$$2\underline{Mg} + \underline{O} + CaO \cdot 2Al_2O_3 \text{ (s)} \qquad [14]$$
$$= 2MgO \cdot Al_2O_3 \text{ (s)} + \underline{Ca}$$

$$\Delta G^\circ_{14} = -98{,}870 - 149.82T \text{ (J/mol)} \qquad [15]$$

$$CaO \text{ (s)} + 2Al_2O_3 \text{ (s)} = CaO \cdot 2Al_2O_3 \text{ (s)} \qquad [16]$$

$$\Delta G^\circ_{16} = 15{,}650 + 25.82T \text{ (J/mol)} \qquad [17]$$

These equilibrium oxides, however, are harmful inclusions in produced steel, so the stability area of liquid nonmetallic inclusion formed by deoxidation has to be shown from the viewpoint of shape control of nonmetallic inclusions.

The activity of each constituent in the CaO-Al_2O_3-MgO system, such as $a_{Al_2O_3}$, a_{MgO}, or a_{CaO}, was quoted in the calculation from our previous study,[11,12] where the regular solution model was applied to evaluate their activities. The calculated stability phase diagram is shown in Figure 5. The evaluated liquid phase area agreed well with the liquidus lines observed in our previous work.[11,12]

The main findings of this study on the thermodynamics of spinel nonmetallic inclusion formation in liquid iron can be summarized as follows.

(1) The equilibrium constants and interaction parameters on calcium, magnesium, and aluminum deoxidation in liquid iron at steelmaking temperature must be expressed by the first-and second-order interaction parameters, including cross-product terms.
(2) Stability phase diagrams of MgO-$MgO \cdot Al_2O_3$-Al_2O_3 and MgO-$MgO \cdot Al_2O_3$-$CaO \cdot 2Al_2O_3$ were drawn at steelmaking temperatures as a function of dissolved magnesium, aluminum, calcium, and oxygen contents in liquid iron.
(3) The liquid oxide phase area in the stability phase diagram of the MgO-Al_2O_3-CaO ternary system was determined at steelmaking temperatures.

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Thermodynamics of Calcium and Oxygen in Molten Ti₃Al

YOSHINAO KOBAYASHI and FUMITAKA TSUKIHASHI

The solubility of Ca and O in molten Ti_3Al equilibrated with solid CaO has been measured at 2003 and 2053 K. The equilibrium constant of reaction CaO (s) = $\underline{Ca}$ (mass pct in Ti_3Al) + $\underline{O}$ (mass pct in Ti_3Al) and the interaction parameter between Ca and O were determined. The standard Gibbs energy of reaction was obtained as follows:

$$\Delta G^\circ = 258{,}000 - 98.0T \text{ J/mol (2003 to 2053 K)}$$

The deoxidation of Ti_3Al using Ca bearing fluxes is discussed in comparison with that of other Ti-Al alloys.

The improvement of mechanical properties of titanium-aluminum alloy is of growing importance in the aircraft and space industry. Eliminating oxygen from the alloy is important for practical applications, because the oxygen degrades the mechanical and physical properties. Calcium has been considered to be a promising reagent for the deoxidation of refractory metals because of its strong affinity for oxygen. Thermodynamic properties of calcium and oxygen in molten Ti and Ti-Al alloys have been investigated[1] using a chemical equilibrium technique. In this study, thermodynamic properties of calcium and oxygen in molten Ti_3Al equilibrated with solid CaO at 2003 and 2053 K were observed to discuss the deoxidation of titanium-aluminum alloys using calcium-based fluxes.

The experimental procedure is the same as that described in a previous article.[1] Samples were a mixture of Ti and TiAl or Al with the composition of Ti_3Al, as shown in Table I. Five grams of sample were equilibrated in a CaO crucible (22-mm o.d., 18-mm i.d., and 60-mm height) manufactured by Yoshizawa Lime Industry Co., Ltd, Tokyo, Japan. A CaO lid was adhered with zirconia cement on the top of the crucible to prevent the evaporation loss of cal-

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YOSHINAO KOBAYASHI, Graduate Student, and FUMITAKA TSUKIHASHI, Associate Professor, are with the Department of Metallurgy, The University of Tokyo, Tokyo 113, Japan.
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Table I. Chemical Composition of Raw Materials

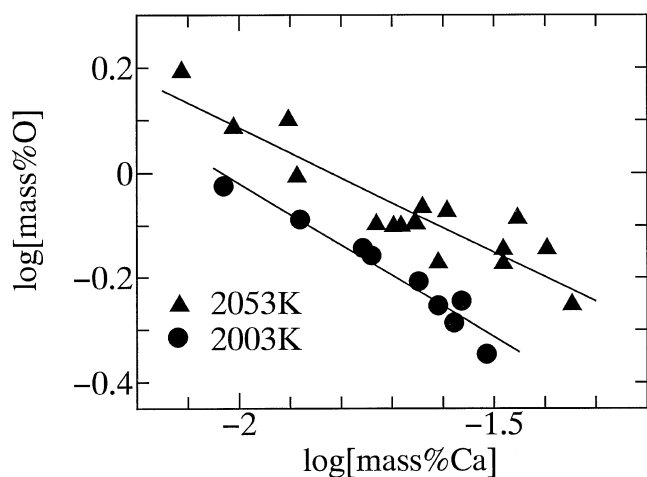| Sample	Mass Pct Al	Mass Pct Ti
Ti	—	99.6
TiAl	38.8	58.1
Al	99.8	—

Fig. 1—The relationship between calcium and oxygen contents of Ti₃Al equilibrated with CaO at 2003 and 2053 K.

Table II. Calcium and Oxygen Contents of Ti₃Al Equilibrated with Solid CaO at 2003 and 2053 K

Temperature (K)	Number	Mass Pct Ca	Mass Pct O
	101	0.0093	0.946
	102	0.0133	0.818
	103	0.0175	0.720
	104	0.0182	0.697
2003	105	0.0225	0.620
	106	0.0246	0.558
	107	0.0264	0.517
	108	0.0273	0.569
	109	0.0306	0.451
	201	0.00772	1.56
	202	0.00976	1.22
	203	0.0125	1.26
	204	0.0130	0.986
	205	0.0186	0.800
	206	0.0201	0.793
	207	0.0208	0.794
	208	0.0221	0.805
2053	209	0.0223	0.801
	210	0.0229	0.862
	211	0.0246	0.675
	212	0.0256	0.848
	213	0.0330	0.715
	214	0.0330	0.671
	215	0.0352	0.822
	216	0.0402	0.717
	217	0.0450	0.559

cium in the metal. A high frequency induction furnace was employed to melt Ti₃Al. A CaO crucible with lid set in a graphite tube (42-mm o.d., 30-mm i.d., and 100-mm length) was placed in a MgO holder. A graphite tube was used as a heating element. The holder was put in a silica reaction tube set in an induction coil. Samples were melted at 2003
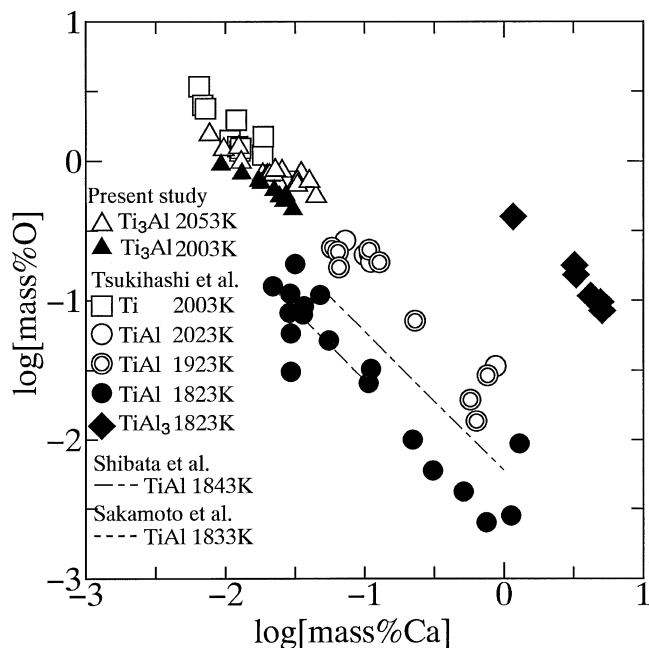

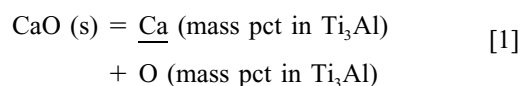Fig. 2—The relationship between calcium and oxygen contents of Ti and Ti-Al alloy equilibrated with CaO.

or 2053 K in a dehydrated and deoxidized argon with the rate of 1000 cm³/min. The holding times were preliminarily determined to be 10 and 5 minutes at 2003 and 2053 K, respectively. The temperature was measured from the top of the crucible through a silica glass window by using a two-color pyrometer and was controlled manually within ±5 K. No composition change was observed throughout the experiments. After equilibration, a CaO crucible was withdrawn from the furnace and the samples were quenched in a Fe holder placed in a water bath. The calcium, titanium, and aluminum contents were determined by inductively coupled plasma emission spectroscopy and oxygen using a LECO* oxygen analyzer.

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

The calcium and oxygen contents of the molten Ti₃Al equilibrated with solid CaO at 2003 and 2053 K are shown in Figure 1 and Table II. The oxygen content decreases with increasing calcium content at each temperature. The product of [mass pct Ca] and [mass pct O] increases with increasing temperature.

The relationship between the calcium and oxygen contents of Ti and Ti-Al alloys[1] is shown in Figure 2 together with the present results. The results for TiAl obtained by Shibata et al.[2] and Sakamoto et al.[3] are also shown in Figure 2 for comparison. The oxygen content of alloys decreases with increasing calcium content.

The reaction between solid CaO and molten Ti₃Al and its equilibrium constant are expressed by Eqs. [1] and [2].

$$\text{CaO (s)} = \underline{\text{Ca}} \text{ (mass pct in Ti}_3\text{Al)} \quad [1]$$
$$+ \underline{\text{O}} \text{ (mass pct in Ti}_3\text{Al)}$$

$$K = \frac{f_{\text{Ca}} \text{ [mass pct Ca]} \cdot f_{\text{O}} \text{ [mass pct O]}}{a_{\text{CaO}}} \quad [2]$$

where a_{CaO} is the activity of CaO relative to pure solid CaO,
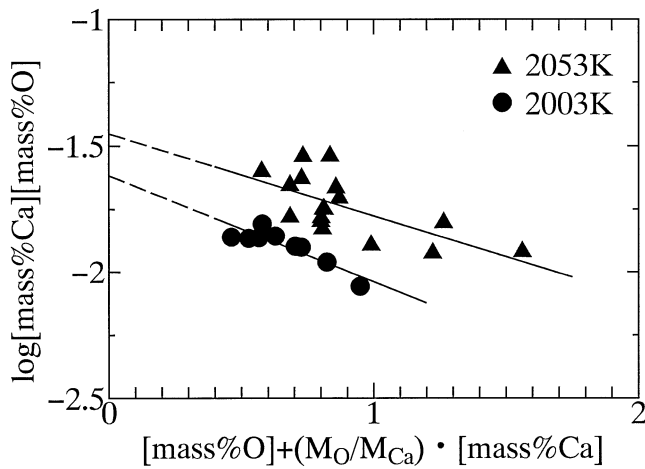
Fig. 3—The relationship between log [mass pct Ca][mass pct O] and [mass pct O] + $(M_O/M_{Ca}) \cdot$ [mass pct Ca].

Table III. Equilibrium Constants of Reaction CaO (s) = <u>Ca</u> (Mass Pct in M) + <u>O</u> (Mass Pct in M) and Interaction Parameter e_{Ca}^O

Solvent	Temperature (K)	Log K	e_{Ca}^O
Ti₃Al (present work)	2003	−1.62	0.42
	2053	−1.45	0.32
Ti[1]	2003	−1.75	−0.019
TiAl[1]	1823	−2.70	−0.969
	1923	−2.03	−0.871
	2023	−1.90	−0.902
TiAl₃[1]	1823	−0.27	0.031
TiAl[2]	1843	−2.3	−0.50
TiAl[3]	1833	−2.8	3.0
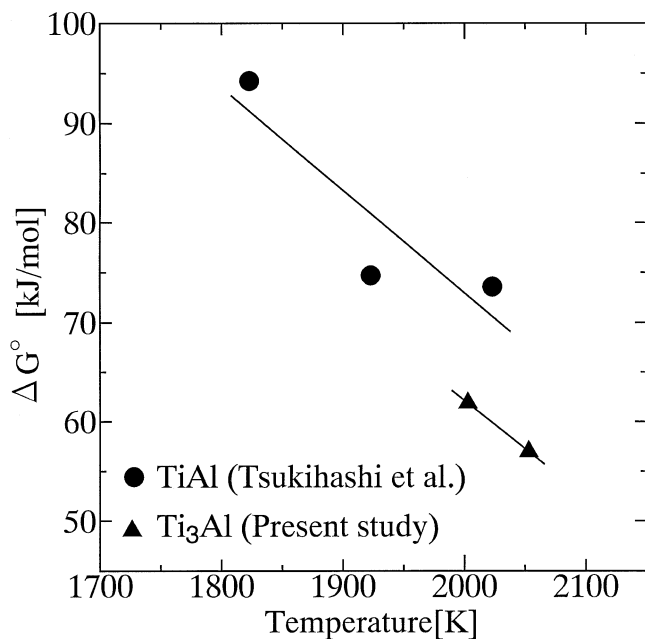
Fig. 4—The standard Gibbs energy of reaction: CaO (s) = <u>Ca</u> (mass pct in M) + <u>O</u> (mass pct in M) (M: TiAl or Ti₃Al).

f_i is the activity coefficient of component i relative to 1 mass pct, and [mass pct i] is the content of component i of molten Ti₃Al in mass pct. Because a CaO crucible was used, a_{CaO} is unity. The activity coefficients of calcium and oxygen, f_{Ca} and f_O, are expressed as Eqs. [3] and [4], respectively, by using the first-order interaction parameters.

$$\log f_{Ca} = e_{Ca}^{Ca} \text{ [mass pct Ca]} + e_{Ca}^O \text{ [mass pct O]} \quad [3]$$

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

Assuming that the self-interaction coefficients e_{Ca}^{Ca} and e_O^O can be ignored because the calcium and oxygen contents are small, Eq. [5] can be obtained by substituting Eqs. [3] and [4] into Eq. [2] and using the thermodynamic relationship of Eq. [6] between the interaction parameters.

$$\log \text{ [mass pct Ca][mass pct O]} = \log K$$
$$- e_{Ca}^O ([\text{mass pct O}] + \frac{M_O}{M_{Ca}} \cdot [\text{mass pct Ca}]) \quad [5]$$

$$e_O^{Ca} = e_{Ca}^O \cdot \frac{M_O}{M_{Ca}} \quad [6]$$

where M_{Ca} and M_O are the molecular weights of calcium and oxygen. Therefore, log [mass pct Ca][mass pct O] is expected to have a linear relationship with [mass pct O] + $(M_O/M_{Ca}) \cdot$ [mass pct Ca]. The equilibrium constant of Reaction [1] and the interaction parameter can be obtained from the intercept and the slope of the straight line shown in Figure 3. The results are summarized in Table III together with the value for the Ti-Al system and Ti.

The interaction parameter between calcium and oxygen, e_{Ca}^O, in molten iron at 1873 K was reported as −580.[4] Furthermore, Wakasugi et al.[5] suggested that a much smaller value of e_{Ca}^O is necessary to describe the equilibrium of the Fe-Ca-O system. Kimura and Suito[6] studied calcium-oxygen equilibrium in molten iron at 1873 K and reported the values of −12,500, −1500, and −150 for e_{Ca}^O depending on the calcium and oxygen contents of molten iron. The value of e_{Ca}^O in nickel was reported to be −3,060 at 1873 K.[7] The interaction parameter in the molten Ti or Ti-Al alloy is much larger than that in the molten iron or nickel because the affinity of oxygen with Ti and Al is stronger than that of oxygen with iron and nickel.

The standard Gibbs energy of Reaction [1] can be obtained from the equilibrium constants. Figure 4 shows the standard Gibbs energy of Reaction [1] together with that for TiAl.[1] The standard Gibbs energy was expressed as follows:

$$\Delta G^\circ = 258,000 - 98.0T \text{ J/mol} \quad (2003 \text{ to } 2053 \text{ K}) \quad [7]$$

The observed oxygen content of TiAl is much lower than that of Ti₃Al, TiAl₃, and Ti, as shown in Figure 2. Therefore, Ca-based fluxes have an effect on the deoxidation of TiAl. On the other hand, it is difficult to remove oxygen from Ti₃Al, TiAl₃, and Ti by using Ca-based fluxes.

The thermodynamic properties of Ca and O in molten Ti₃Al equilibrated with solid CaO at 2003 and 2053 K have been investigated. The findings can be summarized as follows:

1. The standard Gibbs energy of reaction CaO (s) = <u>Ca</u> (mass pct in Ti₃Al) + <u>O</u> (mass pct in Ti₃Al) was determined as follows:

$$\Delta G^\circ = 258,000 - 98.0T \text{ J/mol} \quad (2003 \text{ to } 2053 \text{ K})$$

2. The interaction parameters between Ca and O, e_{Ca}^{O}, in molten Ti_3Al were obtained to be 0.42 and 0.32 at 2003 and 2053 K, respectively.

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Preparation of Fine Ceria Powders by Hydrolysis of Cerium(IV) Carboxylate Solutions

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Many of the technological uses of rare earths often require oxide powders with specific particle size, morphology, and purity. Various preparation routes have been reported for rare earth oxides, using aqueous solutions or alkoxides in alcohols. The hydrometallurgical process called hydrolytic stripping is also a promising route for producing oxide materials, which involves precipitation of oxides by direct hydrolysis of metal-loaded carboxylic acid extractant dissolved in an organic solvent using water at elevated temperatures.[1,2] The hydrolysis of metal carboxylate in the organic phase enables the elimination of anion contamination of the oxide product, because the organic solvent having a low dielectric constant is free from ionic species. Using the hydrolytic stripping technique, powders of α-Fe_2O_3, Fe_3O_4, $CuO + Cu_2O$, $Mg(OH)_2$, γ-Mn_2O_3 ZrO_2, and several ferrites MFe_2O_4 (M: Ni, Co, Zn, or Mn) have been prepared at 130 °C to 245 °C.[3–8] However, no information is available concerning the preparation of rare-earth oxide powders directly from metal carboxylate in the organic phase. The purpose of this study is to establish

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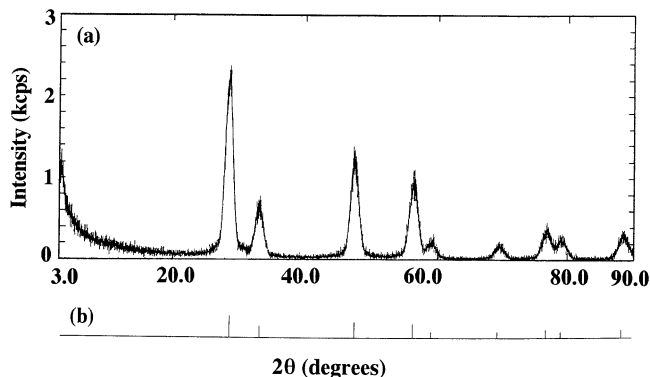Manuscript submitted January 15, 1997.

Fig. 1—X-ray powder diffraction analysis of precipitate from cerium(IV) carboxylate solution in the presence of water and atmospheric oxygen: (*a*) observed XRD pattern; and (*b*) International Center for Diffraction 34-0394. Precipitation conditions: 220 °C, 2.5 MPa, 0.17 $kmol/m^3$ cerium(IV) carboxylate, 1.3 $kmol/m^3$ free carboxylic acid, and 120 min.
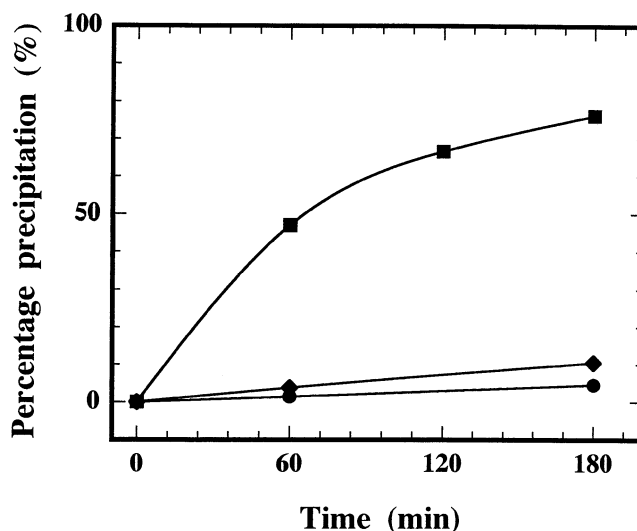

Fig. 2—Extent of ceria precipitation as a function of time at different temperatures and pressures: (■) 220 °C and 2.5 MPa; (♦) 160 °C and 0.61 MPa; and (●) 140 °C and 0.36 MPa. Precipitation conditions: 0.050 $kmol/m^3$ cerium(IV) carboxylate and 0.34 $kmol/m^3$ free carboxylic acid.

conditions for preparation of ceria (cerium(IV) oxide and CeO_2) by treating cerium(IV) carboxylate solutions with water.

In preparation of the organic starting solution, commercially available Versatic 10, a synthetic tertiary aliphatic monocarboxylic acid (Shell Chemical Co., Tokyo, Japan) was used with Exxsol D80, an aliphatic hydrocarbon diluent (Exxon Chemical Co., Tokyo, Japan). Cerium(IV) carboxylate solutions were prepared by exchange extraction; CaO powder was first dissolved in a dilute Versatic 10 solution, and then the resulting calcium-loaded carboxylate solution was shaken with an aqueous $Ce(NH_4)_2(NO_3)_6$ solution for several minutes in a separating funnel. Residual calcium was removed from the cerium(IV)-loaded carboxylate solution by mixing with a very dilute HCl solution (pH 3.0). The cerium(IV) carboxylate solution was washed with distilled water to remove residual anions and then passed through glass fiber paper and phase-separating paper