3F_1 + 2(\Gamma_1^1 - \Gamma_6^1 - \Gamma_1^4 - \Gamma_6^4)F_2$	-0.015
U_3^2	$(\Gamma_2^2 - \Gamma_1^3)F_1 - 2(\Gamma_4^4 + \Gamma_6^4)F_2$	-0.001
U_4^1	$(\Gamma_6^1 - \Gamma_6^4)F_1 + (\Gamma_2^2 - \Gamma_1^5 - \Gamma_6^5)F_2$	0.021
U_4^2	$(\Gamma_1^1 - \Gamma_1^4)F_1 - 2(\Gamma_6^3 + \Gamma_6^5)F_2$	0.046

Table III continued

Displacement	Expression	U/a*
U_5^1	$(\Gamma_3^3 - \Gamma_1^5)F_1 + 2(\Gamma_6^1 + \Gamma_4^4 - \Gamma_6^4 - \Gamma_6^7)F_2$	-0.006
U_5^2	$-\Gamma_6^5F_1 + (\Gamma_1^1 + \Gamma_6^1 - \Gamma_1^4 + \Gamma_2^4 - \Gamma_2^7 - \Gamma_4^7)F_2$	0.005
U_5^3	$-8\Gamma_6^4F_2$	-0.022
U_6^1	$(\Gamma_2^2 - \Gamma_1^3 + \Gamma_6^3 + \Gamma_2^6 - \Gamma_2^8 - \Gamma_6^8)F_2$	0.002
U_6^3	$(\Gamma_1^2 + \Gamma_1^3 - \Gamma_6^3 - \Gamma_1^6 - \Gamma_1^8 - \Gamma_6^8)F_2$	0.020

*2a $\equiv$ lattice parameter, 3.3066 Å for Nb. [28]

The substitutional atom was also assumed to interact with only its first and second nearest neighbors. Therefore, the displacement and force on the atom in position (1,1,1) are (S_1, S_1, S_1) and (F_1, F_1, F_1) , and on the atom in position (2,0,0) are $(S_2, 0, 0)$ and $(F_2, 0, 0)$, respectively, where

$$S_1 = (\Gamma^0 - \Gamma_1^2 + 2\Gamma_2^2 - 2\Gamma_1^3 - 2\Gamma_6^3 + \Gamma_3^3 - \Gamma_1^5 - 2\Gamma_6^5)F_1 \\ + (\Gamma_1^1 - 2\Gamma_6^1 - \Gamma_1^4 - 2\Gamma_6^4)F_2 \quad (23)$$

and

$$S_2 = 4(\Gamma_1^1 - 2\Gamma_6^1 - \Gamma_1^4 - 2\Gamma_6^4)F_1 + (\Gamma^0 - 4\Gamma_6^3 - \Gamma_1^6)F_2 \quad (24)$$

The Kanzaki forces $\underline{F}_1$ and $\underline{F}_2$ induce displacements on all atoms around the defect. Hence, the atom in (2,2,0) is displaced by $(S_3, S_3, 0)$ where

$$S_3 = 2(\Gamma_1^1 + \Gamma_6^1 - \Gamma_1^4 + \Gamma_2^4 - \Gamma_4^4 - \Gamma_6^4 - \Gamma_2^7 - \Gamma_4^7 - \Gamma_6^7)F_1 \\ + (\Gamma_2^2 - 2\Gamma_6^5 - \Gamma_6^8)F_2 \quad (25)$$

The Kanzaki forces are related to the dipole tensor through Eqs. (17) and (18).

$$8\sqrt{3} aF_1 + 12aF_2 = \frac{\text{Trace } P}{3} = K\Delta V \quad (26)$$

where $2a$ is the lattice parameter, K is the bulk modulus and ΔV is the change in the volume of the crystal due to the introduction of the point defect. Equation (26), however,

contains two unknowns which can not be determined without another relation. A proper approach requires, for example, the definition of a pair potential for the solute-solvent interaction which, then, would be used to calculate the forces from Eq. (19). However, the distance from the substitutional solute atom to its second nearest neighbors is only 15% larger than to its first nearest neighbors, and the forces $\underline{F}_1$ and $\underline{F}_2$ are expected to have the same order of magnitude.^[23] Hence, the simplest approximation is to assume

$$|\underline{F}_2| = \alpha |\underline{F}_1| \quad (27)$$

where α is a positive number close to one, and use Eq. (26) to determine the forces $\underline{F}_1$ and $\underline{F}_2$. Table IV presents the lattice distortions around different substitutional solutes in a niobium matrix assuming $\alpha = 1/\sqrt{3}$ and $\alpha = 1$. The displacements of the first and second nearest neighbor atoms around a substitutional solute are slightly dependent on the values chosen for the Kanzaki forces $\underline{F}_1$ and $\underline{F}_2$, while the displacements of the third nearest neighbors are practically independent. Further, all the atoms of the three nearest neighbor shells are either pulled away or pushed towards the substitutional solute, depending on the sign of the variation of the lattice parameter.

Expressions for the first order elastic interaction energy between substitutional and interstitial solute atoms will be given for the two nearest neighbor configurations, for example, positions I and J in Fig. 1. For both configurations it will

Table IV

Lattice Distortions around Substitutional Solutes in Niobium

Solute	V	Ti	Zr	Ta	Hf
$\frac{1}{a} \frac{da}{dc} (\%)^*$	-4.11	-1.29	6.65	-0.26	5.18
Trace P (eV)	-7.17	-2.25	11.61	-0.45	9.03
Approximation $ \underline{F}_1 = \underline{F}_2 $					
F_1 (eV/Å) [°]	-0.042	-0.013	0.068	-0.003	0.053
F_2 (eV/Å) [°]	-0.072	-0.023	0.117	-0.005	0.091
$S_1/a (\%)^{\dagger}$	-0.27	-0.08	0.44	-0.02	0.34
$S_2/a (\%)^{\dagger}$	-0.59	-0.19	0.97	-0.04	0.75
$S_3/a (\%)^{\dagger}$	-0.34	-0.11	0.55	-0.02	0.42
Approximation $ \underline{F}_1 = \sqrt{3} \underline{F}_2 $					
$F_1 = F_2$ (eV/Å) [°]	-0.056	-0.018	0.091	-0.004	0.070
$S_1/a (\%)^{\dagger}$	-0.39	-0.13	0.63	-0.03	0.48
$S_2/a (\%)^{\dagger}$	-0.41	-0.13	0.67	-0.03	0.51
$S_3/a (\%)^{\dagger}$	-0.33	-0.10	0.53	-0.02	0.41

*Calculated from data. [28]

[†]2a $\equiv$ lattice parameter, 3.3066 Å for Nb. [28]

Figure 1. Substitutional and interstitial nearest neighbor configurations.

be assumed that substitutional and interstitial atoms do not have direct interaction, so the net force exerted on each of these atoms by the whole lattice when they are in their relaxed positions is zero. [29] As further simplification, the Kanzaki forces exerted by these atoms on their neighbors are the same as when each of them is alone in the lattice, which is equivalent to assuming that the coupling forces between one defect and the host atoms are not changed by the presence of another defect. Then, Eq. (19) may be rewritten as

$$\Delta E_{el}(S,T) = -\frac{1}{2} \Sigma (F_S U_T + F_T U_S) \quad (28)$$

where the Kanzaki forces F_S and F_T , and displacements U_S and U_T for the defects S and T are calculated when each defect is alone in an otherwise perfect lattice. Hence, the first order elastic interaction energies are

$$\begin{aligned} \Delta E_{el}(I) = & -\frac{1}{2} [F_1 S_2 + 8F_2 S_1 + 4(2U_2 + 2U_4^1 + U_4^2)F_1 \\ & + (U_1 + U_5^3 + 4U_3^2)F_2] \end{aligned} \quad (29)$$

and

$$\begin{aligned} \Delta E_{el}(J) = & - [F_1 S_1 + F_2 (S_2 + S_3) + (U_1 + 2U_3^1 + 2U_3^2 \\ & + U_5^1 + 2U_5^2)F_1 + (U_2 + U_6^3 + U_4^2)F_2] \end{aligned} \quad (30)$$

for the first and second nearest neighbor configurations, respectively (I and J, Fig. 1).

Table V provides the first order elastic interaction energies for different substitutional solutes and interstitial oxygen in niobium. The absolute values of the Kanzaki forces have much smaller effects on the S-I elastic interaction energies than on the lattice distortion around a substitutional solute. Further, the interaction energy for the two nearest neighbor positions has the same sign, being attractive when the substitutional atom dilates the host crystal and vice versa, while continuum elasticity predicts an opposite sign for the S-I interaction energy when the interstitial occupies the nearest neighbor position (position I in Fig. 1).^[3] This result probably reflects the effect of the distribution of the Kanzaki forces among the first and second neighbors of the substitutional solute. However, the inclusion of the changes of the coupling forces between one defect and the host atoms induced by the other defect may reverse the sign of the interaction energies, as pointed out by Dederichs et al.^[30] for the interaction between self-interstitial and substitutional solutes in a fcc crystal. A comparison of these elastic interaction energies with the oxygen binding energies for Nb-based alloys reveals that they are only a small fraction of the experimental binding energies. Hence, these calculations suggest that the experimental binding energies arise mainly from electronic interactions between substitutional and interstitial solutes which may cause changes of the coupling forces (cf. Eqs. (6) and (7)) or direct chemical interaction between substitutional and interstitial solutes.

Table V

First Order Elastic Interaction Energies Between
Substitutional and Oxygen Interstitial Solutes in Niobium

Solute	Experimental Binding Energy ^[50] (eV)	S-I Interaction Energies (eV) [*]			
		Approximation $ \underline{F}_1 = \underline{F}_2 $		Approximation $ \underline{F}_1 = \sqrt{3} \underline{F}_2 $	
		$\Delta E_{el}(I)$	$\Delta E_{el}(J)$	$\Delta E_{el}(I)$	$\Delta E_{el}(J)$
V	0.55	0.064	0.062	0.062	0.054
Ti	0.7	0.021	0.020	0.020	0.017
Zr	0.7	-0.104	-0.101	-0.100	-0.088
Ta	0.3	0.005	0.004	0.004	0.004
Hf	—	-0.080	-0.078	-0.078	-0.069

* I and J refer to alternative interstitial site occupations, Fig. 1.

Unfortunately, similar calculations can not be done for the vanadium-based alloys because an extensive table for the perfect lattice Green's function matrix elements is not available.

1.3 Models for Diffusion with Traps

The activated migration of an interstitial atom from one equilibrium position to another is accomplished whenever the atom acquires enough energy to surmount the barrier between the two potential minima. When no other effects are present, all interstitial sites are equivalent and the atom has the same probability to jump to any site. The introduction of a defect, e.g., a substitutional or an interstitial atom, affects the potential energy of the surrounding interstitial sites. This perturbation may have either a short- or long-range character,^[31] and both the potential maxima and minima may be altered. A trap is formed when the potential energy of a site is lowered with respect to normal sites (Fig. 2). Hence, a particle in a trap site has lower probability to jump to a neighboring site than a particle in a normal site. Figure 2 depicts a trap site which exerts an effective attraction for atoms in its nearest neighbors through the lowering of the potential energy maximum.

Many models have been proposed to explain the effect of traps on the interstitial diffusion. Some models are very general but either require extensive use of a computer^[32-34] or the expressions for the diffusion coefficient are too

Figure 2. Diagram of the potential energy; T trap site, N normal site, ΔE_T trapping energy and ΔE_S change of the saddle point energy.

involved.^[35-37] These models, therefore, can not be easily compared with experimental data. Simple models have their own limitations, however, they provide a consistent description of the experimental data within their validity. Three simple models are presented in this section. The models proposed by Oriani^[38] and McLellan^[39] assume no change of the saddle point energy ($\Delta E_s = 0$ in Fig. 2); hence the atom has the same probability to make any jump until it is trapped. The model proposed by McNabb and Foster^[40] is phenomenological and does not assume any atomistic configuration for the traps.

Oriani's model^[38] is analyzed without the restriction of small trap population and it is shown that it leads to the major characteristics of diffusion with traps.

The flux of interstitial atoms, Fick's first law, can be written in terms of their concentration on normal sites, C_n , or in terms of the total concentration, $C_n + C_t$, where C_t is the concentration upon trap sites. However, the flux must be the same and independent of either formulation. Hence, one obtains a relation between the diffusion coefficient in a normal lattice, D_n , and in a lattice with traps, D :

$$\frac{D}{D_n} = \frac{1}{1 + \frac{dC_t}{dC_n}} \quad (31)$$

The derivative dC_t/dC_n in Eq. (31) may be evaluated if only one kind of traps exists in the crystal and the population of trapped interstitials is in equilibrium with the

population upon normal sites. These conditions lead to the following relation between the fractional occupancy of trap sites, θ_t , and normal sites, θ_n :

$$\frac{\theta_t}{1 - \theta_t} = \frac{\theta_n}{1 - \theta_n} \exp - \frac{\Delta g}{kT} \quad (32)$$

where $\Delta g = \Delta h - T\Delta S$, with Δh , the partial molar enthalpy, and ΔS , the change of the nonconfigurational entropy associated with an atom at a trap site; k and T have their usual meaning.

The concentrations of interstitial solute atoms in trap and normal sites are

$$C_t = \phi N_s \theta_t \quad (33)$$

and

$$C_n = [\beta(N_m + N_s) - \phi N_s] \theta_n, \quad (34)$$

where ϕ is the number of trap sites associated with a substitutional atom, β is the number of interstitial sites per lattice site, N_m and N_s are the number per unit volume of matrix and substitutional atoms, respectively. Expressing C_t as a function of C_n with Eqs. (32)-(34), and performing the derivative,

$$\frac{dC_t}{dC_n} = \frac{\tau}{1 - \tau} \left(\frac{1 - \theta_t}{1 - \theta_n} \right)^2 \exp - \frac{\Delta g}{kT} \quad (35)$$

where

$$\tau = \frac{\phi}{\beta} \frac{N_S}{N_m + N_S} = \frac{\phi}{\beta} X_S, \quad (36)$$

X_S being the atomic fraction of substitutional solute. Hence, Eq. (31) for the diffusion coefficient in a lattice with traps may be written as

$$\frac{D}{D_n} = \frac{1}{1 + \frac{\tau}{1 - \tau} \left(\frac{1 - \theta_t}{1 - \theta_n} \right)^2 \exp - \frac{\Delta g}{kT}}. \quad (37)$$

θ_t and θ_n can be derived from Eq. (32) and an expression for the total concentration of interstitials

$$N_i = C_t + C_n \quad (38)$$

which yields a quadratic equation whose solution is

$$\theta_t = \frac{-[x - (\tau+i)(x-1)] + \{[x - (\tau+i)(x-1)]^2 + 4\tau i(x-1)\}^{1/2}}{2\tau(x-1)} \quad (39)$$

where $i = N_i/\beta(N_m + N_S)$ and $x = \exp \Delta g/kT$. This result is, however, of limited application, since the total concentration of interstitials changes throughout most diffusion experiments. Nonetheless, it is important to know some limiting conditions. At the high temperature limit, $\Delta g/kT \rightarrow 0$, both θ_n and θ_t approach the same value i , and Eq. (37) can be written in its widely used form,

$$\frac{D}{D_n} = \frac{1}{1 + \frac{\tau}{1 - \tau} \exp - \frac{\Delta g}{kT}} \quad (40)$$

which also holds whenever θ_t and θ_n are much less than unity. At the low temperature limit, $|\Delta g|/kT \rightarrow \infty$, two conditions may occur. If the number of interstitials is lower than the number of trap sites, $i < \tau$, then θ_t approaches i/τ and θ_n approaches zero. However, if the number of interstitials is larger than the number of trap sites, $i > \tau$, θ_t approaches 1 and the traps have no effect on the diffusion coefficient, $D = D_n$.

Perkins and Padgett^[41] derived an expression similar to Eq. (40) through the calculation of the interstitial trapping and escape frequency. However, their model is valid even for the more general case sketched in Fig. 2, since their relation depends on the ratio of the jump frequencies from the trap site to its nearest neighbor and vice versa, and this ratio is independent of the change in the saddle point energy, ΔE_s .

McLellan's model^[39] also assumes one species of trap sites and equilibrium between the interstitial population in trapped and normal sites. However, it takes into account the different chemical environments for interstitials in a perfect crystal and in a defect crystal. From the reaction rate theory the expression for the diffusion coefficient is

$$\frac{D}{D_n} = \frac{\gamma^{dc}}{\gamma^{pc}} \cdot f \quad (41)$$

where

$$f = 1 - \frac{C_t}{N_i} + \frac{C_t}{N_i} \exp \frac{\Delta g}{kT} \quad (42)$$

and

$$\frac{\gamma^{dc}}{\gamma^{pc}} = \frac{1 - i}{1 - \theta_t} \cdot \frac{\theta_t}{i} \cdot \exp \frac{\Delta g}{kT} \quad (43)$$

the factor γ^{dc}/γ^{pc} is the ratio of the activity coefficient of interstitial atoms in a defect crystal and in a perfect crystal. The factor f is the ratio of the diffusion coefficients and can be derived from the random walk mean square displacement formalism.^[42] Furthermore, if the fractional occupancy of normal and trap sites are much smaller than unity,

$\theta_n = \theta_t \exp \Delta g/kT$, and from Eqs. (33), (34), (36) and (38),

$$C_t = \frac{\tau \cdot N_i}{\tau + (1 - \tau) \exp \frac{\Delta g}{kT}} \quad (44)$$

Substituting Eq. (44) into Eq. (42) and rearranging the expression:

$$f = \frac{1}{1 - \tau + \tau \exp - \frac{\Delta g}{kT}} = \frac{1}{1 - \tau} \cdot \frac{1}{1 + \frac{\tau}{1 - \tau} \exp - \frac{\Delta g}{kT}}, \quad (45)$$

which is equivalent to Oriani's Eq. (40) and is the relation derived by Koiwa^[32] for the same limits. Hence, from Eq. (45) and the limit of Eq. (43) for $\theta_t, \theta_n \ll 1$, McLellan's model yields the following relation for the diffusion coefficient

$$\left(\frac{D}{D_n}\right)^{1/2} = \frac{1}{1 - \tau + \tau \exp - \frac{\Delta g}{kT}} \quad (46)$$

when the fractional occupancy of trap sites is much smaller than unity.

The main limitation of the models proposed by Oriani and McLellan is the assumption of local equilibrium between the atomic populations in normal and trap sites throughout the diffusion process. Further, the expression for the fractional occupancy, Eq. (39), depends on the total concentration of interstitials which is usually a function of time. Hence, the general relations for the diffusion coefficient, Eqs. (37) and (41), can not be used except, perhaps, in a tracer diffusion technique where the total concentration of interstitials is kept constant.

The restrictions cited in the previous paragraph may be avoided altogether if one uses the general model of diffusion with traps proposed by McNabb and Foster.^[40] Their mathematical analysis of trapping describes diffusion with the relations

$$\frac{\partial C}{\partial t} + N \frac{\partial n}{\partial t} = \nabla \cdot D \nabla C \quad (47)$$

and

$$\frac{\partial n}{\partial t} = \underline{k} C(1 - n) = p n \quad (48)$$

where C is the concentration of diffusing species, N is the concentration of traps per unit volume, n is the fraction of traps occupied (equivalent to θ_t), and k and p are the rate constants for trapping and release, respectively. These nonlinear equations may be employed with most boundary and initial conditions but they do not have a general analytic solution. Caskey and Pillinger^[43] developed an approximate solution to these equations by the finite difference method. Their solution allows the determination of the concentration of diffusing species as a function of time and position. The ratio k/p may then be calculated from experimental data.^[2] The study of the ratio k/p versus temperature provides information on the trap energy.

An attempt was made to compare the Oriani and McLellan models using the oxygen diffusivity data for Nb-based alloys obtained by Lauf.^[2] A nonlinear least-squares program was employed in the analysis. The values of the binding energy that give the best fit to the data are displayed in Table VI. Both models were fitted assuming six trap sites per substitutional solute, $\phi = 6$. The figures in the parentheses are the errors for a 95% confidence level. The results for Oriani's model, Eq. (40), are in good agreement with the previously reported values^[2] (cf. Table I) while the errors are even smaller. The binding energies calculated from McLellan's model, Eq. (46), are slightly less than those from Oriani's model, but the curve fitting was not improved; for example, compare Fig. 3 (a) and (b) for oxygen diffusion in Nb-.95Zr

Figure 3. (a) Arrhenius plot for oxygen diffusion in Nb-0.95Zr alloy. Diffusivities were fitted according to Oriani's model, $\phi = 6$.

Figure 3. (b) Arrhenius plot for oxygen diffusion in Nb-0.95Zr alloy. Diffusivities were fitted according to McLellan's model, $\phi = 6$.

alloy. Thus, it was impossible to discern the most appropriate model solely from this analysis. Even though McNabb and Foster's model gives a reasonable agreement with Oriani's model,^[44] the experimental data are too scarce to allow any definite conclusions.

Since internal friction^[45] and lattice parameter^[46] measurements for the Nb-Zr-O system suggest the possibility of two oxygen atoms associated with a zirconium atom, Oriani's model was also analyzed with the assumption of two trap sites per substitutional solute, $\phi = 2$. The curve fitting was as good as for Oriani's model with $\phi = 6$, but larger binding energies were obtained (Table VI). Furthermore, the fractional occupancy of trap sites, Eq. (39), was greater than 70% over the whole temperature range of these experimental data, so the more general relation Eq. (37) must be used instead of Eq. (40). Since the substitution of the fractional occupancy of normal and trap sites in Eq. (37) results in a barely discernible change of the effective diffusivities instead of the one order of magnitude found in the experiment, it is concluded that more than two trap sites are present for each substitutional solute in Nb.

Table VI
Binding Energies (kJ/mole) Between a
Substitutional Solute and an Oxygen Interstitial in Niobium

Alloy	Models for Diffusion with Traps*			
	McLellan Model		Oriani Model	
	$\phi = 6$		$\phi = 6$	$\phi = 2$
Nb-.9Ti	50.7 (5.1%)		67.3 (5.0%)	79.1 (4.6%)
Nb-.95Zr	51.4 (2.0%)		67.6 (2.4%)	78.9 (2.0%)
Nb-1.4V	42.0 (3.3%)		54.7 (4.0%)	66.1 (3.4%)
Nb-2.7V	33.9 (2.8%)		45.7 (3.2%)	57.5 (3.0%)
Nb-5.1V	36.4 (2.9%)		52.3 (3.6%)	64.7 (3.0%)
Nb-4.1Ta	25.8 (10.2%)		33.8 (5.8%)	44.5 (7.6%)

* Percentages in parentheses refer to twice the standard error of fitting.
 ϕ is defined as the number of trap sites per substitutional solute atom.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Electrolytes

The electrolytes were a solid solution of 92 mole% of ThO_2 and 8 mole% of Y_2O_3 supplied by Zirconium Corporation of America. As received, they were discs of 15 mm diameter and approximately 3 mm thick. In order to improve the response time of the cell, the discs were sliced with a diamond saw to a final thickness of the order of 1 mm and then polished through 1 μ diamond paste.

2.2 Preparation of Alloys

The pure vanadium was donated by the U.S. Bureau of Mines in the form of cast bars. The niobium and tantalum were purchased in rod form from Wah Chang Albany Corp. The chromium was MARZ grade quality supplied by Materials Research Corporation. The titanium and zirconium were polycrystalline bars produced by the iodide process. The chemical analyses of all starting materials are in Table VII.

The alloys 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 separated compartment of the hearth before melting the alloy. The zirconium acted as a getter for residual oxygen and other impurities in the atmosphere. Each alloy was melted four times. Both zirconium and

Table VII
Chemical Analyses of Starting Materials[†]
(atomic ppm)

	V	Ti	Cr	Ni	Zr	Nb	Ta	Hf
Be	—	—	—	—	—	—	< 10	—
Mg	< 100	—	0.5	3	—	—	20	20
Al	40	20	—	2	90	50-200*	100	70
Si	30	3	< 1	8	**	200	200	100
K	8	—	0.2	4	3	< 20	—	8
Ca	100	0.2	2	3	10	< 20	30	100
Ti	20	bal.	—	—	10000	—	5	30
V	bal.	2	3	—	0.3	30	5	1
Cr	100	10	bal.	—	200	30	< 3	100
Fe	100	10	20	3	800	30	< 10	400
Ni	—	—	< 1	bal.	70	—	8	200

Table VII continued

	V	Ti	Cr	Ni	Zr	Nb	Ta	Hf
Cu	100	3	< 0.6	—	20	50	20	100
Zr	—	12	—	—	bal.	400	2	40000
Nb	—	< 0.5	< 0.6	—	1	bal.	20	—
Mo	7	5	< 0.7	—	—	40	3	3
Pd	—	—	—	—	—	—	—	200
Sn	—	—	—	—	10000	—	—	—
Hf	—	20	—	—	200	12	—	bal.
Ta	< 5	—	—	—	**	100	bal.	10
W	—	—	—	**	**	30	30	—

[†]The analyses were done by mass spectrography at the Materials Research Laboratory, University of Illinois, except for the Cr analysis, which is the lot analysis given by the Materials Research Corporation. All other impurities are below the detection limits.

* Aluminum seemed to be inhomogeneous.

** Interference.

alloy ingots were etched to remove any oxide layer picked up during cooling, and turned over between melts.

The resulting ingots were swaged to 3 mm diameter and cold-rolled into strips ~ 0.5 mm thick without intermediate anneals. Sections of each strip were analyzed by mass spectrography and electron microprobe. The chemical analyses of the alloys are shown in Table VIII. The impurities found in the alloys are clearly related to the starting materials. The alloys were never contaminated by the tungsten electrode. The large errors for vanadium alloys containing Ti, Zr, and Hf are due to solute-rich regions. These segregations resulted from a slow quenching coupled with the presence of eutectic reaction in the V-Zr and V-Hf alloys, or else from oxygen contamination. Microprobe analysis of the V-Ti alloys showed a modulated segregation before annealing. Annealing resulted in a fairly uniform concentration of solute within the grains but segregation in the grain boundaries.

It was not possible to eliminate the precipitates in the alloys containing Zr and Hf.

2.3 Electrode Preparation

The samples were prepared by doping the metal strips with measured amounts of oxygen in a high-vacuum Sieverts' apparatus described elsewhere.^[47] The strips were annealed for approximately 3 hours at temperatures from 1350 to 1600°K and pressures from 10^{-4} to 10^{-5} Pa. At about 1600°K, the pumps were valved

Table VIII

Chemical Analyses of the Vanadium-based Alloys[†]

Major Constituents (atomic pct)*

Ti 1.20 ± 0.89; Ti 4.37 ± 1.56; Cr 0.95 ± 0.09

Ni 0.95 ± 0.08; Zr 2.8 ± 9.4

Impurities (atomic ppm)					
Mg	**	**	1	< 1	7
Al	9	20	**	6	25
Si	4	15	4	< 5	20
K	3	3	—	—	8
Ca	1	5	1	< 8	15
Ti	major	major	8	6	20
Cr	20	150	major	30	70
Fe	23	100	45	23	100
Ni	—	—	—	major	—
Cu	63	150	35	47	85
Zr	—	—	—	—	major
Nb	—	—	—	—	—
Mo	5	9	4	4	9
Hf	—	—	—	—	40
Ta	—	< 1	—	—	< 3
W	—	—	—	—	—

Table VIII continued

Major Constituents (atomic pct)*

Nb 1.04 ± 0.12 ; Nb 3.50 ± 0.35 ; Hf 0.6 ± 1.1 ;Ta 0.96 ± 0.06 ; Ta 3.63 ± 0.07

Impurities (atomic ppm)

Mg	1	6	5	2	40
Al	4	3	15	3	20
Si	3	8	20	4	20
K	2	4	—	5	4
Ca	1	5	8	1	2
Ti	7	7	50	8	9
Cr	40	35	150	47	50
Fe	40	25	100	57	40
Ni	—	—	—	—	—
Cu	33	45	150	43	40
Zr	—	—	< 500	—	—
Nb	major	major	—	—	3
Mo	5	4	< 20	4	7
Hf	—	—	major	—	—
Ta	—	< 2	< 1	major	major
W	—	—	—	< 1	3

Table VIII continued

[†]The analyses were done by mass spectrography at the Materials Research Laboratory, University of Illinois.

^{*}95% confidence level, twice the standard error. The nominal compositions for the alloys containing Zr and Hf were 1 at% of these solutes.

^{**}Interference.

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 alloys were doped with 0.7 to 2.5 at% oxygen. The final concentrations were analyzed by Leco Corp. using a vacuum fusion technique. The strips were cut into segments 13 x 6 x 0.5 mm. The surfaces were ground through 600 grit SiC and attack polished with 0.05 μ alumina in a chromic acid slurry.

The zirconium "sinks" were made from a polycrystalline bar of iodide process zirconium. A 10 mm thick slice of the bar, 20 mm in diameter, was cold-rolled to about 3 mm thick which was then sliced to produce rectangular sections with dimensions slightly greater than those of the samples. One face was ground and polished through 0.05 μ alumina. The platinum leads were spot welded onto the other face.

2.4 Experimental Apparatus and Technique

The vacuum furnace used in this study is sketched in Fig. 4. The electrolytic cell was positioned between two high density alumina (Lucalox) rods mounted vertically in the center of the furnace. A platinum ring above and below the cell helped to insure good alignment and tight contact of the cell components at high temperatures by allowing the assembly to creep into place. A stainless steel weight of 1.4 kg placed on the top of

Figure 4. Schematic illustration of the experimental apparatus.

1. electrolytic cell	6. radiation shields
2. platinum rings	7. thermocouple leads
3. Lucalox tube	8. EMF leads
4. furnace element	9. weight
5. ceramic insulators	10. frame

the upper alumina tube helped to compress the platinum rings and produce the tight contact necessary for good operation of the cell. The heating element was a thoriated tungsten filament, operating on alternating current. The temperature was controlled by a proportional controller using the upper thermocouple. The temperature difference between the upper and lower electrodes was typically less than 5°K.

The electrode compartment was separated from the furnace element by a cylindrical niobium sheet which provided a getter for impurities and electrical shielding. Six concentric radiation shields around the entire assembly reduced the heat loss and helped maintain a uniform cell temperature. The pressure was usually 10^{-4} to 10^{-6} Pa. The cell was carefully isolated electrically to assure low leakage and, thus more accurate EMF measurements. The upper electrode support was isolated from the lower by alumina spacers at room temperature. The cell EMF was measured by a high impedance (10^{12} ohm) electrometer with the reference electrode grounded. The output of the electrometer was connected to a digital printer, which printed time, upper and lower temperatures, pressure gauge output, and cell EMF, at intervals from one minute to three hours. The cell configurations for kinetic and equilibrium measurements are shown in Fig. 5. A double configuration, Fig. 5(b), was used for most equilibrium measurements to save time.

The reference electrode in the kinetic study was either a Nb+O (2 phases) or a V+O (1 phase) binary alloy. It was placed

Figure 5. Cell configurations used in this study: (a) and (b), thermodynamic study; (c) kinetic study.

on the bottom, Fig. 5(c), and was not disturbed for several consecutive runs. The temperature was held at 450°K for approximately 14 hours and then brought to 1273°K within two hours. The EMF was recorded as a function of time until the curve showed a distinct straight-line portion. The slope of this line was calculated by a linear regression of at least eight points, then the temperature was changed and a new curve of EMF versus time was obtained. Section 2.5 presents further discussion on this technique.

In the equilibrium study, the time to reach the experimental temperature was not as critical as in the kinetic measurements, hence the temperature was raised to 973°K in about six hours. It was then held at this temperature until the EMF became constant with time, when both the EMF and the actual temperature were recorded before setting the furnace for a new temperature.

2.5 The Kinetic Study

The electrolytic cell technique allows the determination of kinetic data through the monitoring of either its current during transient or steady-state conditions,^[48] or its EMF during transient conditions.^[1] The latter method was proposed by Kirchheim et al.^[1] and uses the cell geometry of Fig. 5(c). The sink must be a material with high oxygen mobility and high solubility for oxygen, and negligible interdiffusion with the sample.^[49] A zirconium block has been used with excellent results for Nb, V^[2,50] and Ta.^[1]

If the cell capacitance is very low, it may be assumed that there is almost no oxygen transport through the electrolyte/sample interface, so that $x = L$ and $t \neq 0$, $\partial c / \partial x = 0$, where $c(x, t)$ is the oxygen concentration as a function of the position x , and time, t . Furthermore, the sink removes all the oxygen from the sample/sink interface, so the boundary condition at this interface is $c(0, t) = 0$. The solution of Fick's second law with the initial condition $c(x, 0) = f(x)$ and the above boundary condition is:

$$c(x, t) = \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2L} \exp \left\{ - \left[\frac{(2n-1)\pi}{2L} \right]^2 Dt \right\}, \quad (49)$$

where A_n are the coefficients of the Fourier transform of $f(x)$, i.e.,

$$f(x) = \sum_{n=1}^{\infty} A_n \sin \frac{(2n-1)\pi x}{2L} \quad (50)$$

For times larger than $4L^2/9\pi^2 D$, $c(x, t)$ can be represented by the first term of the series, and the concentration at the electrolyte/sample interface is,

$$c(L, t) = A_1 \exp \left[- \frac{\pi^2 Dt}{4L^2} \right]. \quad (51)$$

The cell EMF, E , can be determined as a function of the oxygen activity at the sample/electrolyte interface, a , and the corresponding activity of the reference electrode, a_r , so that from the Nernst equation:

$$E = \frac{RT}{2F} \ln \frac{a}{a_r} \quad (52)$$

If Henry's law is obeyed by the sample electrode, $a = \gamma c$, one can rewrite the above equation as:

$$E = \frac{RT}{2F} \ln \frac{\gamma c(L,t)}{a_r} = \frac{RT}{2F} \left(\ln \frac{\gamma A_1}{a_r} - \frac{\pi^2 D t}{4L^2} \right) \quad (53)$$

Therefore, a plot of EMF versus time will be linear with a slope given by

$$\frac{dE}{dt} = - \frac{RT\pi^2 D}{8FL^2} \quad (54)$$

The diffusion coefficient is then calculated from the above equation for each temperature of interest. The relative error of a measurement of D is estimated at less than $\pm 7\%$. 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 an extremely low oxygen partial pressure associated with the oxygen concentration at the electrolyte/sample interface.

2.6 The Equilibrium Study

Oxygen activities were determined in the following galvanic cell:

used either in a single or double cell configuration, Figs. 5 (a) and (b). The reference electrode was a single phase V-6.350* and was always grounded. The EMF produced by this cell is related to the oxygen equilibrium pressure of the reference V-O electrode, $P_{O_2,V}$, and the oxygen equilibrium pressure of the ternary vanadium alloy, $P_{O_2,T}$, by the relation

$$E = - \frac{RT}{4F} \cdot \ln \left(\frac{P_{O_2,V}}{P_{O_2,T}} \right) \quad (55)$$

If $P_{O_2} = 1 \text{ atm}$ ($1.01 \times 10^5 \text{ Pa}$) is selected as the standard state for both the gas phase and the oxygen in solution, the oxygen activity is defined to be $(P_{O_2})^{1/2}$ and the activity coefficient, γ_N , by the relation

$$(P_{O_2})^{1/2} = 1.01 \times 10^5 \cdot \gamma_N \cdot N \quad (56)$$

where N is the atom fraction of oxygen in solution. Hence, the oxygen activity in the ternary electrode can be determined from the measurements of the cell EMF and the oxygen pressure in

* Concentrations in atomic percent are used throughout.

equilibrium with the reference electrode. The activity coefficient for an atom fraction N of oxygen in α -V solid solution is [51]

$$\ln \gamma_N = \left[\left(19.98 - \frac{96470}{T} \right) N + 12.00 - \frac{50770}{T} \right] (1 - N)^2 \quad (57)$$

3. RESULTS

3.1 Metallography

The microstructure of the oxygen-doped vanadium ternary alloys containing Cr, Ni, Nb and Ta was consistent with the presence of a homogeneous solid solution. These alloys had very large grains and a well annealed structure as shown in Fig. 6 for V-3.5Nb-.930.

The oxygen-doped vanadium ternary alloys containing Ti, Zr and Hf, however, presented second phases (Figs. 7-9). Both binary diagrams for V-Zr and V-Hf have an eutectic reaction, so the precipitates were probably formed during the fabrication of these binary alloys. Optical microscopy indeed revealed the existence of precipitates in these alloys prior to doping. The configuration of the precipitate in the V-Zr alloy prior to doping suggests that the precipitates were massive regions fragmented by the swaging and cold-rolling processes (Fig. 10). Scanning electron microscopy and X-ray energy dispersive analysis showed that these precipitates were Zr- and Hf-rich segregations in the V-Zr and V-Hf alloys, respectively. Ion probe analyses performed on the V-Zr alloy showed very small oxygen content in the as-melted alloy. After doping, however, the ZrO mass correlated extremely well with the Zr mass, indicating a large amount of oxygen combined with the Zr-atoms (Figs. 11 (c) and (d)), although some oxygen was left in the vanadium

Figure 6. Optical micrograph of the V-3.5Nb-0.930 alloy.

Figure 7. Optical micrograph of the V-4.4Ti-1.00 alloy.

Figure 8. Optical micrograph of the V-1Zr-2.10 alloy.

Figure 9. Optical micrograph of the V-1Hf-0.80 alloy.

Figure 10. Optical micrograph of the V-1Zr alloy prior to doping.

Figure 11. Ion profile analysis of the V-1Zr-2.10 alloy. Image field is about 150 μm .

- (a) ^{51}V mass signal
- (b) ^{67}VO mass signal
- (c) ^{90}Zr mass signal
- (d) ^{106}ZrO mass signal

matrix and segregated in the grain boundaries as Figs. 11 (a) and (b) show for the V and VO masses, respectively.

It was impossible to resolve in the optical microscope any precipitates in the V-Ti alloys, but electron probe analyses (wavelength dispersive analysis) revealed a modulated segregation in the as-melted alloys. After doping, no composition variations were resolved except in the grain boundaries, where large Ti segregations were found. The microscopy of the V-4.4Ti-1O showed a second phase with well defined geometry within small grains (Fig. 7). However, this second phase was barely visible in the more dilute alloy, which also had larger grains ($\sim 1-3$ mm). Since this second phase was not found in the as-melted alloys (prior to doping), it might be a transformation in the V-Ti-O ternary system, formed at doping temperatures or on cooling. Moreover, the geometric pattern of this phase suggests well defined crystallographic relations between this phase and the matrix. Either a titanium oxide or a high temperature oxygen-stabilized phase^[52] could have been formed; however, transmission electron microscopy is needed to identify the phase.

3.2 Equilibrium

The equilibrium EMF data for the alloys used in the diffusion measurements are presented in Figs. 12 and 13. Straight lines were fitted to the data by least-square analysis whenever it was possible. The resulting EMF equations are given in

Figure 12. EMF versus temperature for the vanadium-based alloys containing Ti, Cr and Ni. The reference electrode was a single phase V-6.35O alloy.

Figure 13. EMF versus temperature for the vanadium-based alloys containing Nb and Ta. The reference electrode was a single phase V-6.350 alloy.

Table IX. The change of the EMF slope for the V-1.2Ti alloy is probably due to some phase transformation since the V-6.50 reference electrode is single phase throughout the experimental temperature range. This behavior is also hinted in the EMF data for vanadium alloys containing Cr and Ni.

The activity coefficient as a function of the oxygen mole fraction is defined by Eq. (56) for a standard state of oxygen gas at 1 atm. (1.01×10^5 Pa), and it can be represented as a function of temperature by the relation

$$RT \ln \gamma_N = \Delta H^{XS} - T\Delta S^{XS} \quad (58)$$

where ΔH^{XS} and ΔS^{XS} are the excess enthalpy and entropy of oxygen in the particular ternary alloy. These excess enthalpies and entropies were computed from the EMF equations in Table IX and, together with the corresponding values for an infinitely dilute solution of oxygen in pure vanadium, Eq. (57) in the limit when the mole fraction approaches zero, are shown in Table X.

3.3 Diffusion

The diffusivities of oxygen in seven substitutional alloys are presented in Figs. 14 through 20. The straight line in these figures corresponds to the oxygen diffusion in pure vanadium (Table XI). Two different oxygen concentrations were used for the V-Cr alloy (Fig. 15). Figure 21 shows the oxygen diffusivities in V-1.50 and V-0.60^[2] binary alloys; the

Table IX

EMF Versus Temperature Equations for the Vanadium-based Alloys

Alloy	Slope $\times 10^{-4}$ (V/°K)	EMF Intercept (V)	Temperature (°K)
V-1.2Ti-2.10	-2.527 -0.825	0.1498 -0.0117	872 - 922* 974 - 1175
V-0.95Cr-2.30	-0.574 0.000	0.0110 -0.0430	874 - 923* 974 - 1123*
V-0.96Ni-2.50	-0.513 0.289	0.0328 -0.0427	874 - 923* 974 - 1123
V-1.0Nb-1.40	-0.427	-0.0429	872 - 1174
V-0.96Ta-2.40	-0.585	-0.0149	872 - 1327
V-3.6Ta-0.870	-0.577	-0.0465	872 - 1275

*The slope and EMF intercept were not calculated by least-squares analysis.

Table X

Excess Enthalpy ΔH^{XS} and Entropy ΔS^{XS} for Oxygen

Solution in the Vanadium-based Alloys

$$RT \ln \gamma = \Delta H^{XS} - T \cdot \Delta S^{XS}$$

Alloy	$\Delta H^{XS}/R$	$\Delta S^{XS}/R$	Temperature (°K)
V-1.2Ti-2.10	-46423 -50171	-6.88 -10.83	872 - 922 974 - 1175
V-0.95Cr-2.30	-49644 -50898	-11.32 -12.66	874 - 923 974 - 1123
V-0.96Ni-2.50	-49138 -50891	-11.38 -13.24	874 - 923 974 - 1123
V-1.0Nb-1.40	-50895	-12.16	872 - 1174
V-0.96Ta-2.40	-50245	-11.26	872 - 1327
V-3.6Ta-0.870	-50979	-12.29	872 - 1275
V-O (infinite dilution)	-50770	-12.00

Figure 14. Arrhenius plot for oxygen diffusion in $\text{V}-1.2\text{Ti}-2.1\text{O}$ alloy (points) compared to oxygen diffusion in pure vanadium (line).

Figure 15. Arrhenius plot for oxygen diffusion in V-0.95Cr-2.20 and V-0.95Cr-0.880 alloys (points) compared to oxygen diffusion in pure vanadium (line).

Figure 16. Arrhenius plot for oxygen diffusion in V-0.96Ni-2.00 alloy (points) compared to oxygen diffusion in pure vanadium (line).

Figure 17. Arrhenius plot for oxygen diffusion in V-1.0Nb-1.4O alloy (points) compared to oxygen diffusion in pure vanadium (line).

Figure 18. Arrhenius plot for oxygen diffusion in V-3.5Nb-0.930 alloy (points). The upper line is for oxygen diffusion in pure vanadium.

Figure 19. Arrhenius plot for oxygen diffusion in V-0.96Ta-2.40 alloy (points) compared to oxygen diffusion in pure vanadium (line).

Figure 20. Arrhenius plot for oxygen diffusion in V-3.6Ta-0.87O alloy (points). The upper line is for oxygen diffusion in pure vanadium.

Table XI
Least-squares Analyses of Arrhenius Relation for
Oxygen Diffusion in Vanadium-based Alloys

Alloy	$\ln D_0^*$ (m^2/s)	Activation Energy* (kJ/mole)	Variance	Correlation Coefficient
V-1.2Ti-2.10	-14.19 ± 0.82	118.0 ± 7.4	0.0512	0.988
V-0.95Cr-2.20	-12.53 ± 0.60	129.8 ± 5.6	0.0294	0.993
V-0.95Cr-0.880	-12.95 ± 0.34	129.1 ± 3.2	0.0044	0.999
V-0.96Ni-2.00	-13.00 ± 0.72	126.5 ± 6.6	0.0372	0.993
V-1.0Nb-1.40	-12.12 ± 0.56	135.1 ± 5.2	0.0229	0.998
V-3.5Nb-0.930	-12.73 ± 0.56	134.5 ± 5.2	0.0089	0.998
V-0.96Ta-2.40	-12.38 ± 1.12	131.9 ± 10.2	0.0771	0.984
V-3.6Ta-0.870	-10.91 ± 2.18	152.0 ± 12.6	0.0606	0.980
Pure V (0.6 & 1.50)	-13.42 ± 0.66	123.7 ± 6.1	0.0579	0.985

* 95% confidence level, twice the standard error.

Figure 21. Arrhenius plot for oxygen diffusion in V-0.60 and V-1.50 binary alloys. The line is the best fit through all the experimental points.

straight line was obtained by least-square fitting through all the experimental points.

The least-square analysis of the Arrhenius relations for oxygen diffusion in all alloys is given in Table XI. The activation energy for oxygen diffusion was usually greater in the substitutional alloys than in pure V, except for the oxygen diffusion in V-1.2Ti (Fig. 14) and V-0.96Ni (Fig. 16) which coincide with pure V within the experimental error. No evidence for oxygen diffusion with traps was found for the more dilute alloys. Both V-3.5Nb (Fig. 18) and V-3.6Ta (Fig. 20) alloys presented oxygen diffusivities below the pure V line. This is characteristic of diffusion in the presence of traps, however, the effect is too small to allow definite conclusions.

The diffusion coefficients could never be reliably determined in V-1Hf-0.80, V-4.4Ti-1.0, V-4.4Ti-1.70, V-1Zr-0.70 and V-1Zr-2.10 alloys. The cell EMF in these samples hardly showed the linear region predicted by Eq. (53). Nonetheless, the cell EMF also decreased with 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. However, the time dependence of the EMF before reaching its equilibrium value was similar to the behavior found in the diffusion measurements. The existence of a local oxygen precipitation process in the alloy is a possible explanation for

this behavior, since Zr- and Hf-rich precipitates and a second phase were found in these vanadium alloys. In particular, the Zr- and Hf-rich precipitates may drain the oxygen in solution, thereby decreasing the cell EMF as a function of time. These precipitates then play the same role as the zirconium sink in the cell configuration for diffusion measurements (Fig. 5(c)), except that the boundary conditions for diffusion are entirely different and thus yield a different solution to Fick's law.

4. DISCUSSION

4.1 Precipitation

The oxygen diffusivities in the vanadium alloys containing Zr, Hf and 4.4Ti could never be reliably determined even though the time dependence of the cell EMF indicated a continuous depletion of the oxygen solution in these alloys. Since this same behavior was found in equilibrium measurements without a Zr sink (Fig. 5 (a) or (b)), a precipitation process was proposed to explain it. It is well known that the elements Zr and Hf have strong affinities to oxygen, that is, they form very stable oxides. Further, the metallographic examination of the alloys containing Zr and Hf revealed the presence of solute-rich precipitates (cf. Section 3.1). Ion probe analyses showed a large amount of oxygen associated with the Zr-rich precipitates although some oxygen still remained in solution in the vanadium matrix (Fig. 11). Therefore, any oxygen present in solid solution in these V-based alloys will tend to migrate to the Zr- or Hf-rich regions causing a continuous depletion of the oxygen in the V-matrix. This oxygen precipitation is most probably diffusion controlled, since the precipitates play a rôle similar to the zirconium sink in the diffusion measurements, where the interface does not seem to limit the oxygen transport into the zirconium. [1,2]

Ham^[53] showed that in a weakly supersaturated solid solution of initially uniform composition, and where the ultimate

precipitate particle size is small compared with their separation, the solute concentration decreases uniformly except within small volumes around the particles according to the following relation

$$c(t) = C_0 \exp - \left(\frac{t}{\tau}\right)^{3/2} \quad (59)$$

and

$$\tau = \frac{r_s^2}{2D} \left(\frac{C_p}{C_0}\right)^{1/3} \quad (60)$$

where r_s is a measure of the separation between the precipitates, D is the diffusion coefficient of solute in the matrix, C_0 and C_p are the initial excess of solute in solution and the amount of solute already precipitated, respectively. Equation (59) is valid for small times and for spheroidal particles which grow with constant eccentricity (without changing their shape). The time dependence of the cell EMF is obtained from Eqs. (52) and (59).

$$E = RT \ln \frac{\gamma C_0}{a_r} - RT \left(\frac{t}{\tau}\right)^{3/2}, \quad (61)$$

therefore, a plot of the EMF versus $(\text{time})^{3/2}$ must yield a straight line of slope

$$\frac{dE}{dt} = - \frac{RT}{\tau^{3/2}}. \quad (62)$$

Figures 22 through 24 show plots of the EMF versus $(\text{time})^{3/2}$ for V-1Hf-0.80 and V-1Zr-2.10 samples using an electrolytic cell configured for equilibrium measurements (Figs. 22 and 23) as well as for diffusion measurements (Fig. 24). The values of $\ln \tau$ from Eq. (62) were determined from these figures and they are plotted in Fig. 25 versus reciprocal temperature. The least-squares analysis of an Arrhenius relation through these points gives an activation energy of 140.2 ± 2.6 kJ/mole for the oxygen diffusion in the vanadium-rich matrix of the V-1Hf-0.80 sample. The two open circles in Fig. 25 were determined for a V-1Zr-2.10 sample during an equilibrium measurement. If a straight line is assumed to join these two points, the activation energy for oxygen diffusion in this sample is ~ 160 kJ/mole. This value was also obtained when the EMF of a cell configured for diffusion measurements with another specimen of V-1Zr-2.10 alloy was analyzed according to Eq. (61), as shown in Fig. 24. This supports the assumption that most oxygen atoms were diffusing toward the precipitates. Both the V-Zr and V-Hf alloys have small precipitates with a large mean separation between them (Figs. 8 and 9), therefore satisfying the assumptions in deriving Eq. (59).

The oxide precipitation in the alloys containing Zr and Hf certainly requires attractive interactions between oxygen and substitutional solute atoms. Moreover, since some Zr and Hf were still in solid solution in the vanadium matrix, the activation energies for oxygen diffusion determined from the

Figure 22. EMF versus $(\text{TIME})^{1.5}$ for V-1Hf-0.8O alloy using an electrolytic cell configured for equilibrium measurements.

Figure 23. EMF versus $(\text{TIME})^{1.5}$ for V-1Zr-2.10 alloy using an electrolytic cell configured for equilibrium measurements.

Figure 24. EMF versus $(\text{TIME})^{1.5}$ for V-1Zr-2.1O alloy using an electrolytic cell configured for diffusion measurements.

Figure 25. Ln (time constant) versus reciprocal temperature.

precipitation process are probably increased by S-I attractive interactions, assuming, of course, that the precipitation process is diffusion controlled. Thus, the difference between the activation energies in these alloys and in pure vanadium gives an estimate for the S-I binding energies, which were ~ 36 kJ/mole and ~ 16 kJ/mole for the Zr and Hf solutes, respectively. However, the errors associated with these estimates are unknown.

It was not possible to analyze the V-4.4Ti alloys according to Eqs. (61) and (62) even though the observed time dependence of the EMF during equilibrium measurements was consistent with oxygen depletion from the solid solution. The metallographic examination of this alloy showed crystallographically oriented platelet precipitates arranged in a grid, where the transformed and untransformed matrix have comparable dimensions (Fig. 7). This suggests that the oxygen atoms diffuse only a small distance before precipitating in the boundaries of the untransformed volume. Ham's model, however, assumes the existence of only a small precipitate in the center of a large volume of unprecipitated matrix and, therefore, it is not adequate for the V-4.4Ti alloys.

Though the experimental data on these alloys are limited, the agreement certainly supports a diffusion-controlled precipitation of oxygen in the Zr- and Hf-rich regions. Furthermore, it demonstrates a new use of solid electrolytic cells for the study of the kinetics of solid-state precipitation

processes. This use could be expanded to other types of reactions, e.g., ordering, martensitic, etc., where the oxygen atom acts essentially as a "probe" to detect changes in the specimen.

4.2 Equilibrium

The equilibrium results showed only small modifications in thermodynamic behavior of oxygen solutions in the V-based alloys containing Cr, Ni, Nb and Ta. The change of the EMF slope for V-1.2Ti (Fig. 12) and the corresponding decrease of the absolute value of the excess entropy at temperatures around 920°K are indications of phase transformation. Indeed, a second phase was found in the two V-Ti alloys used in this research. This phase probably arises from the ability of oxygen to stabilize some ternary phases,^[52] perhaps oxides, since V and Ti form a continuous solid solution^[54] up to 70% Ti at 873°K and the Ti concentration was found homogeneous in the grains (cf. Section 3.1 on these alloys).

Despite the theoretical uncertainties expressed in Section 1.1, the empirical model proposed by Lauf and Altstetter^[2,50] will be employed in the analysis of the present results. The effect of the substitutional atoms on the oxygen properties in the ternary alloys is separated into elastic and chemical terms. The chemical term represents the oxygen affinity for the substitutional solute. It is assumed to be a function of chemical affinity, A , defined as

$$A = \Delta H_{mo}^f - \Delta H_{so}^f \quad (\text{eV/oxygen atom}) \quad (63)$$

where ΔH_{mo}^f and ΔH_{so}^f are the standard formation enthalpies of the oxides of the substitutional and matrix atoms, respectively. The elastic term is due to the interaction of the impurity strain fields which arises from the differences of atomic radius between impurity and matrix atoms. Since Eqs. (17) and (18) provide a relation between the microscopic forces around each impurity and the macroscopic volume change due to the impurity, a meaningful parameter is the change of lattice parameter, a , with solute concentration, c :

$$\eta = \frac{1}{a} \frac{da}{dc} \quad (64)$$

However, this parameter is not always available in the literature and a substitute might be the size factor defined by

$$\Omega = \frac{1}{3} \frac{\Omega_s - \Omega_m}{\Omega_m}$$

Ω_s and Ω_m are the atomic volumes of substitutional and matrix atoms, respectively, when in the pure metallic form. The value of the above parameters and the difference of charge ΔZ between the substitutional impurity and the matrix ionic cores are shown in Table XII for the vanadium alloys. Although the parameters η and Ω have different absolute values, they follow the same trends, and, therefore, the parameter Ω may be used in qualitative comparisons whenever η is unavailable. Furthermore,

Table XII

Parameters Affecting the Thermodynamic and Diffusion
Properties of Oxygen in Vanadium-based Alloys

Solute	Size Factor $\Omega \%$	$\frac{1}{a} \frac{da}{dc}^*$ %	Chemical Affinity (eV/oxygen atom)	ΔZ (ds bands)
Ti	9.23	4.27	-0.89	-1
Cr	-4.39	-6.72	0.31	+1
Ni	-6.93	—	1.72	+5
Zr	22.83	—	-1.50	-1
Nb	10.30	11.89	0.27	0
Hf	20.54	—	-1.56	-1
Ta	9.97	16.50	-0.03	0

* Calculated from data. [28]

the good correlation between ΔZ and the chemical affinity supports the use of either parameter for the present purposes. Thus, a positive value indicates repulsive S-I interactions with a corresponding increase of the oxygen activity, and vice versa.

In order to analyze the effect of substitutional elements on the thermodynamic properties of oxygen, it is convenient to determine the Wagner's interaction parameters^[55] for each alloy. These parameters are defined by

$$\ln \gamma_{N_i} = \ln \gamma_{N_i}^o + N_i \epsilon_i^{(i)} + N_s \epsilon_i^{(s)} \quad (66)$$

where the first order free energy interaction coefficients^[56] $\epsilon_i^{(i)}$ and $\epsilon_i^{(s)}$ are defined by the expressions

$$\epsilon_i^{(i)} = \left(\frac{\partial \ln \gamma_{N_i}}{\partial N_i} \right)_{N_m \rightarrow 1} \quad (67)$$

$$\epsilon_i^{(s)} = \left(\frac{\partial \ln \gamma_{N_i}}{\partial N_s} \right)_{N_m \rightarrow 1} \quad (68)$$

γ_{N_i} being the activity coefficient at infinite dilution in the m-i binary alloy, and N_m , N_s and N_i the mole fractions for matrix element, substitutional solute and interstitial solute, respectively.

Table XIII shows the sum $N_i \epsilon_i^{(i)} + N_s \epsilon_i^{(s)}$ and the first order free energy interaction coefficient $\epsilon_i^{(s)}$ for the studied alloys at 1000°K. The interaction coefficients $\epsilon_i^{(s)}$ were approximated assuming Henry's law for the oxygen solution in

the ternary alloys, that is $\epsilon_i^{(i)} = 0$. Very good agreement is found between the interaction coefficients for the dilute substitutional alloys (~ 1 at%) and the values for chemical affinity and ΔZ as shown in Tables XII and XIII. The plot of the activity coefficient versus reciprocal temperature for the vanadium alloys containing Ti, Cr and Ni (Fig. 26) shows that the trends of the activity coefficient obtained from Table XIII are valid over the whole experimental temperature range for these alloys. The solid line in this figure gives the activity coefficient for an infinitely dilute oxygen solution in pure vanadium (Table X). The values for the activity coefficient for the V-Nb and V-Ta alloys essentially coincides with the solid line in Fig. 26 and are not plotted for better clarity. Therefore, despite the fact that a larger Ta content seems to increase the oxygen activity, instead of causing a further decrease, these results may be within the experimental error. Nonetheless, the same effect was found in the V-Nb alloys, where an extensive study on V-Nb alloys containing more than 14.8% Nb found that at all compositions the solute decreased the oxygen activity, [51,57] while Table XIII indicates an increase. Further work is required on dilute alloys of these two systems. The results from the present study on the effects of Cr, Ti and Zr are consistent with the results of Klueh and Devan on the solubility of oxygen in similar vanadium alloys; viz., Cr lowered the solubility of oxygen in vanadium by raising the oxygen activity [58] while Ti and Zr decreased the oxygen

Table XIII

Wagner's Interaction Coefficients at 1000°K

Alloy	$N_i \epsilon_i^{(i)} + N_s \epsilon_i^{(s)}$	$\epsilon_i^{(s)}$	$\eta = \frac{1}{a} \frac{da}{dc}$	Δz (ds bands)
V-1.2Ti-2.10	-0.57	-47.5	4.27	-1
V-0.95Cr-2.30	0.57	60.0	-6.72	+1
V-0.96Ni-2.50	1.35	140.6	-6.93*	+5
V-1.0Nb-1.40	0.04	4.0	11.89	0
V-0.96Ta-2.40	-0.22	-22.9	16.50	0
V-3.6Ta-0.870	0.08	2.2	16.50	0

* Size factor Ω (%).

Figure 26. Ln (activity coefficient) versus reciprocal temperature.

activity and probably caused internal oxidation.^[59] Also consistent are the internal friction studies which found Cr and Ni to be noninteractive or repulsive^[60] to oxygen and Ti and Zr were attractive to oxygen.^[60,61]

It is worth noting the semiquantitative agreement between the interaction coefficients for Ti, Cr and Ni, and their corresponding values for the chemical affinity and ΔZ , Tables XII and XIII. This correlation was also found in Table I whenever solutes and solvent belong to the same period in the periodic chart. The size parameters η and Ω for elements within the same period also correlate with the chemical affinity and ΔZ . However, if the elements are taken from different periods the correlation is uncertain, e.g., Nb and Ta. The equilibrium data, therefore, suggest that both chemical affinity and ΔZ are equally important parameters in determining the effects of substitutional solutes on the thermodynamic properties of interstitial solutes.

4.3 Diffusion

The excellent agreement of the oxygen diffusivities for vanadium doped with 1.5% and 0.6% of oxygen, Fig. 21, supports the equilibrium results that Henry's law is obeyed in V-O binary alloys up to $\sim 3\%$ O.^[51] Moreover, the high temperature diffusivity measurements in this study and that of Lauf and Altstetter^[50] agree very well with the diffusivity data, based mostly on low temperature measurements, compiled by Boratto

and Reed-Hill.^[62] Their statistical calculations^[63] provided -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 values in Table XI. The reported errors are twice the standard deviations.

In order to assess the effects of surface finishing of electrodes and electrolytes, and the reproducibility of the present technique, the oxygen diffusivities in a Nb-0.9Ti-1.0 sample prepared by Lauf^[2] were determined after repolishing this sample according to the procedure described in the present study. Very good agreement was obtained for the diffusivities measured in the present and previous study as shown in Fig. 27, confirming the previous study and indicating that surface preparation is not critical.

A test for parallelism using the F statistic^[64] was employed to compare the activation energies for oxygen diffusion in alloys and pure vanadium. The activation energies for all alloys, except V-Nb alloys and V-3.6Ta, were found to be equal to the value obtained for pure V within a confidence level of 95%. Nonetheless, the very small changes of the activation energies for oxygen diffusion in the alloys may reflect intrinsic properties. Better precision would be required to justify interpretation of these small effects.

The oxygen diffusivities in the alloys with ~ 1 at% substitutional solutes showed only small deviations from the Arrhenius line for oxygen diffusion in pure V, therefore

Figure 27. Arrhenius plot for oxygen diffusion in Nb-0.9Ti-1.00 alloy. The upper line is for oxygen diffusion in pure niobium.

suggesting that oxygen is not attracted by any substitutional solutes in these alloys. However, the absence of trapping effects could also be due to a fractional occupancy of trap sites close to one ($\theta_t \approx 1$) or else a very small binding energy. The oxygen content relative to substitutional solute content in most samples would suggest that possibly only one or two trap sites exist per substitutional solute, or else there is a binding energy less than ~ 28 kJ/mole, if six trap sites per substitutional solute is assumed. Three different approaches may be attempted to handle the above situation: 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 ionic conductivity range. 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 less oxygen content, providing a better agreement with the diffusivities in pure V (Fig. 15). This effect is most prominent for higher temperatures where the changes are greater than the associate 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-0.96Ta and V-0.96Ni at higher temperatures. The chemical diffusion coefficient arises whenever the activity coefficient depends on the concentration of the diffusing species. Thus, it is related to the diffusion coefficient for an infinitely dilute solution of oxygen, D_∞ , by the expression

$$D = D_\infty \left(1 + \frac{\partial \ln \gamma}{\partial \ln N} \right) \quad (69)$$

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, Eq. (66), the diffusivity in the ternary alloy is

$$D = D_\infty (1 + N \epsilon_i^{(i)}) \quad (70)$$

which can be approximated by an exponential function if

$$|N \epsilon_i^{(i)}| \ll 1^*,$$

$$D = D_\infty \exp N \epsilon_i^{(i)} \quad (71)$$

The interaction coefficient $\epsilon_i^{(i)}$ may be expressed as a function of temperature by

$$\epsilon_i^{(i)} = \frac{\eta_i^{(i)}}{RT} - \frac{\sigma_i^{(i)}}{R} \quad (72)$$

* $\exp x \approx 1 + x$ if $|x| \ll 1$.

where $\eta_i^{(i)}$ and $\sigma_i^{(i)}$ are the first order enthalpy and entropy interaction coefficients, respectively. [56] So the Eqs. (71) and (72) predict a change of both activation energy and pre-exponential 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. 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 proved that these solutes have similar effects on the activity coefficient of oxygen. Hence, the diffusion and equilibrium data for these two alloys suggest that the S-I 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, Figs. 17 and 19, the other two more concentrated Nb and Ta alloys clearly show diffusivities below the Arrhenius line for pure V, Figs. 18 and 20. Both Oriani's and McLellan's models were employed to fit the experimental

Table XIV

Binding Energies (kJ/mole) of Oxygen to Nb and Ta in V
Assuming Six Trap Sites per Substitutional Solute, $\phi = 6$

	Oriani Model	McLellan Model
Nb	18.9 ± 0.9	14.3 ± 0.6
Ta	19.4 ± 2.6	15.1 ± 1.8

diffusivities for these alloys. Table XIV 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 provided smaller binding energies, as were found for the Nb-based alloys in Section 1.3. Figures 18 and 20 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 by assuming a binding energy linearly dependent on the temperature (Fig. 28). A temperature-dependent binding energy is certainly a possibility. Nonetheless, its absence in most Nb-based alloys except Nb-4.1Ta,^[2,50] and in the V-3.5Nb alloy

Figure 28. Arrhenius plot for oxygen diffusion in V-3.6Ta-0.87O alloy (points). The curve represents the diffusivity predicted by the Oriani model with a "binding energy" linearly dependent on the temperature.

raises doubts on this approach. A smaller number of trap sites per substitutional solute or a large fractional occupancy of the trap sites ($\theta_t \approx 1$) 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 dilute V-3.6Ta 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, in the sense of Section 1.3, may not be valid for the V-3.6Ta or Nb-4.1Ta. [2,50]

The presence of trapping effects in the V-3.5Nb and V-3.6Ta alloys, however, may not imply that the oxygen interactions with these substitutional solutes in vanadium are always attractive, since changes of the substitutional solute content may produce significant modifications of the interactions. Furthermore, the equilibrium data on these two alloys appear to contradict the diffusion data; however, the errors associated with equilibrium measurements are greater than with diffusion and may have masked the small observed effects. Therefore, more equilibrium and diffusion measurements are required for these dilute alloys, in particular for the V-Ta alloys.

4.4 Vanadium x Niobium

The present results raise important questions concerning the effect of substitutional solutes on the thermodynamic and transport properties of oxygen in Nb- and V-based transition alloys. For instance, the large effects of substitutional atoms in niobium^[2] sharply contrast with the barely measurable effects in vanadium. Moreover the greater oxygen solubility in vanadium^[51] than in niobium^[65] probably reflects the same fundamental differences between these two bcc metals. The generally good correlation of the thermodynamic and transport properties of oxygen in V- and Nb-based alloys with the chemical affinity and the difference of charge ΔZ between the substitutional impurity and the solvent ionic cores indicates that the main contribution to substitutional-interstitial solute interactions arises from perturbations induced by these solutes on the electronic structure of V and Nb. The much greater binding energies of oxygen to substitutional solutes in niobium than their respective elastic interaction energies corroborate the above conclusion. However, other experiments are certainly required to properly understand the effect of solutes on the properties of these two transition metals.

5. CONCLUSIONS

1. The oxygen diffusion in vanadium was not significantly modified by small additions of Ti, Cr, Ni, Nb and Ta.
2. 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.
3. The oxygen activity was increased by the addition of 1 at% of Cr, Ni and Nb, and decreased by the addition of Ti and Ta. However, the effects in the alloys containing Nb and Ta are very small and seem to reverse when the substitutional solute content is increased.
4. The main contribution to the interactions between substitutional-interstitial solutes is believed to arise from chemical effects through perturbation induced by these solutes on the electronic structure of the solvent atoms.
5. The EMF technique was shown capable of monitoring the kinetics of a precipitation process, and should be extended to other solid-state reactions, e.g., ordering, martensitic, etc., where the oxygen atom would act essentially as a "probe" to detect changes in the specimen.
6. The oxygen precipitation in vanadium alloys containing Ti, Zr and Hf certainly suggests attractive interactions between oxygen and these solutes.

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