

Thermodynamic Properties of Oxygen in Yttrium-Oxygen Solid Solutions

T.H. OKABE, T.N. DEURA, T. OISHI, K. ONO, and D.R. SADOWAY

The oxygen potential in yttrium-oxygen (Y-O) solid solutions was measured by equilibration with titanium-oxygen (Ti-O) solid solutions. Yttrium and titanium samples were immersed in calcium-saturated CaCl_2 melts at temperatures between 1108 and 1438 K, and oxygen levels in the two metals were measured. With the Ti-O system acting as a reference, oxygen potentials in Y-O solid solutions were determined. By this technique, it was possible to make reliable measurements of extremely low oxygen potentials (as low as 10^{-44} atm at 1273 K), far beyond the range of solid oxide electrolyte sensors.

I. INTRODUCTION

IN recent years 99.9999 pct yttrium* has been produced

*Excluding carbon and gaseous elements.

commercially for use in electronics.⁽¹⁾ The major impurity in this material is oxygen, present in the amount of 0.1 to 0.5 pct (5000 ppm by mass). Oxygen removal from yttrium metal is extremely difficult owing to a combination of two factors. Yttrium has a very strong affinity for oxygen (Figure 1⁽²⁾) and dissolves oxygen in large concentrations (Figure 2^(3,4)). As part of a larger study of electrochemical deoxidation of yttrium,⁽⁵⁾ a technique was developed for measuring extremely low oxygen potentials, circa 10^{-44} atm at 1273 K, which is far beyond the range of solid oxide electrolyte sensors.

II. PRINCIPLES OF MEASUREMENT OF ULTRALOW OXYGEN POTENTIALS

Measurement of ultralow oxygen potential in solid solutions of yttrium-oxygen (Y-O) was accomplished by an indirect technique involving equilibration of Y-O specimens with a reference material, namely, a solid solution of titanium and oxygen. Titanium-oxygen (Ti-O) solid solutions were chosen for the reason that the relationship between oxygen concentration ($[\text{O}]$) and oxygen potential (P_{O_2}) is well established in this system and can be extrapolated to extremely low levels of oxygen potential in accordance with Henry's law.

The principle of the technique is illustrated in Figure 3, which gives the relationship between P_{O_2} and $[\text{O}]$ in Ti-O and Y-O at constant temperature. The two lines were determined as follows. The coordinates of point *A* are P_1 and

$[\text{O}]_A$. P_1 is the value of P_{O_2} in equilibrium with pure Ca and CaO (5×10^{-42} atm at $T = 1273$ K) and is well known from having been measured in several investigations.⁽²⁾ $[\text{O}]_A$ is the concentration of oxygen in titanium (500 ppm*) at

*All expressions of concentration in ppm are by mass.

this P_{O_2} , a value confirmed by multiple researchers.⁽⁶⁻⁹⁾ On the assumption that Ti-O solutions are Henrian up to $[\text{O}]_A$, the relationship between P_{O_2} and $[\text{O}]$ in Ti-O solutions is represented by a straight line connecting point *A* and the origin. It is possible to measure $[\text{O}]$ in titanium metal down to concentrations as low as 10 ppm. At these values of $[\text{O}]$ in titanium, the corresponding P_{O_2} is unmeasurable by direct methods but nevertheless can be accurately determined from the Ti-O line in Figure 3. For example, when the concentration of oxygen in titanium is $[\text{O}]_C$ (approximately 30 ppm), the equilibrium P_{O_2} is P_2 (approximately 2×10^{-44} atm at 1273 K). If a Y-O solution is equilibrated with the same atmosphere in which P_{O_2} is equal to P_2 , then $[\text{O}]$ can be measured and found to be $[\text{O}]_E$.

If Y-O solutions obey Henry's law, the relationship between P_{O_2} and $[\text{O}]$ should be represented by a straight line connecting point *E* and the origin. In this study, measurements of the value of P_{O_2} at the solubility limit of oxygen in yttrium place points *D* and *E* on the same line through the origin, and this confirms that Y-O solutions are Henrian across the entire composition range.

III. EXPERIMENTAL

Table I reports the compositions and forms of the starting materials used in this study. The CaCl_2 solvent for CaO was reagent grade (99.9 pct) anhydrous powder which was dried in air at 800 K for 2 days prior to use.

In a typical experiment, 10 to 15 pieces of yttrium and titanium were placed in a titanium cup filled with CaCl_2 , as shown in Figure 4. The titanium and yttrium were separated from one another by means of titanium and tantalum foils, respectively. The cup containing the samples and the CaCl_2 was sealed in a stainless steel vessel with 5 g of calcium shot. The CaCl_2 works as an oxygen reservoir for establishing a homogeneous oxygen concentration in the two metals even at such extremely low oxygen potentials. Metallic calcium is used to set the low oxygen partial pressure in the

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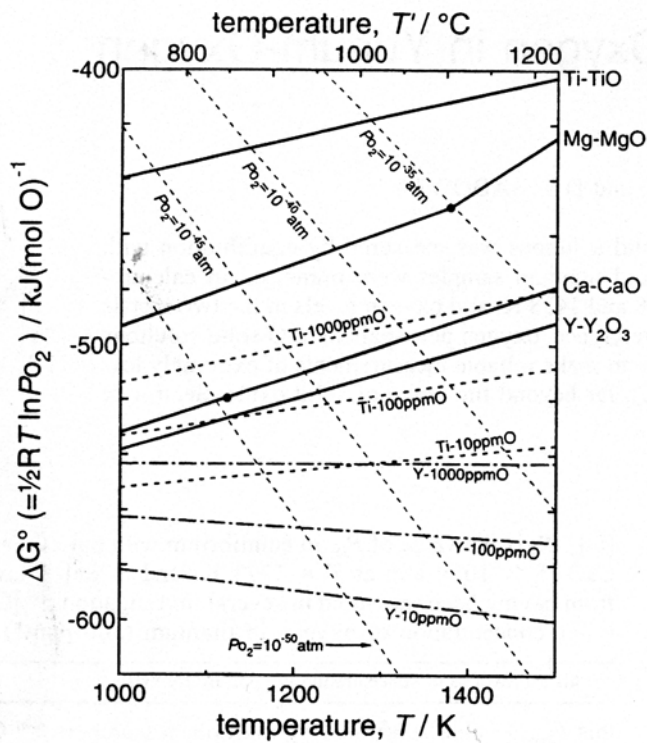


Fig. 1—Ellingham diagram of selected oxides^[2] and solid solutions of Ti-O and Y-O.

vessel. To avoid contamination of the yttrium and titanium by impurities in calcium (mainly oxygen and nitrogen), the calcium was physically isolated from the cup and its contents and was supplied to the CaCl_2 melt in vapor form.

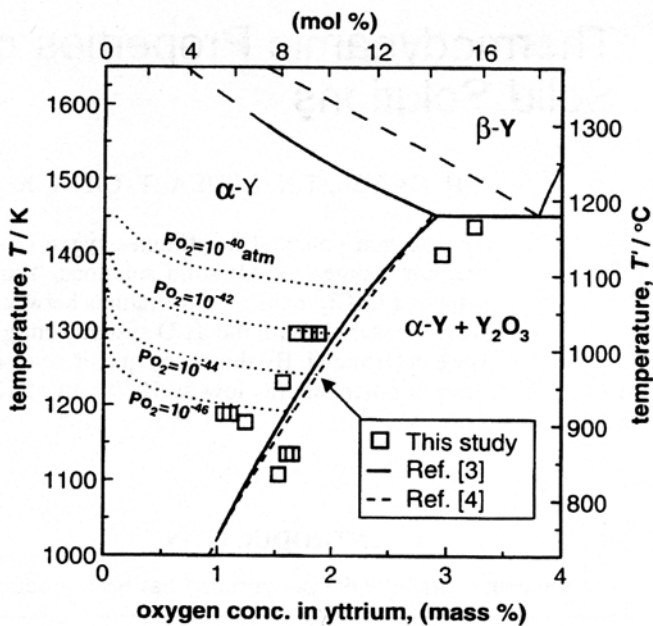


Fig. 2—Phase diagram of the yttrium-rich end of the Y-O system.^[3,4] Lines of constant oxygen potential determined in this study.

In other experiments, 1 g of yttria (Y_2O_3) powder and 2 g of yttrium metal turnings were placed in the titanium cup to establish the equilibrium between yttrium and Y_2O_3 . This experiment was conducted for the purpose of investigating whether oxygen activities in the Y-O solid solutions obey Henry's law up to oxygen saturation (point D in Figure 3).

The assembled, sealed vessel was heated in an electric furnace to a temperature between 1108 and 1438 K. The

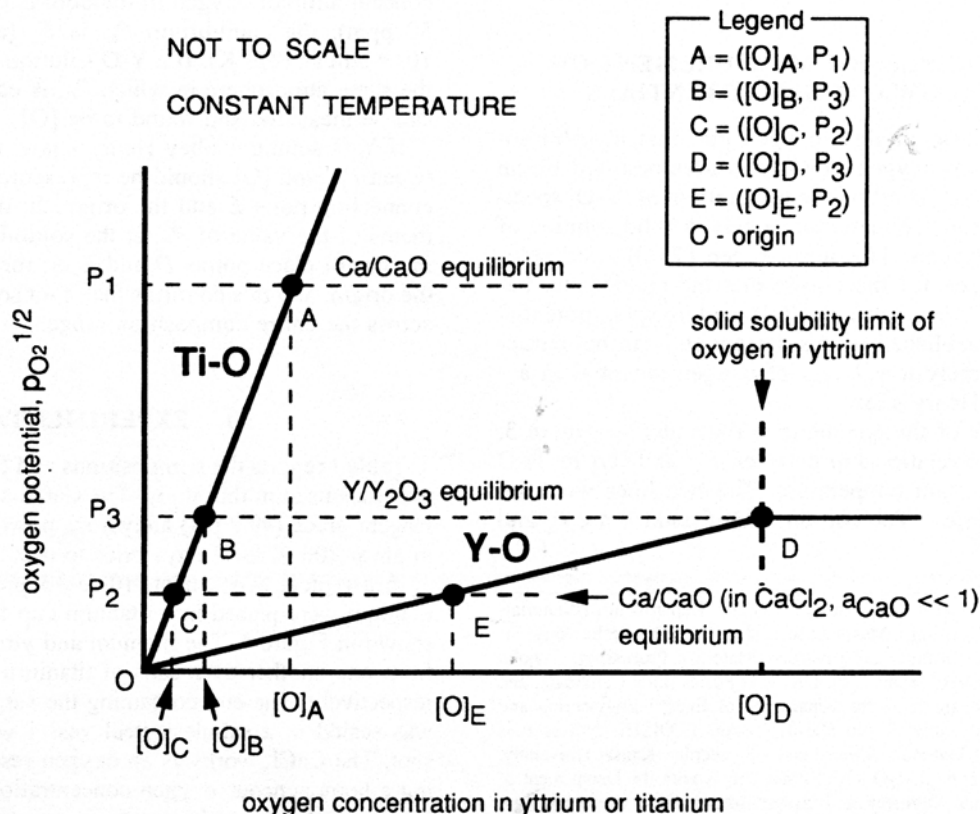


Fig. 3—Relationship between oxygen concentration and oxygen potential in Y-O and Ti-O solid solutions (schematic).

Table I. Chemical Analysis of Yttrium and Titanium Samples Used in This Study

Samples	Grade*	Oxygen Concentration (ppm)	Nitrogen Concentration (ppm)	Configuration
Yttrium-1**	99.9999 pct	4000	70	0.5 to 3-g small pieces
Yttrium-2†	99.9 pct	1300	150	0.5 to 3-g small pieces
Titanium-1‡	99.99 pct	200	20	0.1 to 0.3-g small pieces
Titanium-2†	99.9 pct	1100	50	1.2-mm-diameter wires

*Excluding gaseous elements.

**Electrolytically refined, followed by electron beam melting.^[11]

†Commercial grade.

‡Electron-beam-melted, high-purity sponge.

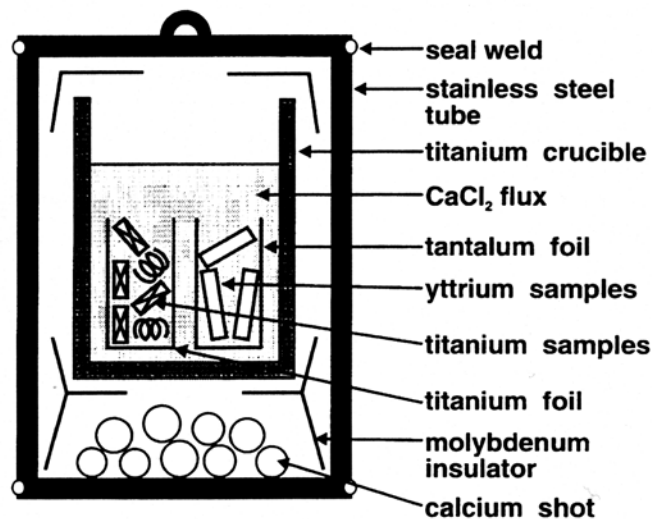


Fig. 4—Reaction vessel used for the measurement of oxygen potential (schematic).

holding time was between 36 ks (10 hours) and 690 ks (8 days), after which time the vessel was removed from the furnace and quenched in water. Previous work with the Ti-O system had established that these times are sufficient for attaining equilibrium.^[8] Furthermore, it is known that oxygen diffusivity in yttrium is higher than in titanium.^[10]

After heat treatment, the calcium-saturated fused salt in the titanium cup was mechanically removed, and yttrium and titanium samples were recovered. The yttrium samples were mechanically polished using files, and the titanium samples were cleaned in warm hydrochloric acid, rinsed in water, alcohol, and acetone, and then allowed to dry.

Oxygen and nitrogen concentrations were determined by an inert gas fusion infrared absorption method (LECO* TC-

*LECO is a trademark of LECO Corporation, St. Joseph, MI.

336 analyzer). Preceding the oxygen and nitrogen analyses, the yttrium samples were again mechanically polished, and the titanium samples were chemically etched with a 1:4:10 mixture of HF:HNO₃:H₂O. For oxygen and nitrogen extraction, 0.1 g of sample enclosed in 1 g of platinum foil was dropped into a graphite crucible and heated to a temperature above 2500 K. The average blank values of oxygen and nitrogen (mainly due to the platinum bath) were 3.6 ± 1.0 and 0.2 ± 0.1 μg, respectively. The concentration of calcium in yttrium was measured by inductively

coupled plasma-atomic emission spectrometry (ICP-AES, Nippon-Jarrell-Ash: ICAP-575II).

IV. RESULTS

Table II reports the results of experiments in which yttrium and titanium specimens were equilibrated with P_{O_2} established by diluting CaO in CaCl₂ (corresponding to $P_{O_2} = P_2$ in Figure 3). The measured value of oxygen concentration in yttrium was found to be independent of the initial oxygen concentration regardless of whether this was greater or less than the final value.

The measured value of nitrogen concentration in the samples was independent of the experimental conditions and, in all cases, increased by about 100 ppm for yttrium and 50 ppm for titanium. The concentration of calcium in yttrium increased from 80 to 100 ppm after experiment.

As the analytical error of the oxygen analysis is 10 ppm, it is not easy to estimate oxygen potentials with high accuracy from the analyzed oxygen concentration in titanium ($[O]_c$ in Figure 3). To address this problem, the oxygen potential in the system was increased by dissolving Y₂O₃ in molten CaCl₂. Measurements made under these conditions are reported in Table III. For experiments in which P_{O_2} was in equilibrium with Y-Y₂O₃ (corresponding to $P_{O_2} = P_3$ in Figure 3), the oxygen concentration in yttrium reached the solubility limit,^[3,4] and the oxygen concentration in titanium increased to about 200 ppm at 1273 K, which can be analyzed with high accuracy.

The temperature dependence of the saturation value of oxygen in yttrium and corresponding equilibrium oxygen concentration in titanium are listed in Table III and plotted in Figure 5. The results listed in Table II are also plotted in the same figure. The lowest values of oxygen concentration in titanium are near the detection limit of analysis with the result that there is considerable scatter in the data for these specimens.

Average distribution coefficients for partitioning oxygen between yttrium and titanium, $[\text{mass pct O}] \text{ in Y} / [\text{mass pct O}] \text{ in Ti}$, were calculated by using data in Tables II and III. In Figure 6, the temperature dependence of the calculated distribution coefficients at different oxygen potentials is plotted. It appears that at any given temperature, the value of the distribution coefficient is almost invariant with oxygen potential. The results also indicate that the distribution coefficient of oxygen increases with temperature. Linear regression analysis of the data in Figure 6 yields the following equation.

Table II. Oxygen Concentration in Samples of Yttrium and Titanium Equilibrated in Calcium-Saturated CaCl₂ (Refer to P₂ in Figure 3)

Experiment Number	Experimental Conditions	Oxygen Concentration (ppm)			
		Yttrium		Titanium	
		Initial	After Experiment	Initial	After Experiment
1D	1115 K (842 °C)	4000	1510, 1630, 1640	200	50, 60
	780 ks (9 days)	1300	1420, 1800	1100	30, 80
1A	1177 K (904 °C)	4000	1970, 2000, 2230	200	10, 40
	260 ks (3 days)	1300	2040	1100	40, 40
1B	1293 K (1020 °C)	4000	2900, 2930, 2940	200	20, 30, 50
	86 ks (1 day)	1300	3100	1100	40, 70
1C	1388 K (1115 °C)	4000	4300, 4420, 4450,	200	40
	56 ks (16 h)		4510	1100	30, 40

Table III. Oxygen Concentration in Samples of Yttrium and Titanium Equilibrated with Y-Y₂O₃ (Refer to P₃ in Figure 3)

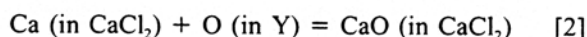
Experiment Number	Experimental Conditions	Oxygen Concentration			
		Yttrium		Titanium	
		Initial	After Experiment (Mass Pct)	Initial	After Experiment (Ppm)
2T	1438 K (1165 °C)	0.400	3.24	200	210, 300
	36 ks (10 h)			1100	380
2Z	1401 K (1128 °C)	0.400	2.96	200	230, 280
	86 ks (1 day)			1100	200, 230
2Y	1296 K (1023 °C)	0.400	1.68, 1.80, 1.88	200	180
	345 ks (4 days)			1100	140, 180
2U	1231 K (958 °C)	0.400	1.56	200	120
	260 ks (3 days)			1100	150, 170
2X2	1188 K (915 °C)	0.400	1.05, 1.11	200	160, 200, 280
	430 ks (5 days)			1100	340
2X	1177 K (904 °C)	0.400	1.07, 1.24, 1.24	200	90, 310, 320
	260 ks (3 days)			1100	90
2V	1135 K (862 °C)	0.400	1.60, 1.65	200	410, 500
	605 ks (7 days)			1100	330, 410
2V2	1108 K (835 °C)	0.400	1.53	200	270
	690 ks (8 days)			1100	720

$$\ln \frac{[\text{mass pct O}]_{\text{inY}}}{[\text{mass pct O}]_{\text{inTi}}} = \frac{-6040 \pm 940}{T} + (9.15 \pm 0.16) \quad [1]$$

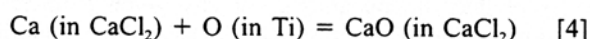
Data below 1155 K (882 °C) were neglected in this regression. This is due to the fact that titanium undergoes a phase transformation at this temperature, and reported values of oxygen activity coefficients in the low-temperature phase (α -titanium) are not consistent.^[7,11-13]

V. DISCUSSION

Reactions between oxygen in yttrium and titanium with calcium dissolved in CaCl₂ are expressed as follows.



$$\Delta G_2^0 = -RT \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot f_{\text{OinY}} \cdot [\text{mass pct O}]_{\text{inY}}} \quad [3]$$



$$\Delta G_4^0 = -RT \ln \frac{a_{\text{CaO}}}{a_{\text{Ca}} \cdot f_{\text{OinTi}} \cdot [\text{mass pct O}]_{\text{inTi}}} \quad [5]$$

where a_i is the activity of component i in molten CaCl₂

relative to pure i at the same temperature. The [mass pct O] in Y and [mass pct O] in Ti are the concentration (in mass pct) of oxygen in yttrium and titanium solid solution, respectively, and f_{OinY} and f_{OinTi} are activity coefficients of oxygen in solution with yttrium and titanium, respectively, and are expressed relative to the 1 mass pct standard state.

In the preceding reactions, a_{CaO} was kept as low as possible. This is due to the fact that at high a_{CaO} , the oxygen concentration in yttrium solid solution reaches saturation even though a_{Ca} is unity. (Note P_{O_2} determined by the Ca-CaO equilibrium (P_1 in Figure 3) is higher than that determined by the Y-Y₂O₃ equilibrium (P_3 in Figure 3).) Coexistence of yttrium and titanium in the calcium-saturated CaCl₂ with a fixed a_{CaO} sets the value of oxygen partial pressure in the system. Thus, one can write

$$\text{O (in Ti)} = \text{O (in Y)} \quad [6]$$

$$\begin{aligned} \Delta G_6^0 &= \Delta G_4^0 - \Delta G_2^0 \\ &= -RT \ln \frac{f_{\text{OinY}} \cdot [\text{mass pct O}]_{\text{inY}}}{f_{\text{OinTi}} \cdot [\text{mass pct O}]_{\text{inTi}}} \end{aligned} \quad [7]$$

Assuming Henry's law to be valid in both the Ti-O and Y-O solutions, *i.e.*, $f_i = 1$, one can calculate the standard free energy change of reaction for Eq. [6] from the values of

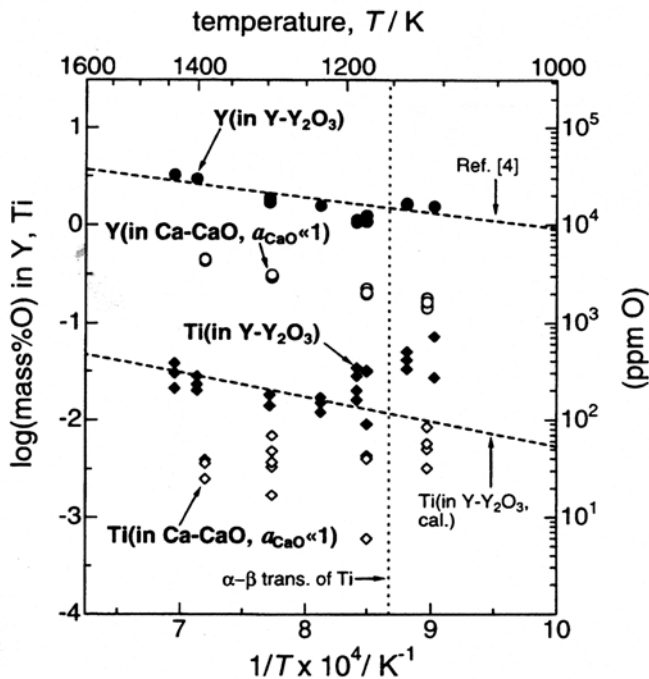


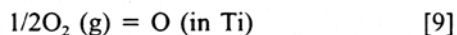
Fig. 5—Oxygen concentration in yttrium and titanium after equilibration. Open circles and diamonds show data from Table II. Filled circles and diamonds show data from Table III.

the distribution coefficient of oxygen in yttrium and titanium obtained in this study. Hence, substitution of Eq. [1] into Eq. [7] yields

$$\Delta G_{\text{O}}^{\circ} = (50,200 \pm 8000) - T \cdot (76.1 \pm 1.3) \quad [1177 \text{ to } 1438 \text{ K}] \quad [\text{J}] \quad [8]$$

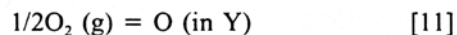
To estimate oxygen potentials in yttrium-oxygen solid solutions, one must first evaluate oxygen potentials in titanium-oxygen solid solutions as a function of oxygen concentration. Oxygen potentials in titanium solid solutions were measured by several researchers,^[6-9] and the reported results are in good agreement with one another.

The Gibbs energy change of solution of oxygen in titanium, $\Delta G_{\text{O}}^{\circ}$, is expressed as follows:



$$\Delta G_{\text{O}}^{\circ} = -RT \ln \frac{[\text{mass pct O}]_{\text{inTi}}}{\sqrt{P_{\text{O}_2}}} \quad [10]$$

The standard Gibbs energy of solution of oxygen in yttrium, shown in Eq. [11], can be determined by Eq. [12] using the standard Gibbs energies of reactions for Eqs. [6] and [9].



$$\Delta G_{\text{O}_1}^{\circ} = \Delta G_{\text{O}}^{\circ} + \Delta G_{\text{O}}^{\circ} \quad [12]$$

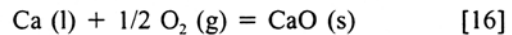
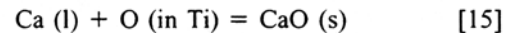
The authors previously determined the value of the Gibbs energy of reaction of Eq. [9], $\Delta G_{\text{O}}^{\circ}$, to be^[8]

$$\Delta G_{\text{O}}^{\circ} = (-583,000) + T \cdot (88.5) \quad [1177 \text{ to } 1373 \text{ K}] \quad [\text{J}] \quad [13]$$

By combining Eqs. [8] and [13], the standard Gibbs energy of solution of oxygen in yttrium, which is expressed by Eq. [11], can be calculated to be

$$\Delta G_{\text{O}_1}^{\circ} = (-533,000 \pm 8000) + T \cdot (12.4 \pm 1.3) \quad [1177 \text{ to } 1438 \text{ K}] \quad [\text{J}] \quad [14]$$

The computed oxygen potentials in yttrium solid solution for Eq. [14] were plotted in Figure 2 for reference. It has to be mentioned that the value of $\Delta G_{\text{O}_1}^{\circ}$ expressed by Eq. [14] includes not only the experimental error in this study but also the error of the Gibbs energy of solution of oxygen in titanium, $\Delta G_{\text{O}}^{\circ}$, in Eq. [13]. For the discussion of the errors in $\Delta G_{\text{O}}^{\circ}$, the following two reactions must be considered:



$$\Delta G_{\text{O}}^{\circ} = \Delta G_{\text{CaO}}^{\circ} - \Delta G_{\text{O}_1}^{\circ} \quad [17]$$

where $\Delta G_{\text{O}_1}^{\circ}$ and $\Delta G_{\text{CaO}}^{\circ}$ are the standard Gibbs energies for Eqs. [15] and [16], respectively. As summarized in Table IV, there is very good agreement between the values of $\Delta G_{\text{O}_1}^{\circ}$ as determined by different researchers,^[8,9] whereas there are large differences in the reported data for $\Delta G_{\text{CaO}}^{\circ}$ in Eq. [16].^[2,14,15] It should be noted that the absolute value of $\Delta G_{\text{O}_1}^{\circ}$ for Eq. [11] determined in this study is directly affected by the error in $\Delta G_{\text{CaO}}^{\circ}$.

There are two other determinations of the value of $\Delta G_{\text{O}_1}^{\circ}$. First, Ran *et al.*^[16] calculated an optimized set of thermodynamic functions in the Y-O system on the basis of the experimentally determined phase diagram and other thermodynamic quantities. The value of $\Delta G_{\text{O}_1}^{\circ}$ based on the work of Ran *et al.* is reported in Table IV. There is considerable uncertainty in this value due to the fact that the Gibbs energy function for the Y-O system is determined by parameter fitting the two-phase coexistence curve by trial and error.^[16]

Second, by using values of maximum solubility^[4] and oxygen potentials in equilibrium with Y-Y₂O₃,^[2] the oxygen potential in the Y-O solid solution has been calculated as a function of temperature on the assumption that Henry's law is valid over the entire solid solution regime.

All three determinations of $\Delta G_{\text{O}_1}^{\circ}$ in Table IV are plotted in Figure 7 as well as $\Delta G_{\text{O}}^{\circ}$ for comparison. As mentioned previously, the plotted data include some uncertainties. Therefore, a more detailed discussion of the absolute values of the calculated oxygen potentials in the yttrium solid solution will be reserved for the future.

VI. CONCLUSIONS

Oxygen distributions in Y-O and Ti-O solid solutions were measured at temperatures between 1177 and 1438 K by equilibrating yttrium and titanium samples submerged in a calcium-saturated CaCl₂ melt. The temperature dependence of the ratio of oxygen concentration in Y-O and Ti-O solid solutions was determined and is expressed by

$$\ln \frac{[\text{mass pct O}]_{\text{inY}}}{[\text{mass pct O}]_{\text{inTi}}} = \frac{-6040 \pm 940}{T} + (9.15 \pm 0.16) \quad [1]$$

With this equation and the reported standard Gibbs energy of solution of oxygen in titanium, oxygen potentials in yttrium solid solution were determined to be

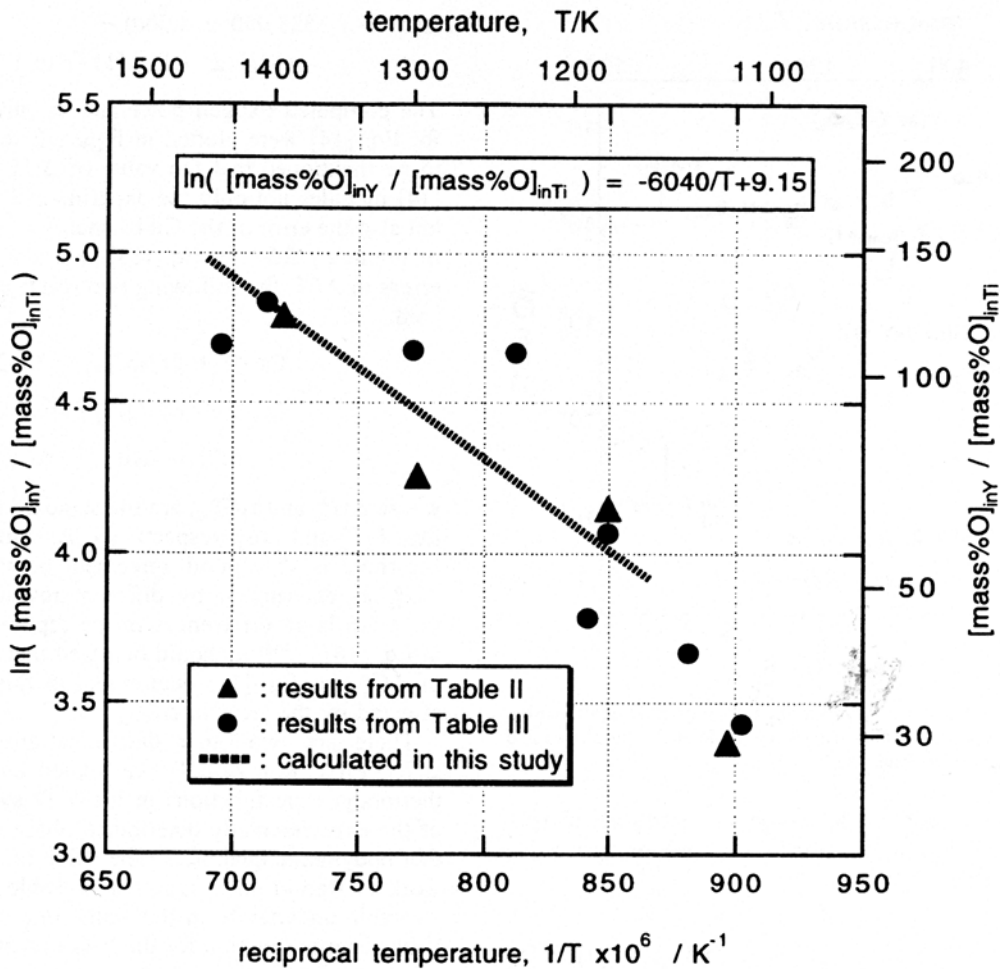
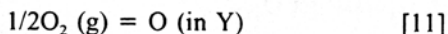


Fig. 6—Temperature dependence of the distribution coefficient for oxygen partitioning between yttrium and titanium.

Table IV. Summary of ΔG_f° 's Used and Obtained in This Study

Reactions	Standard Gibbs Energy of Reaction	Notes
O (in Ti) = O (in Y)	$\Delta G_6^\circ = (50,200 \pm 8000) - (76.1 \pm 1.3)T$	this study
$1/2O_2$ (g) = O (in Y)	$\Delta G_{11}^\circ = \Delta G_6^\circ + \Delta G_{f, CaO}^\circ - \Delta G_{15}^\circ$ $= -533,000 + 12.4T$ [1177 to 1438 K]	calculated in this study calculated from $\Delta G_{f, Y_2O_3}^\circ$ ^[21] and maximum solubility data ^[41]
	$\Delta G_{11}^\circ = -602,000 + 65.0T$	
	$\Delta G_{11}^\circ = -621,000 + 58.0T^*$	Ran <i>et al.</i> ^[16]
Ca (l) + $1/2O_2$ (g) = CaO (s)	$\Delta G_{f, CaO}^\circ = -641,000 + 109T$	JANAF ^[14]
	$\Delta G_{f, CaO}^\circ = -640,000 + 107T$	Barin and Knacke ^[2]
	$\Delta G_{f, CaO}^\circ = -628,000 + 118T$	Wakasugi and Sano ^[15]
Ca (l) + O (in Ti) = CaO (s)	$\Delta G_{15}^\circ = -58,400 + 20.7T$ [1173 to 1373 K]	Okabe <i>et al.</i> ^[18]
	$\Delta G_{15}^\circ = -66,300 + 26.4T$ [1323 to 1573 K]	Niiyama <i>et al.</i> ^[19]
$1/2O_2$ (g) = O (in Ti)	$\Delta G_9^\circ = \Delta G_{f, CaO}^\circ$ ^[14] - ΔG_{15}° ^[18] $= -583,000 + 88.5T$ [1173 to 1373 K]	Okabe <i>et al.</i> ^[18]
	$\Delta G_9^\circ = \Delta G_{f, CaO}^\circ$ ^[15] - ΔG_{15}° ^[19] $= -562,000 + 91.6T$ [1323 to 1573 K]	Niiyama <i>et al.</i> ^[19]
$2/3Y$ (s) + $1/2O_2$ = $1/3Y_2O_3$ (s)	$\Delta G_{f, Y_2O_3}^\circ = -631,000 + 92.4T$	Barin and Knacke ^[2]

*Calculated from the Gibbs energy function for the Y-O system, which is determined by parameter fitting the two-phase coexistence curve by trial and error.



$$\Delta G_{11}^\circ = (-533,000 \pm 8000) + T \cdot (12.4 \pm 1.3) \text{ [1177 to 1438 K] [J] [14]}$$

The value of ΔG_{11}° has a couple of important applications:

the estimation of the theoretical deoxidation limit of yttrium metal and the measurement of ultralow oxygen potentials.

Finally, the methods used in this investigation can be adopted beyond the Y-O system. Many reactive metals, e.g., lanthanides and actinides, have oxygen potentials com-

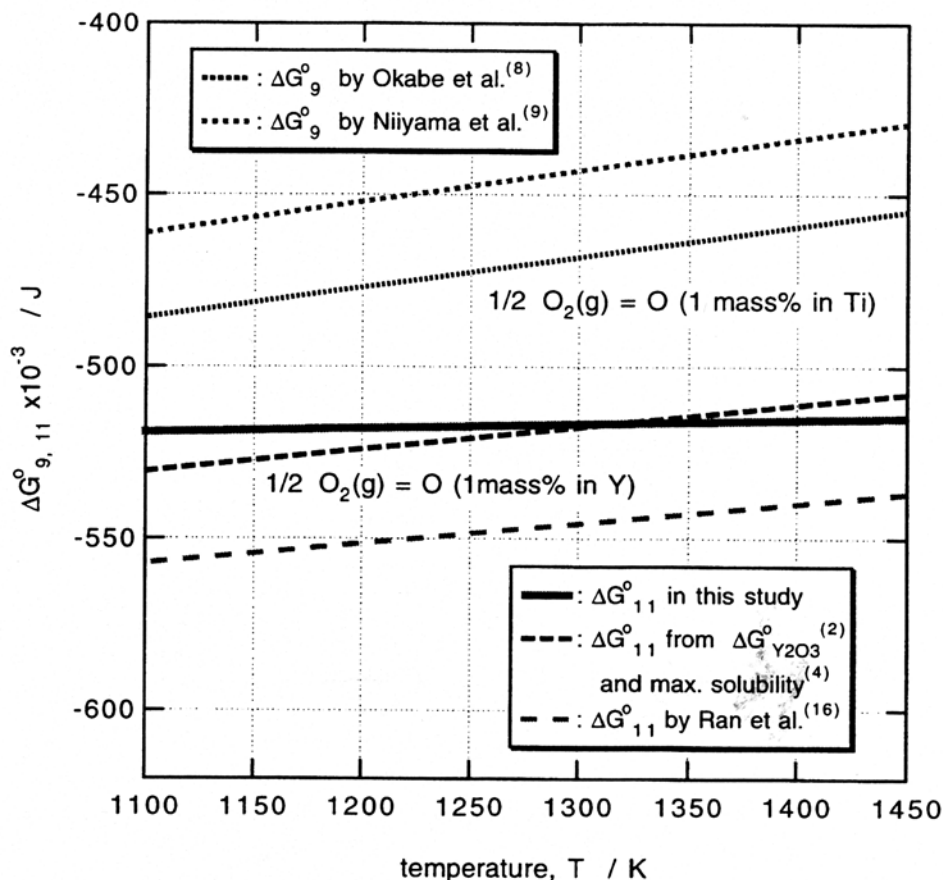


Fig. 7—Temperature dependence of the Gibbs energy of oxygen dissolution in α -yttrium, $\Delta G_{9,11}^0$. The Gibbs energy of oxygen dissolution in β -titanium, $\Delta G_{9,11}^0$, is also plotted for reference.

parable to those encountered in the Y-O system. Ultralow oxygen potentials over those metals can be measured experimentally by a technique similar to that employed in the present study.

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