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Thermodynamic Properties of Dilute Titanium-Oxygen Solid Solution in Beta Phase

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Titanium-oxygen alloys were equilibrated with calcium and calcium oxide at temperatures between 1173 and 1373 K. Equilibrium oxygen concentrations, in the order of 490 mass ppm at 1273 K, were obtained. From the analyzed oxygen concentrations in titanium, thermodynamic properties of oxygen in β -titanium-oxygen alloys were evaluated by using the standard free energy of formation of CaO. A relationship involving oxygen potential, temperature and concentration of oxygen in the β -titanium was determined as follows;

$$1/2 \ln (P_{O_2}/101325 \text{ Pa}) = \ln (\text{mass}\% \text{O}) + 10.6 - 70100/T \quad [1173 - 1373 \text{ K}]$$

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I. Introduction

It is well known that a large amount of oxygen dissolves in titanium to form an interstitial solid solution, as shown in Fig. 1⁽¹⁾. The maximum solubility of oxygen in hexagonal close-packed titanium (α -Ti) is about 33 mol%. The oxygen solubility in the high temperature bcc phase (β -phase) is much lower (about 2 mol% at 1273 K) and the α - β transformation temperature increases sharply with increasing oxygen content.

Oxygen removal directly from titanium-oxygen solid solution to a level below 100 mass ppm level has been deemed to be difficult because titanium has a strong affinity for oxygen. Recently, it has been found that titanium can be deoxidized to a level below 100 mass ppm by using a calcium-halide flux deoxidation method⁽²⁾. In any discussion of the feasibility of preparation of extra-low oxygen titanium, knowledge of the partial molar free energy of oxygen, $\Delta\bar{G}_O$, in β -titanium is needed.

Oxygen activity measurements in β -titanium solid solution are, however, not easy because of the extremely low oxygen partial pressure in titanium-oxygen solid solution⁽³⁾. This low value of oxygen partial pressure makes it difficult to use conventional methods to measure $\Delta\bar{G}_O$. A few thermodynamic investigations have been made by using an indirect method to determine the activity of oxygen in β -titanium⁽⁴⁾⁽⁵⁾, but these values are not consistent with other data.

In this study, the partial pressure of oxygen in β -titanium solid solution was determined by use of calcium-calcium oxide equilibrium. The method chosen in this study is that first used by Kubaschewski and Dench⁽⁶⁾. Titanium samples were allowed to react at a given temperature with an excess amount of mixture of

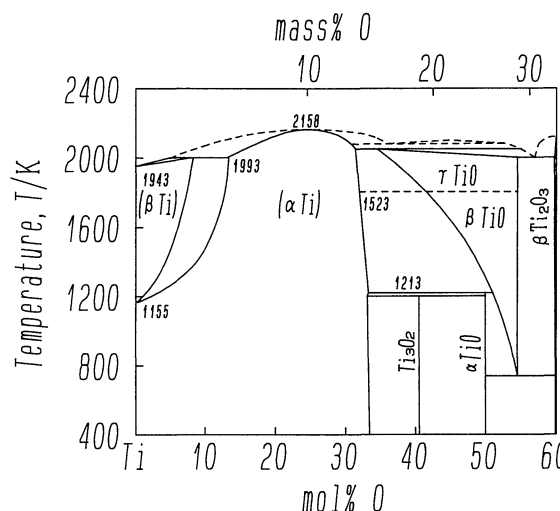
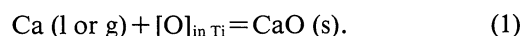


Fig. 1 Phase diagram of the Ti-O system⁽¹⁾.

calcium metal and its oxide until equilibrium was reached. The reaction can be written;



The solubility of calcium in titanium is reported to be very small, about 60 mass ppm at 1273 K⁽⁷⁾, so that the Ti-O alloys in equilibrium with calcium and calcium oxides may be represented by the Ti-O binary system. Thermodynamic properties of oxygen in the solid Ti-O alloys were discussed by using the standard free energy of formation of CaO.

2. Previous studies

Kubaschewski and Dench⁽⁶⁾ measured the activity of oxygen around 1273 K for three compositions of Ti-O solid solution by equilibrating titanium with magnesium, calcium, barium and their respective oxides. They adopted an equilibrium oxygen concentration in titanium, for example, under Ca-CaO coexistence, which was the lowest value of various analytical results ranging

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from 0.07 to 0.24 mass%.

Mah *et al.*⁽⁸⁾ measured the heats of formation and the heat capacities of Ti-O alloys up to 1600 K. They found that the partial molar enthalpy of oxygen at 298 K does not vary significantly with oxygen content up to 25 mol% oxygen. Combining these values, they determined $\Delta\bar{G}_O$ for the α field with the aid of a simple model to estimate configurational entropy. By extrapolating $\Delta\bar{G}_O$ which was deduced from their data for α -solid solution and with various assumptions, they estimated $\Delta\bar{G}_O$ for the β field. Their estimation includes a large amount of uncertainty because they had to use the data on α/β phase boundaries as well as the partial molar heat capacity of oxygen in α -solution.

The method employed by Kubaschewski and Dench⁽⁶⁾ has been extended by Komarek and Silver⁽⁹⁾ who determined $\Delta\bar{G}_O$ for the α -titanium solution in the temperature range between 1073 and 1273 K. $\Delta\bar{H}_O$ and $\Delta\bar{S}_O$ were deduced by differentiating $\Delta\bar{G}_O$.

Based on hydrogen partial pressure measurements in the ternary Ti-O-H system at 1073K, the activities of oxygen in the binary Ti-O system were estimated up to 14 mol% oxygen by Hepworth and Schuhmann⁽¹⁰⁾.

Boureau and Gerdanian⁽¹¹⁾ applied the microcalorimetric method to determine $\Delta\bar{H}_O$ at 1323 K in titanium-oxygen solid solution. $\Delta\bar{S}_O$ in the α and β solutions and $\Delta\bar{G}_O$ within β field were also computed. Tetot *et al.*⁽¹²⁾ improved the experimental apparatus and re-measured $\Delta\bar{H}_O$ with high precision.

Ono and Miyazaki⁽⁴⁾ modified the method employed by Kubaschewski and Dench⁽⁶⁾ to measure the deoxidation limit of titanium by calcium and magnesium at temperatures between 1173 and 1573 K. By using measured oxygen contents, they estimated the thermodynamic properties of oxygen in Ti-O alloys. Recently, Sano and Tsukihashi⁽⁵⁾ used the same method and obtained activities of oxygen in β -titanium in the temperature range 1373–1573 K by using their original value of the standard free energy of formation of CaO⁽¹³⁾. The equilibrium oxygen concentration in titanium obtained by Sano and Tsukihashi⁽⁵⁾ differs significantly from that obtained by Ono and Miyazaki⁽⁴⁾.

II. Experimental

1. Experimental procedures

Titanium samples were placed in a stainless steel container with calcium and CaO as shown in Fig. 2. Several kinds of titanium samples with different initial oxygen concentrations were used as starting materials. Samples containing lower and higher oxygen contents than the equilibrium amount were used as starting materials so as to reach equilibrium from both sides.

Ten to fifteen sample pieces of titanium (about 0.1–0.5 g each) were placed on a titanium dish within a titanium cup, which was filled with calcium and CaO. The cup containing the sample and calcium was set in the stainless steel container. Special care was taken to avoid

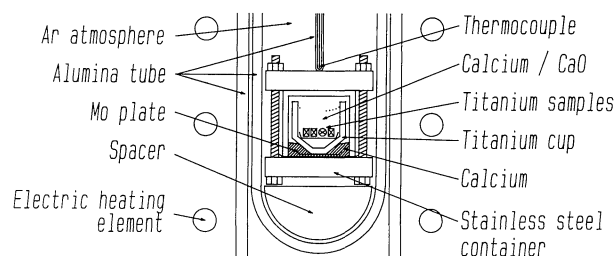


Fig. 2 Schematic illustration of the experimental apparatus.

contamination from the container and the atmosphere (e.g. additional calcium nodules were placed in the space between the titanium cup and the container as a seal to prevent leakage from the container with the liquid calcium when the container was heated to the experimental temperature.)

The assembled container was heated in the furnace to a temperature between 1173 and 1373 K, and the duration of the experimental runs was between 86.4 and 260 ks. The time necessary to reach equilibrium was roughly evaluated by using oxygen diffusivity in titanium⁽¹⁴⁾ and the solid state diffusion model⁽¹⁵⁾, and was confirmed by results of oxygen analysis. The reaction container was then quenched in water. Calcium metal and CaO were removed by leaching with (1+1) acetic acid, and the resulting samples were carefully cleaned in warm HCl aqueous solution, rinsed with water, alcohol and acetone, and then dried.

Oxygen and nitrogen analyses of the samples were made using the inert gas fusion infrared absorption method (LECO TC-336 analyzer). For oxygen extraction, 0.1 g of titanium sample enclosed in a 1 g nickel basket was dropped into a graphite crucible and held above 2300 K. The instrument was calibrated by using 1980 mass ppm oxygen titanium standard samples, and the measured values were cross checked by analyzing different titanium standard samples (440 and 1430 mass ppm). Calcium was chemically analyzed by flame-less atomic absorption spectrometry.

III. Results

1. Oxygen concentration in titanium solid solution

Table 1 shows the analytical results for the oxygen concentration in titanium in equilibrium with calcium and CaO. The oxygen concentrations were essentially independent of specimen history and of the direction from which equilibrium was approached. The results confirm that the reaction time employed in this study was enough to reach equilibrium.

The results in Table 1 are plotted in Fig. 3 together with the reported data^{(4)–(6)}. The results of this work are in good agreement with the data reported most recently by Sano and Tsukihashi⁽⁵⁾. The data reported by Ono and Miyazaki⁽⁴⁾ are the mean values of highly scattered results at a given temperature. Their data are somewhat low in oxygen concentration at temperatures above 1323 K. The

Table 1 Analytical values of oxygen and nitrogen concentrations in titanium. Several kinds of titanium samples with different oxygen concentration were equilibrated with calcium and CaO.

Exp. No.	Reaction temperature (K)	Reaction time (ks)	Oxygen contents (mass ppm)		Nitrogen content (mass ppm)
			Initial	After equilibrium	
Eq-1	1173	260	200	310	430
			720	300	1090
Eq-2	1223	173	200	430	840
			450	380	630
			720	400	1430
Eq-3	1273	86	430	460	340
			1430	470	470
			200	600	880
Eq-4	1323	86	720	580	1760
			1200	590	990
			200	760	260
Eq-5	1373	86	1200	760	540
			200	760	540

scattered values seem to reflect some uncertainty in the determination of the equilibrium oxygen concentration. A plot of data obtained by Kubaschewski and Dench⁽⁶⁾ shows the highest value at 1273 K. The oxygen concentration selected is the lowest value (700 mass ppm) among highly scattered data.

2. Calcium and Nitrogen analyses

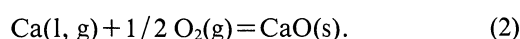
The sample equilibrated at 1273 K for 86 ks contained about 1 mass ppm calcium by chemical analysis. As mentioned above, the maximum solubility of calcium in titanium at 1273 K is about 60 mass ppm. It seems that diffusivity of calcium in titanium is relatively low and that calcium in titanium does not equilibrate completely with calcium metal within the experimental periods.

Nitrogen concentration in the samples was independent of experimental conditions, and increased from the initial values to some extent in all cases. The values at the end of the experiments fall in the range between 340 and 1760 mass ppm randomly. The spread of values seems to result from nitrogen contained in calcium metal as an impurity or possibly from some leakage of the container. Table 1 shows, however, there was no effect on the oxygen solubilities. In the following discussion the increase in nitrogen concentration was neglected and the alloys in equilibrium with calcium and calcium oxides were treated as Ti-O binary solid solution.

IV. Discussion

1. Free energy change of dissolution of oxygen in titanium

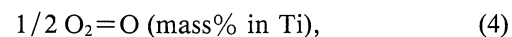
There exist three phases, calcium, CaO and Ti-O alloy under the experimental conditions of this study. At equilibrium, the partial pressure of oxygen dissolved in titanium is equal to the partial pressure of oxygen (P_{O_2}) given by the reaction



The standard free energy of formation of CaO ($\Delta G_{\text{CaO}}^\circ$) for eq. (2) is expressed by eq. (3).

$$\Delta G_{\text{CaO}}^\circ = RT \ln (P_{O_2}/P^\circ)^{1/2}, \quad (3)$$

where P° denotes 101325 Pa. The free energy change of dissolution of oxygen in titanium solid solution, according to the reaction;



can be expressed by eq. (6) by using eq. (3) as follows:

$$\Delta G = -RT \ln \{(\text{mass}\% \text{O}) / (P_{O_2}/P^\circ)^{1/2}\} \quad (5)$$

$$= \Delta G_{\text{CaO}}^\circ - RT \ln (\text{mass}\% \text{O}), \quad (6)$$

where (mass%O) is the oxygen concentration in mass percent. Reported values of free energy change associated with eq. (4) cannot be compared directly with each other, because each author has used different the $\Delta G_{\text{CaO}}^\circ$ values in eq. (3) to calculate the free energy change of eq. (4). As indicated by Wakasugi and Sano⁽⁵⁾, there are large discrepancies among the measurements of $\Delta G_{\text{CaO}}^\circ$ made by various investigators. In this study $\Delta G_{\text{CaO}}^\circ$ which is published in JANAF⁽¹⁶⁾ and is shown in eq. (7), in the temperature range of 1100 to 1500 K, was adopted.

$$\Delta G_{\text{CaO}}^\circ = -641000 + 109T \text{ (J/mol O) [1100–1500 K]}. \quad (7)$$

As illustrated by Fig. 3, the dependence of oxygen concentration in titanium in equilibrium with Ca and CaO on temperature can be expressed in the form;

$$\ln (\text{mass}\% \text{O}) = -7020/T + 2.49 \text{ [1173–1373 K]}. \quad (8)$$

For comparison the data determined by Sano and Tsukihashi⁽⁵⁾ and by Ono and Miyazaki⁽⁴⁾ are given in eqs. (9) and (10), respectively.

$$\ln (\text{mass}\% \text{O}) = -7970/T + 3.17 \text{ [1373–1573 K]}. \quad (9)$$

$$\ln (\text{mass}\% \text{O}) = -5180/T + 0.889 \text{ [1173–1573 K]}. \quad (10)$$

By substituting eqs. (7) and (8) into eq. (6), ΔG for eq. (4) can be calculated as shown by eq. (11).

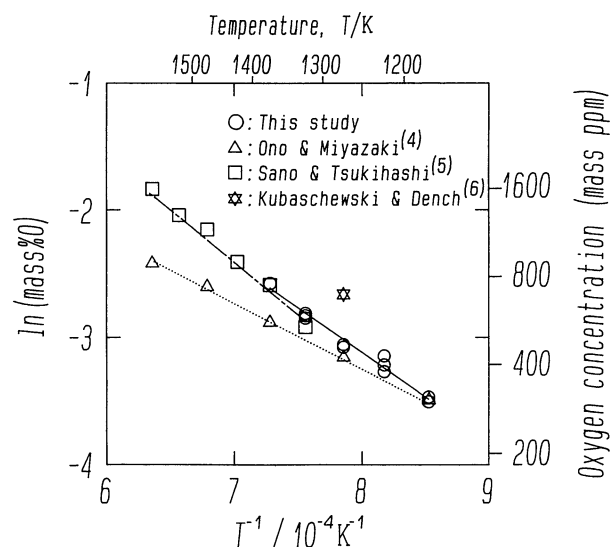


Fig. 3 Temperature dependence of equilibrium oxygen concentration under Ca-CaO existence.

$$\Delta G = -583000 + 88.5T \text{ (J/mol O)} \quad [1173-1373 \text{ K}]. \quad (11)$$

This equation can be rewritten by combining with eq. (5) as follows:

$$1/2 \ln (P_{O_2}/P^\circ) = \ln (\text{mass\%O}) + 10.6 - 70100/T \quad [1173-1373 \text{ K}]. \quad (12)$$

2. Partial molar free energy of oxygen in titanium

The partial molar free energy of oxygen in titanium ($\Delta \bar{G}_O = RT \ln P_{O_2}^{1/2}$) can be written in the form:

$$\Delta \bar{G}_O = \Delta \bar{H}_O - T\Delta \bar{S}_O. \quad (13)$$

The configurational part of $\Delta \bar{S}_O$ may be obtained as a function of composition by considering the existence of three interstitial sites per atom of titanium⁽⁸⁾⁽¹¹⁾:

$$\Delta \bar{S}^{\text{conf}} = R \ln \{(3 - 4No)/No\}, \quad (14)$$

where No is the mole fraction of oxygen, and R is the gas constant. The eq. (13) can be rewritten by eq. (15).

$$\begin{aligned} \Delta \bar{G}_O &= RT \ln P_{O_2}^{1/2} \\ &= \Delta \bar{H}_O - T(\Delta \bar{S}^{\text{th}} + R \ln \{(3 - 4No)/No\}), \end{aligned} \quad (15)$$

where $\Delta \bar{S}^{\text{th}}$ is the thermal part of $\Delta \bar{S}_O$. For dilute solutions at temperatures between 1173 and 1323 K, it can be assumed that $\Delta \bar{H}_O$ and $\Delta \bar{S}^{\text{th}}$ are independent of concentration and change slightly with temperature. By combining eq. (7) and eq. (15), $\Delta \bar{G}_O$ in β -titanium can be expressed as

$$-641000 + 109T = \Delta \bar{H}_O - T(\Delta \bar{S}^{\text{th}} + R \ln \{(3 - 4No)/No\}). \quad (16)$$

Assuming

$$\ln \{(3 - 4No)/No\} = \ln (3/No),$$

and

$$(\text{mass\%O}) = No \times 16 \times 100/47.9,$$

one can obtain eq. (17),

$$\Delta \bar{H}_O - T\Delta \bar{S}^{\text{th}} = -583000 + 127T \quad [1173-1373 \text{ K}]. \quad (17)$$

Neglecting the small temperature dependence of $\Delta \bar{H}_O$ and $\Delta \bar{S}_O$, $\Delta \bar{H}_O$ and $\Delta \bar{S}^{\text{th}}$ in eq. (17) correspond to -583000 J/mol O and -127 J/K , respectively. These constant values are the average values within the temperature and oxygen concentration ranges in this study.

As mentioned above Tetot *et al.*⁽¹²⁾ directly measured $\Delta \bar{H}_O$ at 1323 K and determined the value, $\Delta \bar{H}_O = -627000 \text{ J/mol O}$. The difference with our data is considerably large. Assuming that $\Delta \bar{H}_O$ obtained by Tetot *et al.* is constant within the temperature range 1173–1373 K, the temperature dependence of the equilibrium oxygen concentration in β -titanium under Ca and CaO existence can be calculated by substituting $\Delta \bar{H}_O = -627000 \text{ J/mol O}$ into eq. (16). By making the same approximations used in eq. (17), one can obtain eq. (18),

$$\ln (\text{mass\%O}) = -1740/T + C, \quad (18)$$

where C is a constant which cannot be determined by

ΔG_{CaO} and $\Delta \bar{H}_O$ at 1323 K. The calculated value using eq. (18) rather small compared to the value in eq. (8). In other words, the temperature dependence of oxygen concentration in titanium calculated from eq. (18) is very small compared to that determined in this study. This difference cannot be explained at this stage.

V. Conclusion

Thermodynamic properties of oxygen in titanium-oxygen alloys have been determined by equilibrating titanium-oxygen alloys with calcium and CaO at temperatures between 1173 and 1373 K. From the analyzed oxygen content in β -titanium, the partial molar free energies of formation of oxygen in β -titanium have been calculated by using the standard free energy of formation of CaO. A relationship involving oxygen potential, temperature and concentration of oxygen in the β -titanium was determined as follows;

$$\begin{aligned} RT \ln (P_{O_2}/101325 \text{ Pa})^{1/2} \\ = -583000 - T(-127 + R \ln \{(3 - 4No)/No\}) \end{aligned}$$

or

$$\begin{aligned} 1/2 \ln (P_{O_2}/101325 \text{ Pa}) \\ = \ln (\text{mass\%O}) + 10.6 - 70100/T \quad [1173-1373 \text{ K}] \end{aligned}$$

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