Thermodynamics of Yttrium and Oxygen in Molten Ti, Ti_3Al, and TiAl

YOSHINAO KOBAYASHI and FUMITAKA TSUKIHASHI

The solubility of yttrium and oxygen in molten Ti, Ti_3Al, and TiAl equilibrated with solid Y_2O_3 has been measured from 1793 to 2093 K. The equilibrium constant of reaction Y_2O_3 (s) = $2\underline{Y}$ (mass pct) + $3\underline{O}$ (mass pct) and the interaction parameter between yttrium and oxygen in molten metals were determined. The standard Gibbs energy of reaction was also obtained as a function of temperature. The deoxidation of Ti, Ti_3Al, and TiAl by using yttrium-based fluxes is discussed and the deoxidation ability of yttrium is compared with that of calcium.

I. INTRODUCTION

The improvement of the mechanical properties of titanium and its alloys such as specific strength, heat resistance, and corrosion resistance is of growing importance for the application in the space and aircraft industry. Since the impurities such as oxygen degrade the mechanical properties of the alloys, the elimination of them is very important for use as the industrial materials. However, it is very difficult to remove oxygen from these metals because of strong affinity with the oxygen.

Yahata *et al.*[1] reported that Ti-Al alloy can be deoxidized to about 0.05 to 0.01 mass pct oxygen in a few minutes by adding aluminum to the melt in an electron-beam furnace. The activity of aluminum for the melt was estimated from the evaporation rate of aluminum. However, the composition of metal cannot be well controlled.

Calcium is a promising element for the deoxidation of titanium and its alloys because of its strong affinity with oxygen. Therefore, several investigations have been conducted by using calcium-based fluxes. Okabe *et al.*[2] investigated the deoxidation of solid Ti and Ti-Al alloys by using calcium bearing flux. The oxygen content of Ti and TiAl lowers to 0.0060 mass pct at 1273 K and 0.0066 mass pct at 1373 K, respectively, by using Ca-$CaCl_2$ flux. Sakamoto *et al.*[3] observed the thermodynamic properties of calcium and oxygen in molten TiAl in a CaO crucible at 1833 K and reported the interaction parameters. Shibata *et al.*[4] investigated the deoxidation of molten TiAl in a cold crucible by adding Ca-Al alloy at 1843 K, obtaining the oxygen content as low as 0.01 mass pct. One of the authors[5] reported the equilibrium of calcium and oxygen in molten Ti and Ti-Al alloys and the thermodynamic properties of calcium and oxygen in molten Ti and Ti-Al alloys, equilibrating these metals with solid CaO at 1823 to 2003 K.

However, because calcium is easy to evaporate at high temperature, the evaporation loss is significant when calcium is applied for the deoxidation.

As yttrium has a strong affinity with oxygen and its boiling point is as high as 3200 K, yttrium can be used for the deoxidation of titanium and its alloys. However, the thermodynamic properties of yttrium and oxygen in molten Ti and Ti-Al alloys have not been known. In the present study, the thermodynamic properties of yttrium and oxygen in molten Ti, Ti_3Al, and TiAl equilibrated with solid Y_2O_3 have been observed and the deoxidation by yttrium-based fluxes is discussed.

II. EXPERIMENTAL

The experimental procedure is the same as that conducted in the previous study.[5] Sponge titanium (99.99 pct purity) was used as a specimen. The Ti_3Al and TiAl alloy were prepared by melting the mixture of sponge titanium and aluminum rod (99.99 pct purity). The compositions of Ti_3Al and TiAl are Ti-25.0 mol pct Al and Ti-53.9 mol pct Al, respectively. A yttrium oxide pellet was prepared by pressing reagent grade Y_2O_3 powder (99.9 pct purity) and by sintering in a graphite crucible in an Ar atmosphere at 1673 K for 24 hours. Ten grams of metal and 0.5 g of Y_2O_3 pellet were set in the high frequency induction furnace with the cold crucible (30-mm i.d.). Metallic yttrium turnings (99.9 pct purity) were added to the samples and powder TiO_2 (99.9 pct purity) was added to titanium and Ti_3Al during melting to control the yttrium and oxygen content of metal. A schematic cross section of the experimental apparatus is shown in Figure 1. The molten metal was levitated by electromagnetic force and was equilibrated with solid Y_2O_3 pellet from 1793 to 2093 K. Argon (99.9999 pct purity) was flowing during an experiment. The temperature was measured from the top of the chamber through a silica glass window by using a two-color pyrometer and controlled manually within ± 2 K. The holding times were preliminarily determined to be 5 minutes for Ti and Ti_3Al and 10 minutes for TiAl, as shown in Figure 2, which were enough to be equilibrium. No composition change was observed throughout the experiments for Ti_3Al and TiAl. After equilibration, the sample was quenched by contact with the water-cooling copper crucible. The yttrium, titanium, and aluminum contents were determined by inductively coupled plasma emission spectroscopy and oxygen by a LECO* oxygen analyzer.

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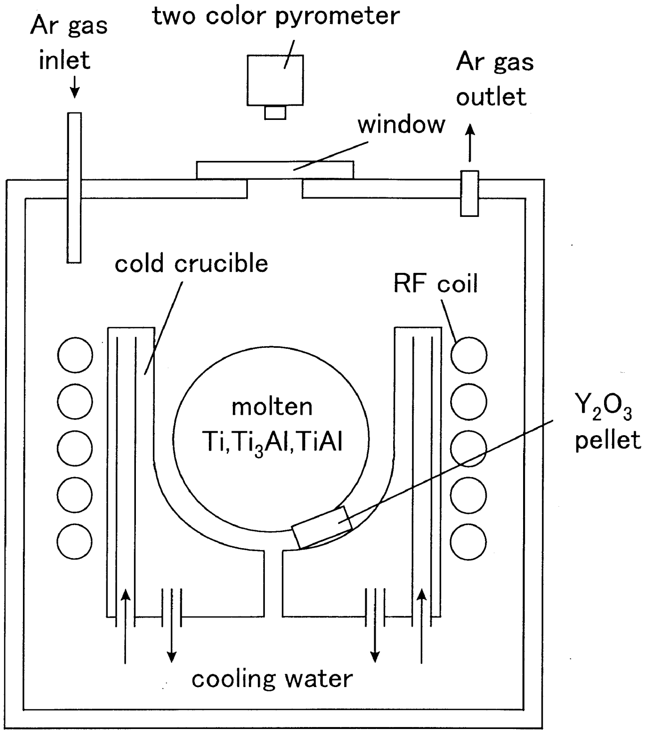

Fig. 1—Schematic cross section of experimental apparatus.

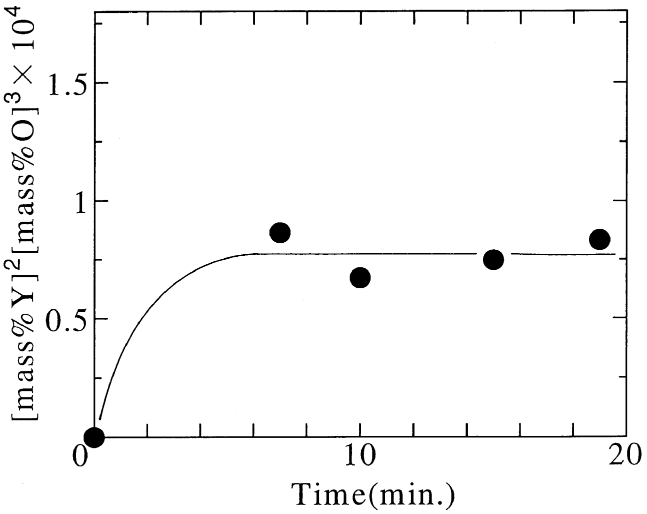

Fig. 2—Relationship between the holding time and the solubility product of yttrium and oxygen in TiAl at 1793 K.

Table I. Yttrium and Oxygen Contents of Molten Ti Equilibrated with Solid Y_2O_3 at 1991, 2042, and 2093 K

Experimental Number	[Mass Pct Y]	[Mass Pct O]
1991 K		
101	0.879	0.409
102	0.914	0.368
103	0.994	0.344
104	1.11	0.299
105	1.23	0.287
106	1.36	0.270
107	1.68	0.262
108	1.70	0.264
109	2.07	0.242
2042 K		
201	0.967	0.459
202	1.13	0.398
203	1.35	0.327
204	1.56	0.301
205	1.90	0.281
206	2.59	0.263
2093 K		
301	0.842	0.630
302	0.846	0.631
303	1.03	0.544
304	1.34	0.471
305	1.35	0.476
306	1.38	0.433
307	1.43	0.427
308	2.09	0.355
309	2.47	0.334

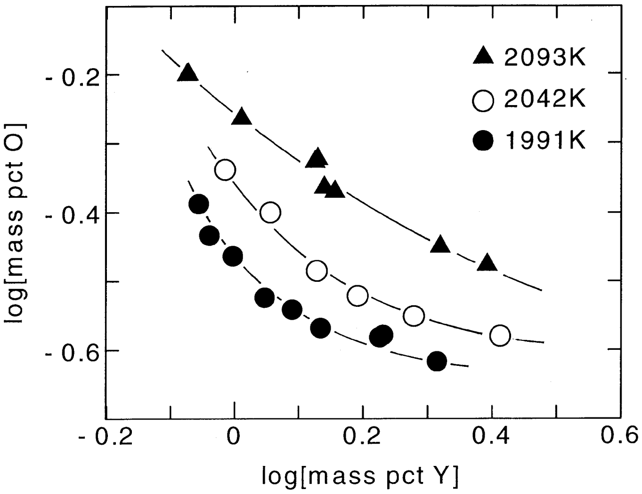

Fig. 3—Relationship between yttrium and oxygen contents of Ti equilibrated with Y_2O_3 at 1991, 2042, and 2093 K.

III. RESULTS

The yttrium and oxygen contents of molten Ti equilibrated with solid Y_2O_3 are shown in Table I and Figure 3. The oxygen content decreases with increasing yttrium content. The solubility product, [mass pct Y]^2[mass pct O]^3, increases with increasing temperature.

The reaction between molten metal and solid Y_2O_3 and its equilibrium constant are expressed by Eqs. [1] and [2].

$$Y_2O_3\ (s) = 2\underline{Y}\ (\text{mass pct in M}) + 3\underline{O}\ (\text{mass pct in M})\ (\text{M: Ti, Ti}_3\text{Al, TiAl}) \quad [1]$$

$$K = \frac{(f_Y\ [\text{mass pct Y}])^2 \cdot (f_O\ [\text{mass pct O}])^3}{a_{Y_2O_3}} \quad [2]$$

where $a_{Y_2O_3}$ is the activity of Y_2O_3 relative to pure solid Y_2O_3, f_Y and f_O are the activity coefficients of yttrium and oxygen relative to 1 mass pct in metal, and [mass pct Y] and [mass pct O] are yttrium and oxygen contents of molten metal in mass pct, respectively. Since solid Y_2O_3 is in the system, $a_{Y_2O_3}$ is unity. The activity coefficients of yttrium and oxygen, f_Y and f_O, are expressed as Eqs. [3] and [4] using the first-order interaction parameters.

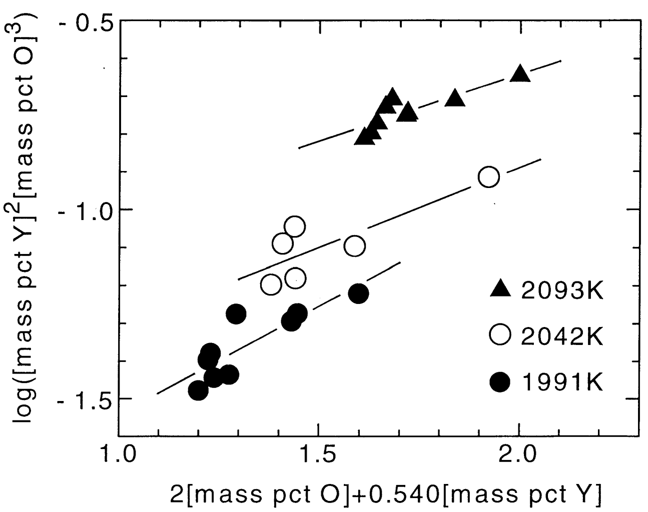

Fig. 4—Relationship between 2 [mass pct O] + 0.540 [mass pct Y] and log ([mass pct Y]^2[mass pct O]^3) for Ti at 1991, 2042, and 2093 K.

Table II. Equilibrium Constant of Reaction Y_2O_3 (s) = 2$\underline{Y}$ (Mass Pct) + 3$\underline{O}$ (Mass Pct) and Interaction Parameter e_Y^O in Molten Ti, Ti_3Al, and TiAl

Solvent	Temperature (K)	Log K	e_Y^O
Ti	1991	−2.14	−0.589
	2042	−1.73	−0.421
	2093	−1.40	−0.377
Ti_3Al	1993	−2.16	−0.478
	2043	−1.81	−0.359
	2093	−1.53	−0.375
TiAl	1793	−4.96	−2.41
	1843	−4.26	−1.32
	1893	−3.74	−0.508

$$\log f_Y = e_Y^Y \text{ [mass pct Y]} + e_Y^O \text{ [mass pct O]} \quad [3]$$

$$\log f_O = e_O^Y \text{ [mass pct Y]} + e_O^O \text{ [mass pct O]} \quad [4]$$

Assuming that the self-interaction parameters e_Y^Y and e_O^O can be ignored, Eq. [2] can be rewritten as Eq. [5] using the thermodynamic relationship of Eq. [6] between the interaction parameters.

$$\log (\text{[mass pct Y]}^2\text{[mass pct O]}^3) = \log K - e_Y^O(2 \text{ [mass pct O]} + 3(M_O/M_Y) \text{ [mass pct Y]}) \quad [5]$$

$$e_O^Y = e_Y^O \cdot (M_O/M_Y) \quad [6]$$

where M_Y and M_O are the molecular weights of yttrium and oxygen. Therefore, log ([mass pct Y]^2[mass pct O]^3) is expected to have a linear relationship with 2 [mass pct O] + 3(M_O/M_Y)·[mass pct Y]. Figure 4 shows the relationship between 2 [mass pct O] + 3(M_O/M_Y)·[mass pct Y] and log ([mass pct Y]^2[mass pct O]^3). The equilibrium constant of Reaction [1] for Ti and the interaction parameter e_Y^O in molten Ti obtained from the intercept and the slope of the regression line are shown in Table II. The yttrium and oxygen contents of molten Ti_3Al equilibrated with solid Y_2O_3 are shown in Table III and Figure 5. The oxygen content decreases with increasing yttrium content. The solubility product, [mass pct Y]^2[mass pct O]^3, increases with increasing temperature. Figure 6 shows the relationship between 2 [mass pct O] + 3(M_O/M_Y) · [mass pct Y] and log ([mass pct Y]^2[mass pct O]^3). The equilibrium constant of Reaction [1] for Ti_3Al and the interaction parameter e_Y^O in molten Ti_3Al obtained from the regression line in Figure 6 are shown in Table II. The yttrium and oxygen contents of molten TiAl equilibrated with solid Y_2O_3 are shown in Table IV and Figure 7. There is a possibility that aluminum is oxidized and formed an intermediate compound, $2Y_2O_3 \cdot Al_2O_3$, due to large activity of aluminum[6] in molten TiAl. However, $2Y_2O_3 \cdot Al_2O_3$ was not detected by X-ray dif-

Table III. Yttrium and Oxygen Contents of Molten Ti_3Al Equilibrated with Solid Y_2O_3 at 1993, 2043, and 2093 K

Experimental Number	[Mass Pct Y]	[Mass Pct O]
1993 K		
401	0.407	0.518
402	0.610	0.382
403	0.882	0.312
404	1.13	0.273
405	1.22	0.276
406	1.37	0.243
407	1.60	0.227
2043 K		
501	0.452	0.603
502	0.761	0.432
503	0.815	0.420
504	1.07	0.335
505	1.26	0.298
506	1.32	0.292
507	1.47	0.265
508	1.60	0.274
509	1.69	0.271
2093 K		
601	0.598	0.681
602	0.993	0.476
603	1.36	0.379
604	1.45	0.384
605	1.58	0.383
606	1.85	0.333
607	1.92	0.326

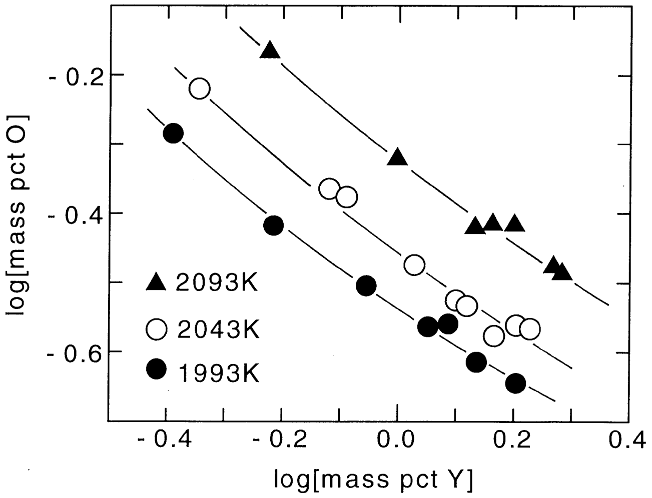

Fig. 5—Relationship between yttrium and oxygen contents of Ti_3Al equilibrated with Y_2O_3 at 1993, 2043, and 2093 K.

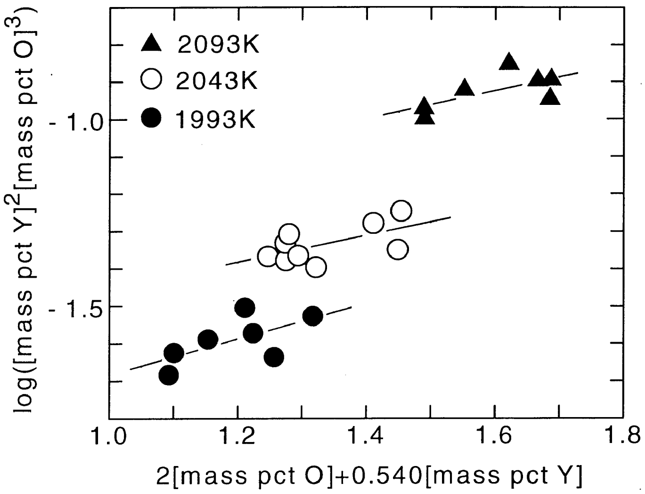

Fig. 6—Relationship between 2 [mass pct O] + 0.540 [mass pct Y] and log ([mass pct Y]^2[mass pct O]^3) for Ti_3Al at 1993, 2043, and 2093 K.

Table IV. Yttrium and Oxygen Contents of Molten TiAl Equilibrated with Solid Y_2O_3 at 1793, 1843, and 1893 K

Experimental Number	[Mass Pct Y]	[Mass Pct O]
1793K		
701	0.221	0.120
702	0.240	0.109
703	0.260	0.100
704	0.334	0.0918
705	0.505	0.0800
706	0.751	0.0743
1843K		
801	0.252	0.145
802	0.336	0.118
803	0.347	0.122
804	0.389	0.111
805	0.412	0.115
806	0.511	0.0906
807	0.557	0.0907
1893K		
901	0.364	0.139
902	0.443	0.116
903	0.573	0.0985
904	0.840	0.0817

fraction analysis in the present study. The oxygen content decreases with increasing yttrium content. The solubility product, [mass pct Y]^2[mass pct O]^3, increases with increasing temperature. Figure 8 shows the relationship between 2 [mass pct O] + $3(M_O/M_Y) \cdot$ [mass pct Y] and log ([mass pct Y]^2[mass pct O]^3). The equilibrium constant of Reaction [1] for TiAl and the interaction parameter e_Y^O in molten TiAl are shown in Table II.

Since the oxygen content of TiAl is lower than that of Ti and Ti_3Al at the same yttrium content, the oxygen can be removed very easily from TiAl by using metal yttrium.

IV. DISCUSSION

The interaction parameters reach zero with increasing temperature, which indicates that yttrium and oxygen behave more ideally in molten metal.

The standard Gibbs energy of Reaction [1] as a function

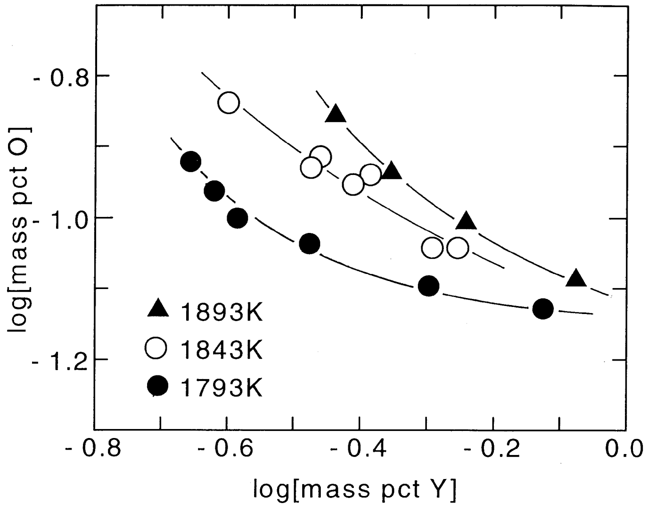

Fig. 7—Relationship between yttrium and oxygen contents of TiAl equilibrated with Y_2O_3 at 1793, 1843, and 1893 K.

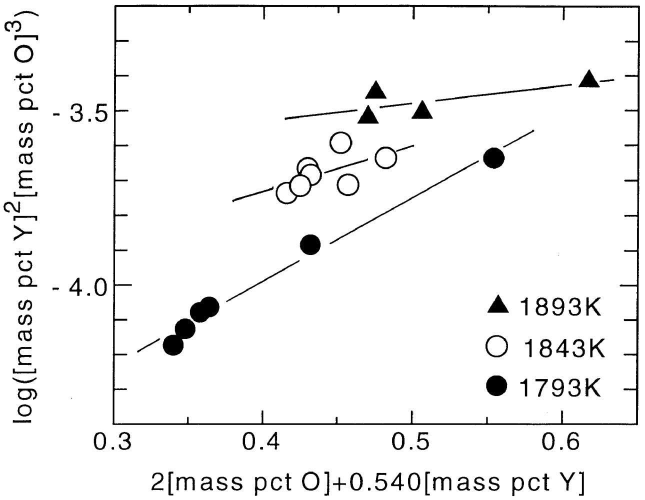

Fig. 8—Relationship between 2 [mass pct O] + 0.540 [mass pct Y] and log ([mass pct Y]^2[mass pct O]^3) for TiAl at 1793, 1843, and 1893 K.

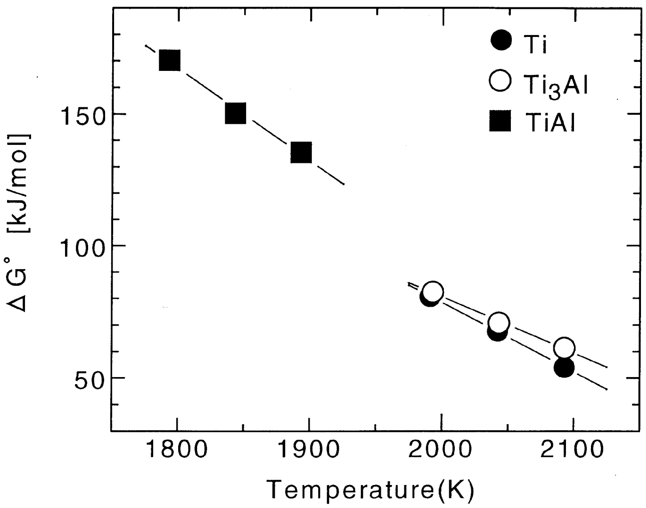

Fig. 9—The standard Gibbs energy of the reaction Y_2O_3 (s) = $2\underline{Y}$ (mass pct in M) + $3\underline{O}$ (mass pct in M), (M: Ti, Ti_3Al, TiAl).

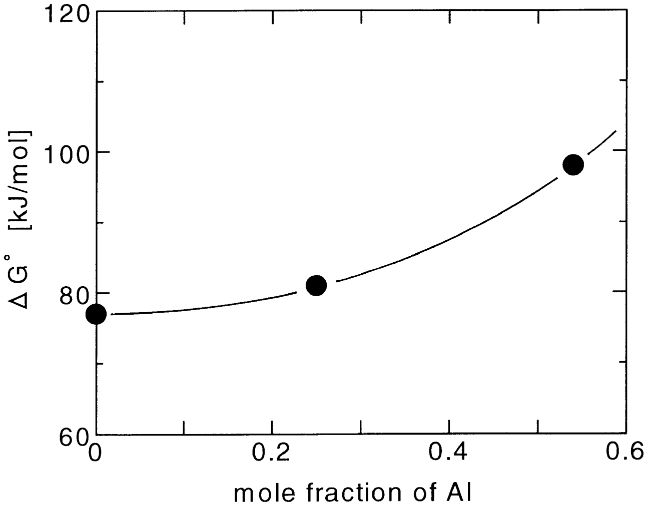

Fig. 10—Relationship between the mole fraction of Al and the standard Gibbs energy of the reaction Y_2O_3 (s) = $2\underline{Y}$ (mass pct in M) + $3\underline{O}$ (mass pct in M), (M: Ti, Ti_3Al, TiAl) at 2000 K.

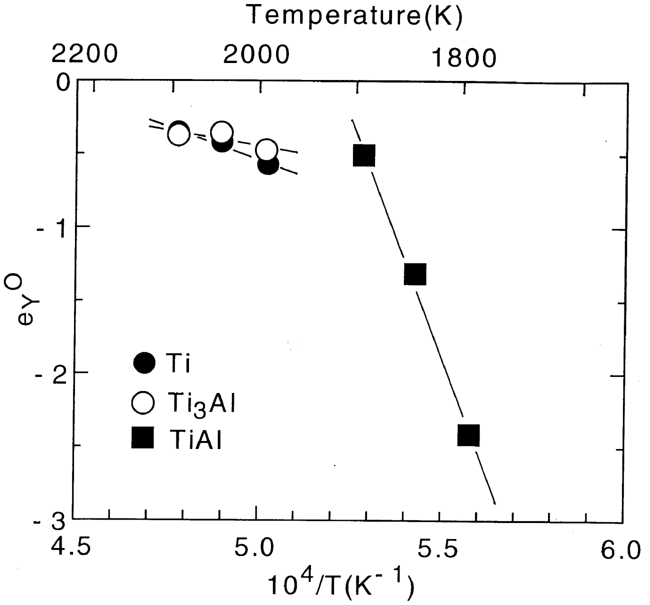

Fig. 11—Temperature dependence of the interaction parameter e_Y^O in molten Ti, Ti_3Al, and TiAl.

of temperature for each metal is shown in Figure 9 and expressed as Eqs. [7] through [9].

$$\text{Ti: } \Delta G^\circ = 601{,}000 - 262T \quad (\pm 2600)\ [\text{J/mol}]\ (1991 \text{ to } 2093 \text{ K}) \qquad [7]$$

$$\text{Ti}_3\text{Al: } \Delta G^\circ = 503{,}000 - 211T \quad (\pm 500)\ [\text{J/mol}]\ (1993 \text{ to } 2093 \text{ K}) \qquad [8]$$

$$\text{TiAl: } \Delta G^\circ = 794{,}000 - 348T \quad (\pm 1200)\ [\text{J/mol}]\ (1793 \text{ to } 1893 \text{ K}) \qquad [9]$$

The standard Gibbs energies of Reaction [1] for Ti, Ti_3Al, and TiAl at 2000 K are compared in Figure 10. The ΔG° increases with increasing Al content. Tsukihashi *et al.*[5] have investigated thermodynamic properties of calcium and oxygen in molten Ti and Ti-Al alloy and reported the standard Gibbs energy for Reaction [10] as Eq. [11].

$$\text{CaO (s)} = \underline{\text{Ca}} \text{ (mass pct in TiAl)} + \underline{\text{O}} \text{ (mass pct in TiAl)} \qquad [10]$$

$$\Delta G^\circ = 279{,}000 - 103T\ [\text{J/mol}]\ (1823 \text{ to } 2023 \text{ K}) \qquad [11]$$

$$1/3\text{Y}_2\text{O}_3 \text{ (s)} = 2/3\underline{\text{Y}} \text{ (mass pct in TiAl)} + \underline{\text{O}} \text{ (mass pct in TiAl)} \qquad [12]$$

Since the ΔG° at 2000 K of Eq. [10] is larger than that of Eq. [12], deoxidation by calcium is thermodynamically more effective than deoxidation by yttrium.

Ishii and Ban-ya[7] reported the equilibrium constant of Reaction [13] for iron and nickel as expressed by Eqs. [14] and [15].

$$\text{Y}_2\text{O}_3 \text{ (s)} = 2\underline{\text{Y}} \text{ (mass pct in M)} + 3\underline{\text{O}} \text{ (mass pct in M) (M: Fe, Ni)} \qquad [13]$$

$$\text{Fe: } \log K = -36{,}160/T + 7.33 \qquad [14]$$

$$\text{Ni: } \log K = -36{,}250/T + 6.36 \qquad [15]$$

The values $\log K = -12.0$ for iron and -13.0 for nickel at 1873 K are much smaller than the values for Ti and TiAl. Therefore, iron and nickel are more easily deoxidized than Ti and Ti-Al alloys because oxygen has a stronger affinity with Ti than with iron and nickel.

The temperature dependencies of interaction parameter e_Y^O for Ti, Ti_3Al, and TiAl are shown in Figure 11 and expressed as Eqs. [16] through [18].

$$\text{Ti: } e_Y^O = -9040/T + 3.99\ (1991 \text{ to } 2093 \text{ K}) \qquad [16]$$

$$\text{Ti}_3\text{Al: } e_Y^O = -4300/T + 1.70\ (1993 \text{ to } 2093 \text{ K}) \qquad [17]$$

$$\text{TiAl: } e_Y^O = -64{,}900/T + 33.8\ (1793 \text{ to } 1893 \text{ K}) \qquad [18]$$

Ishii and Ban-ya[7] reported the values of -6.12 for e_O^Y in molten iron and -6.47 in molten nickel at 1873 K, which are much smaller than the values for Ti, Ti_3Al, and TiAl obtained in the present study.

The oxygen contents of Ti and Ti-Al alloys are estimated when calcium- and yttrium-based fluxes are applied for refining. To decrease the activity of CaO, Y_2O_3 in the flux, fluorides such as CaF_2 and YF_3 can be used to form fluxes for practical application. The relationship between the activity of CaO and Y_2O_3 and the oxygen content of molten TiAl is calculated at 1773 K according to Reactions [1] and [10], as shown in Figure 12. The calcium and yttrium contents are assumed to be constant at 0.1 mass pct. The thermodynamic properties for yttrium and oxygen shown in Table II and those for calcium and oxygen in molten TiAl[5] are used for the calculation. The oxygen contents in the CaO system are smaller than those in the Y_2O_3 system. The oxygen content by yttrium deoxidation can be lowered 0.06 mass pct if the activity of Y_2O_3 is less than 0.1. This shows that utilization of calcium- and yttrium-based fluxes is thermodynamically effective for the deoxidation of molten TiAl.

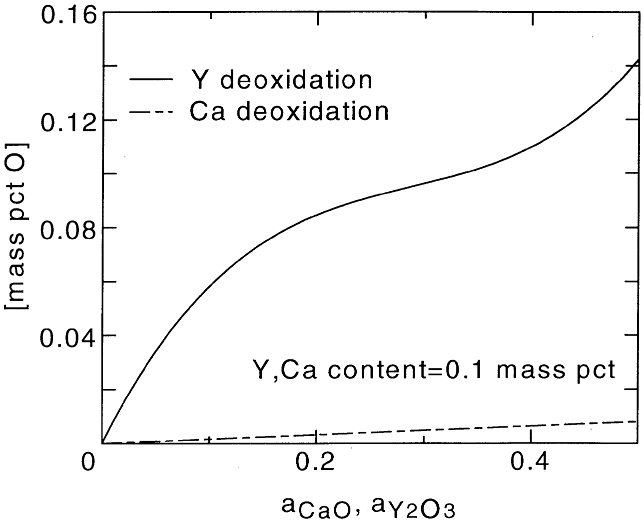

Fig. 12—Relationship between estimated oxygen content of molten TiAl and the activity of oxide in the systems at 1773 K.

V. CONCLUSIONS

The thermodynamic properties of yttrium and oxygen in molten Ti, Ti_3Al, and TiAl equilibrated with solid Y_2O_3 have been measured from 1793 to 2093 K. The results are summarized as follows.

1. The standard Gibbs energy was determined as follows:

$$Y_2O_3\ (s) = 2\underline{Y}\ (\text{mass pct in M}) + 3\underline{O}\ (\text{mass pct in M})$$
$$(\text{M:Ti, } Ti_3Al\text{, TiAl})$$
$$\text{Ti: } \Delta G^\circ = 601{,}000 - 262T\ (\pm 2600)\ [\text{J/mol}]$$
$$(1991 \text{ to } 2093 \text{ K})$$
$$Ti_3Al\text{: } \Delta G^\circ = 503{,}000 - 211T\ (\pm 500)\ [\text{J/mol}]$$
$$(1993 \text{ to } 2093 \text{ K})$$
$$\text{TiAl: } \Delta G^\circ = 794{,}000 - 348T\ (\pm 1200)\ [\text{J/mol}]$$
$$(1793 \text{ to } 1893 \text{ K})$$

2. The interaction parameter e_Y^O in molten Ti, Ti_3Al, and TiAl was obtained as follows:

$$\text{Ti: } e_Y^O = -9040/T + 3.99\ (1991 \text{ to } 2093 \text{ K})$$
$$Ti_3Al\text{: } e_Y^O = -4300/T + 1.70\ (1993 \text{ to } 2093 \text{ K})$$
$$\text{TiAl: } e_Y^O = -64{,}900/T + 33.8\ (1793 \text{ to } 1893 \text{ K})$$

3. The deoxidation behavior of molten TiAl by calcium- and yttrium-based fluxes is estimated. These fluxes are thermodynamically effective for the deoxidation of molten TiAl.

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