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Oxygen Vacancies in $Nb_{22}O_{54-x}$, $Nb_{25}O_{62-x}$, and $Nb_{28}O_{70-x}$

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The isolated oxygen vacancies in $Nb_{22}O_{54-x}$, $Nb_{25}O_{62-x}$ and $Nb_{28}O_{70-x}$ at temperatures above 1300°C were examined thermodynamically using gravimetric data obtained previously by Kimura. The concentrations of oxygen vacancies in $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ were estimated from isothermal changes in weight and found to be proportional to $Po_2^{-1/2}$. With $Nb_{28}O_{70-x}$, on the other hand, the concentration of oxygen vacancies was proportional to $Po_2^{-1/4}$. These results can be explained well on the assumption that the main defects, which all depend upon the partial pressure of oxygen in the surrounding atmosphere, are oxygen vacancies with one trapped electron, quasifree electrons, and tetravalent niobium ions.

1. Introduction

The phase equilibrium study on the system NbO_2–Nb_2O_5 by Schäfer, Bergner, and Gruehn (*1*) showed that five compounds, $Nb_{12}O_{29}$, $Nb_{22}O_{54}$, $Nb_{47}O_{116}$, $Nb_{25}O_{62}$, and $Nb_{53}O_{132}$, are stable at 1300°C in the composition range between NbO_2 and Nb_2O_5. Later, Kimura (*2*) confirmed the above-stated observation at temperatures higher than 1300°C but found that $Nb_{22}O_{54}$, $Nb_{25}O_{62}$, and $Nb_{28}O_{70}$ (Nb_2O_5) show considerable deficiencies in oxygen.

The deviations from stoichiometry observed in this family of materials had been explained as being due to Wadsley defects (*3*, *4*), until Allpress and Roth (*5*) suggested the presence of anion vacancies or metal interstitials in these compounds.

However, Iijima, Kimura, and Goto (*6*) recently studied Kimura's samples of $Nb_{22}O_{54-x}$ and found the presence of some Wadsley defects which mostly correspond to $Nb_{12}O_{29}$, together with two kinds of point defects. These authors thought that even well-equilibrated samples are allowed to have at least one type of Wadsley defect and concluded that the nonstoichiometry of $Nb_{22}O_{54}$ must result from the net effects of the Wadsley defect and the point defects.

On the other hand, there is some evidence to support the view that these compounds have contained no or a very small proportion of the Wadsley defect at high temperatures. With careful observations on lattice images, Browne, Hutchison, and Anderson (*7*), and recently Goto and Kikuchi (*8*), reached an identical conclusion that the transformation of one type of the Wadsley defect to another may be achieved by a "cooperative movement" of atoms, as was first suggested by Andersson and Wadsley (*9*). This implies that the energy required for the formation of the Wadsley defect may be small. Therefore, it is suggested that the Wadsley defect can easily appear during the quenching of samples containing an oxygen-deficient point defect, provided that the two-phase region is more extended at a lower temperature, which is still high enough to allow the rearrangement of atoms in the structure. This view is also suggested by the experiments of Allpress and Roth (*5*). They showed that the Wadsley defects found in stoichiometric Nb–W oxides disappeared after a prolonged annealing at about 1350°C but those found in nonstoichiometric samples were never entirely removed from the samples. Nimmo and Anderson (*10*) obtained a similar result, i.e., that no Wadsley defects were observable in the $Nb_{28}O_{70-x}$ at compositions down to $NbO_{2.495}$. They suspected that oxygen deficient point defects occur in those samples.

Several models for point defects deficient in oxygen have been proposed recently in relation to the question mentioned above (*7, 8, 11*). All the models were proposed, in fact, to explain unusual contrast often observed in the lattice images of Nb_2O_{5-x} in relation to particular tetrahedral sites. It is, however, obvious that electron microscopy can reveal very little about defects caused by light atoms, such as isolated oxygen vacancies, for which a classical approach of the Kröger style (*12*) is still unavoidable.

In the present paper, the possibility and nature of isolated oxygen vacancies in the Nb_2O_{5-x} block structures were examined by a gravimetric study using experimental data collected from Kimura's work (*2*) on the system of NbO_2–Nb_2O_5.

2. Gravimetric Considerations

The reaction by which Nb_2O_5 is reduced to Nb_2O_{5-x} can be expressed as

$$1/x\,Nb_2O_5 = 1/x\,Nb_2O_{5-x} + \tfrac{1}{2}O_2. \qquad (1)$$

If the deviation in stoichiometry x is caused by oxygen vacancies, the reaction involves an elementary reaction expressed as

$$O_O{}^x = V_O{}^x + \tfrac{1}{2}O_2 \qquad (2)$$

where $O_O{}^x$ is an oxygen atom in a normal oxygen lattice site with neutral charge state (denoted by an x superscript) and $V_O{}^x$ is an oxygen vacancy with neutral state. The trapped electrons may be excited into the conduction band according to

$$V_O{}^x = V_O{}^{\cdot} + e^- \qquad (3)$$

and

$$V_O{}^{\cdot} = V_O{}^{\cdot\cdot} + e^-, \qquad (4)$$

where $V_O{}^{\cdot}$ is a singly ionized vacancy and $V_O{}^{\cdot\cdot}$ is a doubly ionized one.

Applying the law of mass action to the above equations, we obtain:

$$K_1 = [V_O{}^x]\,Po_2^{1/2} \qquad (5)$$

$$K_2[V_O{}^x] = [V_O{}^{\cdot}]\,[e^-] \qquad (6)$$

$$K_3[V_O{}^{\cdot}] = [V_O{}^{\cdot\cdot}]\,[e^-]. \qquad (7)$$

If the first electrons are partially or completely excited while the second are not, the combination of Eqs. (5) and (6) leads to

$$[e^-] = [V_O{}^{\cdot}] = (K_1 K_2)^{1/2}\,Po_2^{-1/4}. \qquad (8)$$

Equation (8) is the case indicated by Greener *et al.* (*13, 14*), which includes the extreme one where all the oxygen vacancies, $[V_O]_{tot}$, have been singly ionized to the state of $V_O{}^{\cdot}$, and therefore

$$[V_O{}^{\cdot}]_{tot} = [V_O{}^{\cdot}] \propto Po_2^{-1/4}. \qquad (9)$$

If all oxygen vacancies are completely ionized to the state of $V_O{}^{\cdot\cdot}$, the case proposed

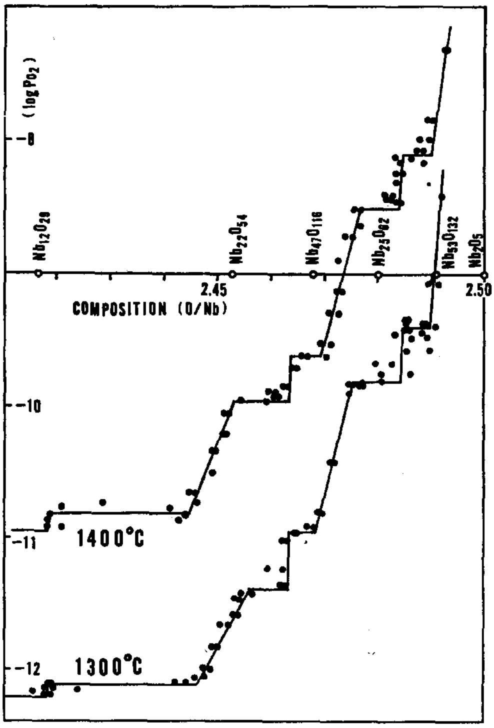

FIG. 1. System of the NbO_2–Nb_2O_5 at 1300 and 1400°C studied by Kimura (*2*).

by Kofstad and Anderson (*15*) can be represented as:

$$[V_O]_{tot} = [V_O^{\cdot\cdot}] = (\tfrac{1}{4})^{1/3}(K_1K_2K_3)^{1/3}Po_2^{-1/6}. \qquad (10)$$

Kofstad and Anderson adopted a range of Po_2 about 10^{-7} to 10^{-12} atm for their experiments which were at 1300°C. According to phase equilibrium studies (*1*, *2*), however, Nb_2O_{5-x} phase ($Nb_{28}O_{70}$ with nonstoichiometry region) can be stable at 1300°C at values of Po_2 above $10^{-9.5}$ atm, and changes, through several homologous compounds such as $Nb_{25}O_{62}$, $Nb_{22}O_{54}$, and $Nb_{12}O_{29}$, into NbO_2 at 10^{-12} atm as shown in Fig. 1. Therefore, it may be supposed that during the experiments their samples could have changed into other homologs or have involved a

TABLE I

THERMOCHEMICAL DATA CITED IN FIGS. 2 AND 3

	Composition (O/Nb) from		$\log [V_o]_{tot}$ from			
$\log Po_2$	Nb_2O_5	NbO_2	Nb_2O_5	NbO_2	$\log [Nb^{4+}]$	$\log K_4K_5$
			($Nb_{22}O_{54-x}$ at 1300°C)			
−12.12	2.443	2.444	−2.33	−2.37	−0.95	
−12.08	2.448	2.446	−2.57	−2.46	−0.98	−9.53
−12.02	2.448	2.449	−2.57	−2.65	−0.99	−9.61
−11.84	2.450	2.450	−2.73	−2.73	−1.00	−9.65
−11.67	2.451	2.452	−2.84	−2.98	−1.01	−9.75
			($Nb_{22}O_{54-x}$ at 1400°C)			
−10.83	2.444	2.419	−2.37			
−10.78	2.441	2.422	−2.26			
−10.74	2.446	2.429	−2.46			
−10.66	2.445	2.446	−2.41	−2.46	−0.96	−8.73
−10.51	2.449	2.449	−2.65	−2.65	−0.99	−8.89
−10.35	2.450	2.450	−2.73	−2.73	−1.00	−8.91
−10.21	2.451	2.451	−2.84	−2.84	−1.01	−8.95
−10.06	2.451	2.452	−2.84	−2.98	−1.01	−8.95
−10.00	2.451		−2.84			
			($Nb_{25}O_{62-x}$ at 1300°C)			
−10.98		2.464		−2.19		
−10.94	2.467	2.469	−2.28	−2.35	−1.19	−8.98
−10.84	2.468	2.469	−2.32	−2.35	−1.20	−8.95
−10.46	2.472	2.472	−2.49	−2.49	−1.25	−8.97
−9.92	2.475		−2.70		−1.30	−8.96
−9.88	2.478	2.477	−3.09	−2.92	−1.35	−9.28
−9.86	2.475		−2.70			
			($Nb_{25}O_{62-x}$ at 1400°C)			
−9.73		2.466		−2.25		
−9.62	2.466	2.467	−2.25	−2.28		
−9.48	2.467	2.469	−2.29	−2.35	−1.19	−8.25
−9.30	2.471	2.473	−2.44	−2.55	−1.25	−8.39
−9.13	2.473	2.473	−2.55	−2.55	−1.27	−8.38
−8.91	2.473	2.472	−2.55	−2.49	−1.26	−8.23
−8.72	2.475	2.474	−2.70	−2.62	−1.29	−8.31
−8.64	2.477	2.477	−2.92	−2.92	−1.34	−8.59
−8.55	2.477	2.476	−2.92	−2.79		

considerable amount of Wadsley defects, for which the deficiency in oxygen atoms cannot be attributed wholly to the formation of oxygen vacancies.

In the present paper, the relation between $[V_O]_{tot}$ and Po_2 was examined for $Nb_{22}O_{54-x}$, $Nb_{25}O_{62-x}$, and $Nb_{28}O_{70-x}$ separately, using the experimental data obtained by Kimura in his study on phase equilibria in the system NbO_2-Nb_2O_5. The data are listed in the first and second columns of Table I. For these samples, the value of $[V_O]_{tot}$ was estimated as $[V_O]_{tot} = (X - Y)/X$, if the chemical composition of a stoichiometric compound is expressed by NbO_X and that of a nonstoichiometric compound derived from it by NbO_Y.

The values of $[V_O]_{tot}$ thus obtained and the corresponding values of Po_2 are given in Table I, and the plots of $[V_O]_{tot}$ versus Po_2 for $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ are given in Figs. 2 and 3, respectively. According to Kimura (*2*), the samples brought from Nb_2O_5 into equilibrium with a given oxygen pressure were often found to have been more reduced than the samples oxidized from NbO_2 at the same oxygen pressure. Moreover, when the running conditions were close to that for a two-phase region, the reaction had been considerably sluggish and often could not reach to the equilibrium even after 15 to 70 hr. The limits of Po_2 for the single-phase region were also shown in the figures as broken lines drawn vertical to the Po_2 axis. As seen from these figures, the plots include data for the samples for which the equilibration was thought to be insufficient. The plots for the single phase regions of $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$, however, can preferably be regarded as lines with slopes of about $-\frac{1}{2}$ showing the following relationship:

$$[V_O]_{tot} \propto Po_2^{-1/2}. \qquad (11)$$

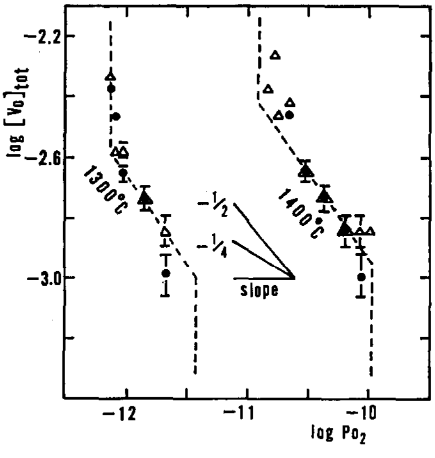

FIG. 2. Plots of $[V_O]_{tot}$ versus Po_2 for $Nb_{22}O_{54-x}$. Open triangles are the data derived from Nb_2O_5 and dots are those derived from NbO_2.

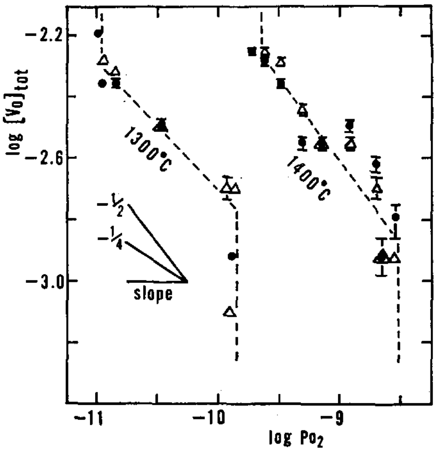

FIG. 3. Plots of $[V_O]_{tot}$ versus Po_2 for $Nb_{25}O_{62-x}$. Open triangles are the data derived from Nb_2O_5 and dots are those derived from NbO_2.

Equation (11) corresponds to the conditions described by the Eqs. (2) and (5), and seems to suggest that all oxygen vacancies in $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ are neutral ones. According to the estimate by Greener *et al.* (*13*), the energy of excitation required for the first electron to be released from a neutral oxygen vacancy is 0.15 eV, which is about the thermal energy at 1300–1400°C. Therefore, the population of oxygen vacancies at such high temperatures must contain a large proportion of $V_O^{\cdot}$.

3. Formation of Nb^{4+}

In previous works on Nb_2O_{5-x}, V_O^{x}, $V_O^{\cdot}$, $V_O^{\cdot\cdot}$, and e^- but not Nb^{4+} have been considered as the chemical entities participating in the reaction. However, it may be quite reasonable to suppose that some of the quasi-free electrons liberated from oxygen vacancies can be retrapped in the valence band of some Nb^{5+} ions, thus changing the Nb^{5+} ions to Nb^{4+}. If this is so, then the mode of the dependence of $[V_O]_{tot}$ on Po_2 certainly must be modified.

Let us consider firstly that the oxygen vacancies in Nb_2O_{5-x} series are exclusively the singly ionized ones, that is $[V_O]_{tot} = [V_O^{\cdot}]$; then we have

$$O_O^{x} = V_O^{\cdot} + e^- + \tfrac{1}{2}O_2 \qquad (12)$$

and

$$e^- + Nb^{5+} = Nb^{4+}. \qquad (13)$$

Equation (13) means that the electrons thermally excited from Nb^{4+} sites can give rise to the electron concentration as proposed for TiO_{2-x} by Frederikse (*16*). Applying the law of mass action, we obtain

$$K_4 = [V_O^{\cdot}]\,[e^-]\,Po_2^{1/2} \qquad (14)$$

$$[e^-]\,K_5 = [Nb^{4+}] \qquad (15)$$

$$K_4 K_5 = [V_O^{\cdot}]\,[Nb^{4+}]\,Po_2^{1/2}. \qquad (16)$$

When we deal not only with $Nb_{28}O_{70-x}$ but also with $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$, we must define a quantity $[Nb^{4+}]_{in}$, which is the concentration of the intrinsic Nb^{4+} ions originally present in a stoichiometric compound such as $Nb_{22}O_{54}$ or $Nb_{25}O_{62}$, and $[Nb^{4+}]_{ad}$ which is the concentration of the Nb^{4+} ions formed in the production of oxygen vacancies. Therefore, $[Nb^{4+}]$ in the Eq. (16) is expressed as

$$[Nb^{4+}] = [Nb^{4+}]_{in} + [Nb^{4+}]_{ad}. \qquad (17)$$

For $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ the values of $[Nb^{4+}]_{in}$ are constant, and $[Nb^{4+}]_{in} \gg [Nb^{4+}]_{ad}$ within the observed ranges of composition of both compounds. Therefore, Eq. (16) can be modified for $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ as follows:

$$\begin{aligned}[V_O]_{tot} = [V_O^{\cdot}] &= K_4 K_5 [Nb^{4+}]^{-1}\, Po_2^{-1/2} \\ &= \text{constant} \times Po_2^{-1/2} \qquad (18)\end{aligned}$$

For $Nb_{28}O_{70-x}$, $[Nb^{4+}]_{in} = 0$ and therefore $[Nb^{4+}] = [Nb^{4+}]_{ad}$, so we have

$$[V_O^{\cdot}] = [e^-] + [Nb^{4+}] \qquad (19)$$

and from Eqs. (15) and (16),

$$\begin{aligned}[V_O]_{tot} = [V_O^{\cdot}] &= K_4^{1/2}(1 + K_5)^{1/2}\, Po_2^{-1/4} \\ &= \text{constant} \times Po_2^{-1/4}. \qquad (20)\end{aligned}$$

If the oxygen vacancies are exclusively in the doubly ionized state $V_O^{\cdot\cdot}$,

$$O_O^{x} = V_O^{\cdot\cdot} + 2e^- + \tfrac{1}{2}O_2 \qquad (21)$$

and

$$K_6 = [V_O^{\cdot\cdot}]\,[e^-]^2\, Po_2^{1/2} \qquad (22)$$

and, with use of Eq. (15) we obtain

$$K_5^{\,2} K_6 = [V_O^{\cdot\cdot}]\,[Nb^{4+}]^2\, Po_2^{1/2}. \qquad (23)$$

For $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ in which Nb^{4+} are constant, Eq. (23) can be modified as:

$$\begin{aligned}[V_O]_{tot} = [V_O^{\cdot\cdot}] &= K_5^{\,2} K_6 [Nb^{4+}]^{-2}\, Po_2^{-1/2} \\ &= \text{constant} \times Po_2^{-1/2}, \qquad (24)\end{aligned}$$

and for $Nb_{28}O_{70-x}$ in which $[Nb^{4+}]$ is not constant but equal to $[Nb^{4+}]_{ad}$:

$$2[V_O^{\cdot\cdot}] = [e^-] + [Nb^{4+}],$$

so we have,

$$\begin{aligned}[V_O]_{tot} = [V_O^{\cdot\cdot}] &= (\tfrac{1}{4})^{1/3}(1 + K_5)^{2/3}\, K_6^{1/3}\, Po_2^{-1/6} \\ &= \text{constant} \times Po_2^{-1/6}. \qquad (25)\end{aligned}$$

As shown in Eqs. (18) and (24), the ionic state of the oxygen vacancies in $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$ cannot be determined from the mode of the dependence of $[V_O]_{tot}$ on Po_2, since for both compounds the $[V_O]_{tot}$ is proportional to $Po_2^{-1/2}$, whether the defects are exclusively in the state of $V_O^{\cdot}$ or in the fully ionized state of $V_O^{\cdot\cdot}$.

For $Nb_{28}O_{70-x}$, however, the mode of the dependence on Po_2 changes with the ionic state of the vacancy; the $[V_O]_{tot}$ is proportional to $Po_2^{-1/4}$ when the oxygen vacancies are $V_O^{\cdot}$, and to $Po_2^{-1/6}$ when they are $V_O^{\cdot\cdot}$. An isothermal weight loss measurement for $Nb_{28}O_{70-x}$ carried out slightly below the melting temperature (at 1485°C) by Kimura (*17*) showed a $Po_2^{-1/4}$ dependence as seen in Fig. 4.

Since $Nb_{22}O_{54}$ are structurally very similar to $Nb_{28}O_{70}$, it may be supposed that the oxygen vacancies in these compounds are also in the state of $V_O^{\cdot}$.

The values of log K_4K_5 in Eq. (18) are listed in the last column of Table I. For this, the concentrations of Nb^{4+} were evaluated on the assumption: $Nb_{ad}^{4+} = 2x$ for $Nb_{22}O_{54-x}$ and $Nb_{25}O_{62-x}$. The heat of formation ΔH of the

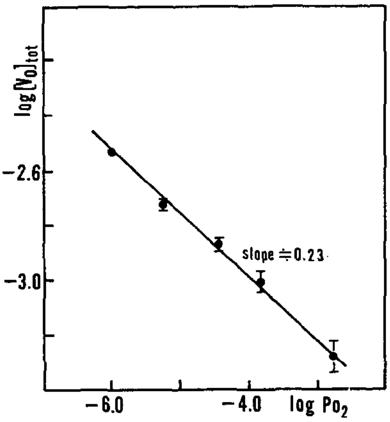

FIG. 4. Plots of $[V_o]_{tot}$ versus Po$_2$ for $Nb_{28}O_{70-x}$ at 1485°C.

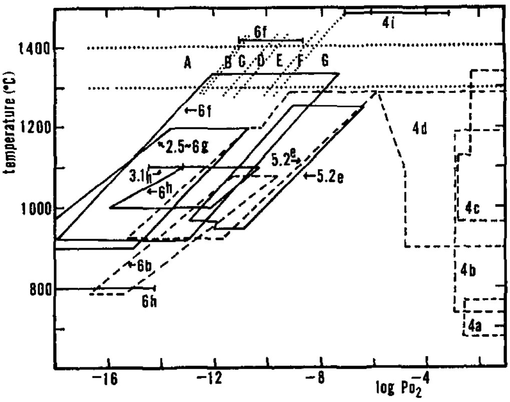

FIG. 5. Observed ranges of Po$_2$ and temperature for the Po$_2$ dependences previously reported.

singly ionized oxygen vacancy $V_O^{\cdot}$ estimated from the values of log K_4K_5 at 1300 and 1400°C is 89 kcal for $Nb_{22}O_{54-x}$ and 77 kcal for $Nb_{25}O_{62-x}$. These are comparable with the 73 kcal for Nb_2O_{5-x}($Nb_{28}O_{70-x}$) given by Greener *et al.* (*13*).

Now, it is concluded that the singly ionized oxygen vacancies, the quasi-free electrons and the Nb^{4+} ions formed in consequence of retrapping of some of the electrons in the valence band of the constituent Nb^{5+} ions are the most probable species of the defects in slightly reduced $Nb_{22}O_{54}$, $Nb_{25}O_{62}$, and $Nb_{28}O_{70}$.

4. Discussion

The conclusion of the present work might raise some arguments because it shows an obvious disagreement with the prevailing interpretation based on many previous works. The Po$_2$ dependence of the weight change of Nb_2O_{5-x} has been investigated by various authors over wide ranges of Po$_2$ and temperature, as shown in Fig. 5. In this figure, the areas enclosed with the solid lines indicate the regions where the values of n for $Po_2^{-1/n}$ were determined from gravimetric measurements, and the areas shown by broken lines are the regions where the values of n were obtained by electrical measurements. Small letters indicate the references: a (*13*), b (*20*), c (*14*), d (*21*), e (*22*), f (*15*), g (*18*), h (*19*), and i (the present paper). Capital letters indicate the compounds, A (NbO_2), B ($Nb_{12}O_{29}$), C ($Nb_{22}O_{54}$), D ($Nb_{47}O_{116}$), E ($Nb_{25}O_{62}$), F ($Nb_{53}O_{132}$), and G ($Nb_{28}O_{70}$), which are stable under the respective Po$_2$ ranges shown by the dotted lines (*1*, *2*).

In those works, the weight changes were observed to be proportional to $Po_2^{-1/6}$, or at least $Po_2^{-1/n}$ where $n > 4$, in most fields except for comparatively high Po$_2$ ranges where the gravimetric measurement is not effective. There are various interpretations (*21–24*) on this fact. The commonly accepted one may be that the oxygen vacancies in Nb_2O_{5-x} are mostly in the state of $V_O^{\cdot\cdot}$, and that the apparent dependence on $Po_2^{-1/4}$ in the fields of high oxygen pressures may be caused not by the exclusive presence of $V_O^{\cdot}$ but by the presence of lower valent impurities (*22*, *24*).

Therefore, our result must be examined in regard to two questions; whether the concentration of lower valent impurities in our samples was so high that they could modify the Po$_2$ dependence of the weight change from $Po_2^{-1/6}$ to $Po_2^{-1/4}$, and whether our samples contained any other factors which produce a similar effect as brought by lower valent impurities.

4.1. *Effect of Impurities*

If we assume that oxygen vacancies in Nb_2O_{5-x} are mostly in the state of $V_O^{\cdot\cdot}$, and that some tetravalent impurities such as Ti^{4+}

occupy normal niobium sites of the structures, the following relations between the concentration of the impurities $[F_M']$ and that of the doubly ionized oxygen vacancies $[V_O^{\cdot\cdot}]$ can be obtained

$$2[V_O^{\cdot\cdot}] = [F_M'] + [e^-] \qquad (26)$$

and

$$[V_O^{\cdot\cdot}]_{\text{obs}} = [V_O^{\cdot\cdot}] - \tfrac{1}{2}[F_M'], \qquad (27)$$

where $[V_O^{\cdot\cdot}]_{\text{obs}}$ denotes the apparent concentration of the doubly ionized oxygen vacancies that is measurable by a gravimetric mean. The combination of Eqs. (26), (27), and (22) leads to

$$K_6 = 4([V_O^{\cdot\cdot}]_{\text{obs}} + \tfrac{1}{2}[F_M'])\,[V_O^{\cdot\cdot}]^2_{\text{obs}}\,\text{Po}_2^{1/2}. \qquad (28)$$

The Po_2 dependence of $[V_O^{\cdot\cdot}]_{\text{obs}}$ in $Nb_{28}O_{70-x}$ was calculated from Eq. (28) for various values of $[F_M']$ and for the values of x from 0.02 to 0.003, which correspond to the composition range of our Nb_2O_{5-x} samples. The results are shown in Fig. 6. The figure indicates that the Po_2 dependencies of $[V_O^{\cdot\cdot}]_{\text{obs}}$ in $Nb_{28}O_{70-x}$ deviate gradually from $\text{Po}_2^{-1/6}$ to $\text{Po}_2^{-1/4}$ with increasing concentrations of F_M' and that the deviation becomes notable when the impurity exceeds a value of about 2000 ppm for the $Nb_{28}O_{70-x}$ having compositions equivalent to those of our samples.

The starting material used in the present work has been analyzed by the supplier (Johnson Matthey Chemicals Ltd.) to be 99.97% pure Nb_2O_5 with impurities shown in Table II. After experiment, an arbitrarily chosen sample was chemically treated and analyzed by the X-ray fluorescence method. It was shown by this analysis that metal elements such as Ti, Fe, W, and Mo were not detectable, that is, the concentrations of these elements were less than the detectable limits of the method as follows: 1 ppm for Fe, 3 ppm for Ti, 10 ppm for W, and 3 ppm for Mo. It is quite obvious from these analytical data that the concentrations of lower valent impurities in our samples are not so high that they could modify the Po_2 dependence curves to any appreciable degree, much less the deviation from $\text{Po}_2^{-1/6}$ to $\text{Po}_2^{-1/4}$.

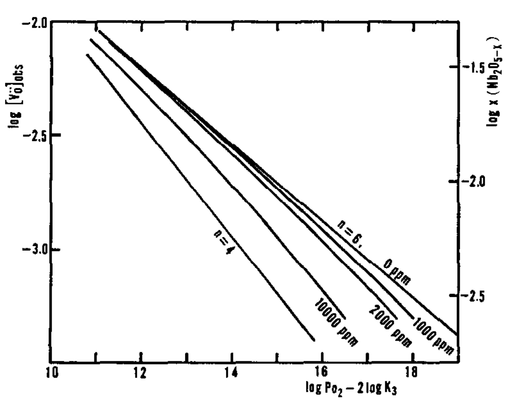

FIG. 6. Variation of the Po_2 dependence with varying tetravalent impurities.

TABLE II

SPECTROGRAPHIC ANALYSIS OF Nb_2O_5

Fe	2 ppm
Mg	1 ppm
Ta	100 ppm

Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, W, Zn, and Zr were undetectable.

4.2. *Effect of Wadsley Defects*

It has been well known that Nb_2O_{5-x} prepared by ordinary methods, such as reducing Nb_2O_5 or oxidizing other lower oxides of niobium, usually contains large proportions of equilibrium and nonequilibrium Wadsley defects and in some cases even domains of neighboring phases. A long duration at high temperatures is required to equilibrate the nonequilibrium extended defects. It was described by Kimura (*2*) that a sample with a composition near $Nb_{53}O_{132}$ could not have been equilibrated by heating for 75 hr at 1400°C.

Iijima et al. (*6*) have suggested that Wadsley defects can be thermodynamically stable and only neighboring phases of the host structure are allowed to be Wadsley defects in well-equilibrated materials, which contain certain amounts of oxygen vacancies. This implies that the proportion of such an equilibrium Wadsley defect relative to that of the oxygen vacancies will increase with decreasing temperature.

For examining the effect of the Wadsley equilibrium defects in the Po_2 dependence curve, it may be possible to apply a similar approach that was used for oxygen point vacancies, as already discussed. The formation of the $Nb_{25}O_{62}$ Wadsley defect in the $Nb_{28}O_{70}$ phase, for example, can be expressed as

$$25\,Nb_{28}O_{70} = 28\,Nb_{25}O_{62} + 7\,O_2. \quad (29)$$

The reaction involves two elementary reactions,

$$25/28\,Nb_{28}O_{70} = V^{x}_{\mathrm{wad}} + \tfrac{1}{4}O_2 \quad (30)$$

and

$$V^{x}_{\mathrm{wad}} = V^{\cdot}_{\mathrm{wad}} + e^{-}, \quad (31)$$

where V^{x}_{wad} and $V^{\cdot}_{\mathrm{wad}}$ are the $Nb_{25}O_{62}$ defects with respective electrical charge states. If the reaction Eq. (30) is prevailing, most of the $Nb_{25}O_{62}$ Wadsley defects are electrically neutral with the formation of one Nb^{4+} ion per molecule, and their concentration must be dependent on $Po_2^{-1/4}$. On the other hand, the reaction Eq. (31) represents the case in which the Wadsley defects are in the singly ionized state with one electron excited to the conduction band. The defect concentration in this case must be proportional to $Po_2^{-1/8}$.

The above results suggest that most of the Nb_2O_{5-x} samples used in our and other works might have contained a proportion of Wadsley defects which could modify the Po_2 dependence curve from $Po_2^{-1/4}$ toward $Po_2^{-1/8}$ if they are singly ionized. This effect may become appreciable when the concentration of the Wadsley defects relative to that of the coexisting oxygen vacancies is increased and an apparent dependence-curve proportional to $Po_2^{-1/n}$, where n is a value somewhat larger than 4, may be attained.

The structures and proportions of the Wadsley defects in the samples used in the present work have been carefully examined by observing the lattice images with high-resolution electron microscopy (*8*, *17*). It was shown by this examination that all samples in the series 4*i* in Fig. 5, which were prepared at 1485°C, contained no Wadsley defect. We therefore suspect that dependence on $Po_2^{-1/6}$ observed in previous works might result from samples containing comparatively large proportion of Wadsley defects, since the temperatures of the experiments of most of the previous works are lower than ours, and durations are also probably shorter.

4.3. *Precision of Experiment*

The impurity of 0.003% (99.97% pure Nb_2O_5) corresponds to an accuracy of ±0.00075 for the values of O/Nb determined by analysis. However, the precision of the experiments must be considerably higher than the accuracy of ±0.00075 because the impurity of the largest quantity in the starting material is Ta^{5+} which does not affect the Po_2 dependence curve and because the compositional variations in the samples made from the same material may be identical. The precisions estimated on the basis of the above consideration are ±0.0002 for the O/Nb value of the samples in series 4*i* in Fig. 5, and ±0.0005 for the other samples. The accuracies of weighing the samples and measuring the Po_2 are within the ranges of the precision mentioned above.

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References

1. H. SCHÄFER, D. BERGNER, AND R. GRUEHN, *Z. Anorg. Allg. Chem.* **365**, 31 (1969).
2. S. KIMURA, *J. Solid State Chem.* **6**, 438 (1973).
3. J. G. ALLPRESS, *J. Solid State Chem.* **1**, 66 (1969).
4. J. G. ALLPRESS, *J. Solid State Chem.* **2**, 78 (1970).
5. J. G. ALLPRESS AND R. S. ROTH, *J. Solid State Chem.* **3**, 209 (1971).
6. S. IIJIMA, S. KIMURA, AND M. GOTO, *Acta Crystallogr.* **A30**, 251 (1974).
7. J. M. BROWNE, J. L. HUTCHISON, AND J. S. ANDERSON, *in* "Proceedings of 7th International Symposium on Reactivity of Solids," p. 116, Bristol (1972).
8. M. GOTO AND T. KIKUCHI, *in* "International Conference on Diffraction Studies of Real Atoms and Real Crystals," p. 147, Melbourne (1974).

9. S. ANDERSSON AND A. D. WADSLEY, *Nature (London)* **211**, 581 (1966).
10. K. M. NIMMO AND J. S. ANDERSON, *J. Chem. Soc. Dalton*, 2328 (1972)
11. J. S. ANDERSON, J. M. BROWNE, A. K. CHEETHAM, R. V. DREELE, J. L. HUTCHISON, D. J. M. BEVAN, AND J. STRAEHLE, *Nature (London)* **243**, 81 (1973).
12. F. A. KRÖGER AND H. J. VINK, *in* "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. 3, p. 307, Academic Press, New York (1956).
13. E. H. GREENER, D. H. WHITMORE, AND M. E. FINE, *J. Chem. Phys.* **34**, 1017 (1961).
14. E. H. GREENER, G. A. FEHR, AND W. M. HIRTHE, *J. Chem. Phys.* **38**, 133 (1963).
15. P. KOFSTAD AND P. B. ANDERSON, *J. Phys. Chem. Solids* **21**, 280 (1961).
16. H. P. R. FREDERIKSE, *J. Appl. Phys.* **32**, 2211 (1961).
17. S. KIMURA, in preparation (1975).
18. R. N. BLUMENTHAL, J. B. MOSER, AND D. H. WHITMORE, *J. Amer. Ceram. Soc.* **48**, 617 (1965).
19. J. F. MARUCCO, *J. Solid State Chem.* **10**, 211 (1974).
20. P. KOFSTAD, *J. Phys. Chem. Solids* **23**, 1571 (1962).
21. W. K. CHEN AND R. A. SWALIN, *J. Phys. Chem. Solids* **27**, 57 (1966).
22. J. M. WIMMER AND W. C. TRIPP, Aerospace Research Laboratories, ARL 73-0157 (1973).
23. R. F. JANNINCK AND D. H. WHITMORE, *J. Chem. Phys.* **37**, 2750 (1962).
24. P. KOFSTAD, *J. Less Comm. Met.* **14**, 153 (1968).