Thermodynamics of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ Oxide System at 1873 K

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Isothermal phase relations for the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system have been investigated under strongly reducing conditions, achieved by equilibrium between graphite and CO gas, $P_{\text{O}_2}=4.56\times 10^{-16}$ atm at 1873 K, in equilibria with a saturating oxide tablet.

Activities of Al_2O_3 and SiO_2 were measured by the Knudsen effusion method. Activities of SiO_2 were also measured by the chemical equilibrium between the oxide and the Fe–Si–C alloy. Activity of TiO_x was also estimated from the composition of the Si–Al–Ti alloy in equilibrium with the oxide assuming that the alloy conformed to a regular solution. In addition, steel composition equilibrated with the oxide of arbitrary composition has been calculated by the activities of each component of the oxide system obtained in the present study.

KEY WORDS: oxide metallurgy; inclusion; phase diagram; activity measurement; Knudsen effusion method.

1. Introduction

Inclusions in steels have been considered to be harmful to quality of final product of steels, and extensive studies on removal of inclusions or making them harmless, have been mostly concentrated. Al_2O_3 formed by aluminum deoxidation in a secondary steel refining process is known to cause a defect like a flaw and a crack. Therefore, a substitution of simple deoxidation of aluminum is required.

On the other hand, an innovative attempt called “oxide metallurgy” has been made to improve steel properties by controlling the size, composition and distribution of non-metallic inclusions in steels.¹⁾ In such a process, an appropriate oxide will act as a precipitation site of MnS that is a transformation site of intragranular ferrite from austenite. If the oxides were finely dispersed in steels, MnS formed on the oxide should make the ferrite grains so fine that the toughness of steels could be enhanced. Sawai *et al.*²⁾ have reported that the complex deoxidization by strong and weak deoxidizing agents is effective for the fine dispersion of deoxidation product, and they have also reported that an oxide with high sulfide capacity was preferable for MnS precipitation. Moreover, Ogibayashi³⁾ reported that low liquidus temperature of the oxide would promote the MnS precipitation.

Thus, thermodynamic properties of the oxide inclusions in steels must be investigated in order to optimize the processes concerned with the inclusions. Some thermodynamic studies of oxide systems satisfying the conditions mentioned above have been done.

Amitani *et al.*⁴⁾ investigated the phase relations for the MnO– SiO_2 – TiO_x system at 1573 K and 1773 K. Ito *et al.*⁵⁾ measured the activity of MnO and sulfide capacity for the MnO– SiO_2 – TiO_2 system at 1673 K. Authors have investigated phase relations and activities of each component for

the MnO– Al_2O_3 – TiO_2 system at 1673 K and 1873 K.⁶⁾ According to these studies, the compositions of low liquidus temperature and high sulfide capacity for the oxide system including MnO and TiO_2 have been obtained. Moreover, steel compositions equilibrated with the oxide have been calculated with the activity data.

However, in the practical process, TiO_2 is not the equilibrium state as titanium oxide because of the low partial pressure of oxygen. Ti^{3+} and Ti^{4+} are reported to coexist in a melt of the oxide under the strongly reducing condition.⁴⁾ In addition, aluminum is the strong deoxidant enough to reduce MnO in the oxide phase. Therefore, the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ oxide system will be formed as deoxidation product in secondary refining process practically.

In this paper, phase relations of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system as well as the activities of Al_2O_3 and SiO_2 have been investigated at 1873 K. Also, the steel composition equilibrated with the oxide has been calculated.

2. Experimental Method

2.1. Measurement of the Phase Relations

A MoSi₂ electric resistance furnace connected to a proportional integral differential (PID) controller with a Pt/6%Rh–Pt/30%Rh thermocouple was used for all the experiments in the present study. Temperature was controlled at 1873 ± 1 K over a length of 50 mm in a mullite tube settled in the furnace. A graphite crucible with 4 g of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_2$ oxide and a tablet of the saturating oxide was placed in the furnace for 24 h. After the experiment, the crucible was taken out of the furnace and cooled by argon flush. The molten oxide phase was separated from the tablet, broken and ground into fine powder, and was subjected to chemical analysis. Silicon in the oxide was determined by the gravimetry, aluminum and total titanium con-

Table 1. Conditions of X-ray diffraction analyses.

Tube voltage	40 kV
Tube current	200 mA
Step	0.02 deg
Scanning rate	5.0 deg/min
Source	1.54056 Å (K α_1 , Cu)
Divergence slit	0.5 deg
Scatter slit	0.5 deg
Receiving slit	0.3 mm

tent by ICP-AES, and trivalent titanium content by a titration of potassium dichromate. X-ray diffraction analysis was done on the boundary between the oxide and the tablet to confirm the solid phase in equilibrium. Analytic condition is shown in **Table 1**.

2.2. Activity Measurement by the Equilibrium between the Oxide and the Fe–Si–C Alloy

A graphite or SiC crucible with 4 g of the oxide and 10 g of the Fe–Si–C alloy was placed in the furnace at 1 873 K for more than 48 h. Carbon monoxide gas was flown into the furnace to maintain $P_{\text{CO}}=1.013 \times 10^5$ Pa. After the experiment, the specimen was taken out of the furnace and cooled by argon flush. Both phases were separated into the oxide and the alloy, and the composition of the oxide was measured by chemical analyses. Silicon in the alloy was measured by the gravimetry method. Carbon content in the alloy was measured by LECO combustion analyzer. The other components were also measured by the same way as in the investigation of the phase relations.

Equilibria between the oxides and the alloys can be represented as the following equations.

$$K_1 = \frac{X_{\text{Si}} \cdot \gamma_{\text{Si}} \cdot P_{\text{CO}}^2}{a_{\text{SiO}_2} \cdot a_{\text{C}}^2}$$

$$K_2 = \frac{X_{\text{Si}}^3 \cdot \gamma_{\text{Si}}^3 \cdot P_{\text{CO}}^2}{a_{\text{SiO}_2} \cdot a_{\text{SiC}}^2}$$

SiC is stable when silicon content is larger than 22.4 mass% in Fe–Si–C alloy.⁷⁾ Thus, Eq. (2) was adopted in such a condition. Activity of SiO_2 in the oxide can be obtained by measurement of silicon content in the alloy with activity coefficient of silicon in the alloy reported by Rein *et al.*⁷⁾ because activity of graphite or SiC and the partial pressure of CO gas are unity.

2.3. Activity Measurement by Knudsen Effusion Method

The Knudsen effusion method was employed to measure activities of Al_2O_3 and SiO_2 . The Al_2O_3 – SiO_2 – TiO_x oxide and the Al–Si–Ti alloy were equilibrated in a graphite cru-

cible for more than 48 h under $P_{\text{CO}}=1.013 \times 10^5$ Pa at 1 873 K, then subjected to chemical analyses. About 0.1 g of the oxide and the alloy were put into a BN crucible covered by a BN lid with an orifice of 0.2 mm in diameter. The crucible was settled in the center of the furnace heated by tantalum heating elements at 1 873 K. Ion current was measured regarding the molecular weight of 27, 28, 43 and 44 by a quadrupole mass spectrometer. The molecular weight of 27, 28, 43 and 44 correspond to Al, Si, AlO and SiO, respectively.

Equilibria between Al_2O_3 and SiO_2 in the oxide and aluminum and silicon in the alloy are represented as following equations.

$$K_3 = \frac{a_{\text{Si}}^{1/2} \cdot a_{\text{SiO}_2}^{1/2}}{P_{\text{SiO}}}$$

$$K_4 = \frac{a_{\text{Al}}^{1/3} \cdot a_{\text{Al}_2\text{O}_3}^{1/2}}{P_{\text{AlO}}}$$

Therefore, activities of Al_2O_3 and SiO_2 were obtained by the following equations.

$$a_{\text{SiO}_2} = \frac{K_3^2 \cdot P_{\text{SiO}}^2}{P_{\text{Si}} / P_{\text{Si}}^\circ} \quad \text{.....(5)}$$

$$a_{\text{Al}_2\text{O}_3} = \frac{K_4^3 \cdot P_{\text{AlO}}^3}{P_{\text{Al}} / P_{\text{Al}}^\circ} \quad \text{.....(6)}$$

where P_i represents a partial pressure of i component and P_i° is a partial pressure of i component of standard state.

On the other hand, relationship between the ion current and the partial pressure of the component i was represented as follows.

$$P_i = k_i \cdot I_i \cdot T \quad \text{.....(7)}$$

where P_i is a partial pressure of i component, k_i is the apparatus constant including the ionization cross section of i species, and T is temperature.

In the present study, the apparatus constant was determined as follows. $\text{Al}_6\text{Si}_2\text{O}_{13}$, Al_2O_3 and the Al–Si alloy were equilibrated in the BN crucible and the ion current values were monitored which corresponds to Al, Si, AlO and SiO by mass spectrometer. Equilibrium among $\text{Al}_6\text{Si}_2\text{O}_{13}$, Al_2O_3 , Al and Si is represented as follows.

$$\Delta G_8^\circ = 138\,600 - 23.89T \quad (\text{J/mol})^{8)}$$

Activities of $\text{Al}_6\text{Si}_2\text{O}_{13}$ and Al_2O_3 are unity and that of silicon is almost unity because compositions of other components are very low. That of aluminum is calculated to 1.8×10^{-3} with the Gibbs energy change of Eq. (8). Thus, activities of all components in Eqs. (3) and (4), and the apparatus constants of respective components could be obtained by measurement of ion current.

Preliminarily, the measurement for ion current corre-

Fig. 1. Phase diagram of the Al_2O_3 - Ti_2O_3 binary system.⁹⁾

Fig. 2. X-ray diffraction pattern of the Al_2O_3 - Ti_2O_3 mixture and the sintering tablet of the mixture at 1873 K.

Table 2. Measurement of lattice spacing and calculation of reciprocal solid solubility for the Al_2O_3 - Ti_2O_3 system.

hkl	Al_2O_3 (ss)				Ti_2O_3 (ss)			
	d_0 (Å)	d_{mix} (Å)	Ti_2O_3 (mol%)	Ti_2O_3 (mass%)	d_0 (Å)	d_{mix} (Å)	Al_2O_3 (mol%)	Al_2O_3 (mass%)
220	1.1861	1.1917	5.63	7.76	1.2856	1.2800	5.63	4.06
306	1.1618	1.1653	4.23	5.86	1.2445	1.2412	3.99	2.86
0210	1.0992	1.1008	3.56	4.95	1.1618	1.1584	5.43	3.91
		Ave.	4.5	6.2		Ave.	5.0	3.6

sponding to Si and SiO under the equilibrium between Si and SiO_2 were repeated. As a result, changes of apparatus constant for Si and SiO were within 10%. In the derivation of activities, it was assumed that the constant would not change between the preliminary measurement for the constant determination and the practical measurement.

3. Results and Discussion

3.1. Phase Relations for the Al_2O_3 - Ti_2O_3 Binary System at 1873 K

Phase diagram of the Al_2O_3 - Ti_2O_3 system have been reported in a literature as shown in Fig. 1.⁹⁾ However, details about solid solubility were incomplete. On the other hand, the Al_2O_3 - TiO_2 system obtained in air is known to have intermediate compound, $\text{Al}_2\text{O}_3 \cdot \text{TiO}_2$.⁹⁾ Thus, phase relations for the Al_2O_3 - Ti_2O_3 binary system were investigated in prior to those for the Al_2O_3 - SiO_2 - TiO_x system.

A mixture of the 50mass% Al_2O_3 -50mass% Ti_2O_3 powder was pressed and shaped into a tablet. The tablet was sintered under the same condition as the measurement of phase relations for the Al_2O_3 - SiO_2 - TiO_x system mentioned in Sec. 2.1. This sample was analyzed by X-ray diffraction (XRD). The XRD pattern of the sintered specimen compared with the simply mixed powder is shown in Fig. 2. It is found that there is no intermediate compound in the Al_2O_3 - Ti_2O_3 binary system according to the diffraction spectra. Since Al_2O_3 and Ti_2O_3 have the same crystal structure, the reciprocal solid solubilities of Al_2O_3 and Ti_2O_3 can be obtained from the shift of spectra based on the following equation assuming that the lattice spacing has a linear relation with the solid solubility.

$$x = (d_{\text{TiO}_{1.5}} - d_{\text{obs}}) / (d_{\text{TiO}_{1.5}} - d_{\text{AlO}_{1.5}}) \quad \dots\dots\dots (9)$$

where x denotes solid solubility described as the molar fraction of Al_2O_3 in Ti_2O_3 solid phase and d is the lattice spacing. The molar fraction of Ti_2O_3 in Al_2O_3 can be also obtained by the same way. There is an error more than 2% as the dependence on the accuracy of measurement of the lattice spacing in this way.

Measurements were done on (220), (306) and (0210) planes and the average values of these inter-planar distances were calculated. Results of these measurements and calculation are shown in Table 2, where the results of practical measurements on the raw mixture of Al_2O_3 and Ti_2O_3 are adopted as values of d_0 . According to the results, solid solubility of Al_2O_3 into Ti_2O_3 is 3.6 mass% and that of Ti_2O_3 into Al_2O_3 is 6.2 mass%. Thus, Al_2O_3 and Ti_2O_3 will coexist with those reciprocal solubilities although these solid solubilities are smaller than those deduced from Fig. 1.

3.2. Phase Relations for the Al_2O_3 - SiO_2 - TiO_x System at 1873 K

The results of the measurement of the Al_2O_3 - SiO_2 - TiO_x system at 1873 K are shown in Table 3. All the equilibrium compositions were obtained by more than twice experiments as mentioned Sec. 2.1. For instance, change of experimental composition for the 15.79mass% Al_2O_3 -67.36mass% SiO_2 -16.85mass% TiO_x is shown in Fig. 3. Isothermal phase diagram of the Al_2O_3 - SiO_2 - TiO_x system at 1873 K is shown in Fig. 4. Liquidus of the Al_2O_3 - SiO_2 - TiO_2 investigated in air is also shown by broken line in Fig. 4. In this study, species of TiO_x equilibrated with liquid phase was observed to be Ti_2O_3 , which is consistent with the results of Amitani *et al.*⁴⁾ As mentioned in the previous section, Al_2O_3 and Ti_2O_3 coexist with the reciprocal

Table 3. Experimental results for the phase relations for the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system at 1873 K.

Sample No.	Composition of the oxide (mass%)				Saturating phase
	Al_2O_3	SiO_2	TiO_x	$\text{Ti}^{4+}/\text{Ti}^{3+}$	
101	15.4	72.2	12.4	1.12	$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$
102	15.8	67.4	16.9	0.67	$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$
103	18.6	62.0	19.4	0.54	$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$
104	16.6	48.2	35.2	1.09	Al_2O_3
105	10.2	71.6	18.3	1.36	Ti_2O_3
106	7.1	66.1	26.8	1.19	Ti_2O_3
107	12.3	65.0	22.7	1.01	Ti_2O_3
108	12.0	43.2	44.8	1.50	Ti_2O_3
109	14.1	54.9	31.0	0.79	Ti_2O_3
110	8.6	79.5	11.9	1.20	$\text{SiO}_2, \text{Ti}_2\text{O}_3$
111	21.0	52.6	26.4	0.89	$\text{Al}_2\text{O}_3, 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$
112	12.4	39.2	48.4	1.43	$\text{Al}_2\text{O}_3, \text{Ti}_2\text{O}_3$
113	8.8	85.4	6.2	1.78	SiO_2

Fig. 3. Change of the composition among the experiments for the measurements of phase equilibria. **Fig. 4.** Isothermal phase diagram of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system at 1873 K. ($P_{\text{O}_2} = 4.56 \times 10^{-16}$ atm)

solubilities, so the pure Al_2O_3 and Ti_2O_3 may not be in equilibrium with the liquid. Hence, the tie lines around the Al_2O_3 and the Ti_2O_3 corners are drawn as broken ones in this figure for convenience.

Maximum solubility of Al_2O_3 is 28 mass% and that of TiO_x is 50 mass%. Liquid area of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system is narrow compared with the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_2$ system in the region of the lower SiO_2 content. This difference is similar to that between the $\text{MnO--SiO}_2\text{--TiO}_2$ and the

Table 4. Experimental results for the measurements of the doubly saturated composition in the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x\text{--}3.7\sim 5.4\text{mass\% MnO}$ system at 1873 K.

No.	Composition of the oxide (mass%)					Saturating phase
	Al_2O_3	SiO_2	TiO_x	MnO	$\text{Ti}^{4+}/\text{Ti}^{3+}$	
201	7.7	78.6	9.6	4.2	0.96	$\text{SiO}_2, \text{Ti}_2\text{O}_3$
202	24.0	49.1	21.6	5.4	0.86	$\text{Al}_2\text{O}_3, 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$
203	15.3	30.6	50.4	3.7	0.54	$\text{Al}_2\text{O}_3, \text{Ti}_2\text{O}_3$

□ Doubly saturated point for the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x\text{--}5\text{mass\% MnO}$
($\text{A}_3\text{S}_2: 3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$)

Fig. 5. Compositions of the doubly saturated point and deduced liquidus lines in the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x\text{--}3.7\sim 5.4$ mass% MnO at 1873 K.

$\text{MnO--SiO}_2\text{--TiO}_x$ systems.⁴⁾

3.3. Liquidus for the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x\text{--}5\text{mass\% MnO}$ System

In order to investigate the effect of MnO considerably contained in the originally formed oxide, the doubly saturated compositions of each component in the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x\text{--MnO}$ system were determined. Initial amount of MnO addition was 5 mass% into the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ oxide. Equilibrium composition obtained in these measurements is shown in **Table 4**. Final MnO contents were fluctuated from 3.7 mass% to 5.4 mass%. Deduced liquidus of that system is shown in **Fig. 5**. Liquidus is drawn as the pseudo-ternary system without MnO content. Addition of a small amount of MnO enlarges the liquidus area of the $\text{Al}_2\text{O}_3\text{--SiO}_2\text{--TiO}_x$ system. Thus, it is found that liquidus would be shrinking with reducing MnO in the practical process.

3.4. Behavior of Trivalent and Tetravalent Titanium in the Oxide Melts

The dependence of valence of titanium on the composition of the melts has been investigated along the composition of $(\text{mass\% Al}_2\text{O}_3)/(\text{mass\% TiO}_x) \approx 0.67$. Relationship between $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio and SiO_2 content in the oxide is shown in **Fig. 6**. $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio increases with SiO_2 content, which suggests that $\text{TiO}_{1.5}$ is more acidic than TiO_2 . This tendency is inconsistent with the $\text{MnO--SiO}_2\text{--TiO}_x$ system by Amitani *et al.*⁴⁾ and the $\text{CaO--SiO}_2\text{--Al}_2\text{O}_3\text{--TiO}_x$ system by Ito *et al.*¹⁰⁾ They have concluded that tetravalent titanium is more acidic than trivalent one in the oxide melt.

Fig. 6. Relationship between $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio and the SiO_2 content in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ system at 1873 K. [(mass% Al_2O_3)/(mass% TiO_x) ≈ 0.67]

Fig. 7. Relationship between $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio and the TiO_x content in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ system at 1873 K. [(mass% Al_2O_3)/(mass% SiO_2) ≈ 0.28]

In the $\text{MnO-SiO}_2\text{-TiO}_x$ system with higher basicity than the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ system, red-ox equilibrium of Ti in such oxide is considered as follows.

Tetravalent titanium forms structure unit of complex anion like TiO_3^{2-} . This anion is decomposed into single trivalent titanium as partial pressure of oxygen decreased or basicity of the melt decreased.

On the other hand, relationship between $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio and TiO_x content along the composition of (mass% Al_2O_3)/(mass% SiO_2) ≈ 0.28 is shown in Fig. 7. $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio increases with TiO_x content. Thus, it is found that TiO_x as well as SiO_2 influenced $\text{Ti}^{4+}/\text{Ti}^{3+}$ ratio.

In order to examine the contradiction between the present work and others, structure of some samples was investigated by the Raman spectrometry. Conditions for the measurements are shown in Table 5 and Raman spectra are shown in Fig. 8. According to the results, although relative intensities are weak, only 1600 cm^{-1} band corresponding to 3-D network is observed while other band peaks corresponding to structure of broken network of silica such like monomer, dimer, chain and sheet are hardly recognized. Thus, Al_2O_3 and Ti_2O_3 do not seem to behave as network-modifiers, but may be incorporated in silicate network structures. Then, ratio of intensity of 1600 cm^{-1} peak and that around

Table 5. Conditions for the measurements by the Raman spectrometry.

Sample No.	Composition of the oxide(mass%)			$P_{\text{O}_2}(\times 10^{-16}\text{ atm})$	$I_{1100\text{cm}^{-1}}/I_{1600\text{cm}^{-1}}$
	Al_2O_3	SiO_2	TiO_x		
T1	10	80	10	4.56	0.47
T2	10	80	10	3.22	0.51
T3	10	80	10	2.28	0.59
T4	10	80	10	1.14	1.27
T5	15	50	35	4.56	0.98

Fig. 8. Raman spectra with various oxygen partial pressures for the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ system.

Fig. 9. Relationship between the ratio of $I_{1100\text{cm}^{-1}}/I_{1600\text{cm}^{-1}}$ and oxygen partial pressure for the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_x$ system.

1100 cm^{-1} corresponding to the structure of sheet of silica were investigated as an index of breakage of network structure. Dependence of the ratio of intensities upon the oxygen partial pressure is shown in Fig. 9. Relative intensity of 1600 cm^{-1} decreases with the decrease of oxygen partial pressure. On the other hand, relative intensity of 1600 cm^{-1} decreases as SiO_2 content decreases compared between T1 and T5 with the same oxygen partial pressure. According to the tendency, it seems that tetravalent titanium ions form the network structure with silicon and oxygen described as Fig. 10, schematically. Both of the tetravalent and trivalent titanium form the complex structure with oxygen and silicon. 3-D network of Si-Ti-O including tetravalent titanium is partially broken into the network including non-bonding oxygen as oxygen partial pressure decreases or basicity of the melt increases.

Fig. 10. Schematic image of structure of the Si-Ti-O in the oxide melt.

Fig. 11. Activities of SiO_2 and $\text{AlO}_{1.5}$ in the Al_2O_3 - SiO_2 - TiO_x system at 1873 K.

3.5. Activities of $\text{AlO}_{1.5}$ and SiO_2 in the Al_2O_3 - SiO_2 - TiO_x System

Activities of $\text{AlO}_{1.5}$ and SiO_2 obtained by the chemical equilibrium between the oxide and the Fe-Si-C alloy and those by Knudsen effusion method are shown in Fig. 11 and Table 6. Activities of SiO_2 measured by both methods are in good agreement. For instance, activity value of SiO_2 of the composition doubly saturated with Al_2O_3 and $\text{Al}_6\text{Si}_2\text{O}_{13}$ is obtained to be 0.45 by the chemical equilibrium and 0.46 by Knudsen effusion method while it is calculated to be 0.462 by the standard free energy of formation of $\text{Al}_6\text{Si}_2\text{O}_{13}$. Thus, the results of activity measurement of $\text{AlO}_{1.5}$ by Knudsen effusion method also seem to be reasonable.

When SiO_2 replaces TiO_x from (mass% SiO_2)=45 to 75 along the composition of (mass% Al_2O_3)=15, activity of $\text{AlO}_{1.5}$ drops near the liquidus of saturated by Al_2O_3 , then decreases gradually from 0.66 to 0.57. This phenomenon seemed to reflect that both of the SiO_2 and TiO_x behave as network-former in the melts mentioned in the previous section.

3.6. Estimation of TiO_x Activity from the Composition and Activity of Each Component of the Si-Al-Ti Alloy in Equilibrium with the Oxide Melt

Composition of the Si-Al-Ti alloy equilibrated with the oxide melt in some of the activity measurements was deter-

Table 6. Activities of SiO_2 and $\text{AlO}_{1.5}$ in the Al_2O_3 - SiO_2 - TiO_x system at 1873 K.

Chemical equilibrium					
Sample No.	Composition of the oxide (mass%)				
	Al_2O_3	SiO_2	TiO_x	a_{Si}	a_{SiO_2}
301	16.3	56.8	26.9	0.0698	0.49
302	22.8	51.5	25.7	0.0678	0.45
303	12.8	43.0	44.2	0.0462	0.21
304	17.1	74.9	8.0	0.0712	0.52
305	21.1	60.5	18.4	0.0703	0.5
306	12.8	80.6	6.6	0.0771	0.66
307	8.8	85.4	6.2	0.1070	0.92
Knudsen effusion method					
Sample No.	Composition of the oxide (mass%)				
	Al_2O_3	SiO_2	TiO_x	$a_{\text{AlO}_{1.5}}$	a_{SiO_2}
308	25.2	51.7	23.1	1.00	0.46
309	13.5	76.0	10.5	0.57	0.75
310	12.9	48.1	39.0	0.94	0.23
311	9.8	77.9	12.3	0.57	0.81
312	12.0	67.8	20.2	0.65	0.44
313	18.1	55.0	27.0	0.66	0.49

mined assuming that composition of alloy did not change during the measurement by the Knudsen cell. The activity of each component of the alloy can be calculated from the composition by Toop's method¹¹⁾ described as follows when the Si-Al-Ti alloy behaves as a regular solution.

$$\log \gamma_{2(1-2-3)} = \left[\frac{N_2}{1-N_2} \log \gamma_{2(1-2)} + \frac{N_3}{1-N_3} \log \gamma_{2(2-3)} \right]_{N_2} - (1-N_2)^2 \left[\frac{G_{1-3}^E}{19.144T} \right]_{N_1/N_3} \dots \dots \dots (11)$$

where subscripts of 1-2-3, 1-2 and 2-3 denote the ternary of 1-2-3, the binary of 1-2 and that of 2-3, respectively. G^E represents excess free energy. In the method, activity coefficient of component 2 in ternary system can be calculated with activity coefficients of 2 in two binary systems and excess free energy of the other binary system. $\gamma_{1(1-2-3)}$ and $\gamma_{3(1-2-3)}$ can be derived in the same way. In the present analysis, the data reported by Desai¹²⁾ are adopted as the thermodynamic property of the Al-Si and the Al-Ti and those by Miki *et al.*¹³⁾ for the Si-Ti binary system, respectively.

Composition and activities of each component of the Si-Al-Ti alloy equilibrated with the oxide are shown in Table 7. Oxygen partial pressure in the system can be determined by the equilibrium between SiO_2 in the oxide and silicon in the alloy. Activities of $\text{TiO}_{1.5}$ and TiO_2 are calculated from the oxygen partial pressure, activity of titanium in the alloy and standard free energies of formation of $\text{TiO}_{1.5}$ and TiO_2 .¹⁴⁾ These results are shown in Fig. 12. This figure shows also activities of $\text{TiO}_{1.5}$ and TiO_2 in the Ti_2O_3 saturated point.

When the content of SiO_2 increases from 55 mass% to 80 mass% along the composition of (mass% Al_2O_3)/(mass% TiO_x) $\approx$ 0.43, activity coefficient of TiO_2 changes

Table 7. Composition and activities of each component of the Si–Al–Ti alloy in equilibrium with the Al_2O_3 – SiO_2 – TiO_x system and estimated activity of TiO_x .

No.	Composition of the oxide (mass%)			Composition of the alloy (mass%)		a_{Ti}	a_{Si}	a_{Ti}	a_{TiO_2}	$a_{\text{TiO}_{1.5}}$
	Al_2O_3	SiO_2	TiO_x	Al	Ti					
311	9.8	77.9	12.3	1.55	6.7	5.7×10^{-4}	0.90	5.4×10^{-3}	5.12×10^{-2}	0.88
312	12.0	67.8	20.2	2.27	9.8	9.5×10^{-4}	0.86	5.5×10^{-3}	4.60×10^{-2}	0.79
313	18.1	55.0	27.0	3.71	12.2	8.7×10^{-5}	0.75	5.5×10^{-3}	3.55×10^{-2}	0.67

Fig. 12. Estimated activity of $\text{TiO}_{1.5}$ and TiO_2 in the Al_2O_3 – SiO_2 – TiO_x system at 1873 K.

from 0.04 to 0.13 while that of $\text{TiO}_{1.5}$ increases from 3.9 to 29, and ratio of $\gamma_{\text{TiO}_2}/\gamma_{\text{TiO}_{1.5}}$ changes from 1.03×10^{-2} to 1.45×10^{-2} . The phenomenon that TiO_2 is more stable than $\text{TiO}_{1.5}$ with lower basicity is in agreement with the structural model described in Sec. 3.4.

3.7. Calculation of the Steel Composition in Equilibrium with the Oxide

Steel composition equilibrated with the oxide of arbitrary composition can be calculated using the data obtained in the present work. Deoxidation equilibrium about metal component; M in the steel is represented as follows.

$$m\text{M}_i = n\text{O} = \text{M}_i\text{O}_n(\text{s}) \quad (\text{M}_i: \text{Al, Si and Ti}) \quad \dots (12)$$

$$\log K = \log a_{\text{M}_i\text{O}_n} - m \log f_{\text{M}_i} - m \log [\text{mass}\% \text{M}_i] - n \log f_{\text{O}} - n \log [\text{mass}\% \text{O}] \quad \dots (13)$$

$$\log f_{\text{M}_i} = \sum_j e_{\text{M}_i}^{\text{M}_j} [\text{mass}\% \text{M}_j] + e_{\text{M}_i}^{\text{O}} [\text{mass}\% \text{O}] \quad \dots (14)$$

where f_{M_i} is activity coefficient of M_i in referred to 1 mass% of M_i and e_i^j is an interaction parameter between i and j in the steel, respectively. Interaction parameters used in the calculation are shown in Table 8.

Calculation was done along $(\text{mass}\% \text{Al}_2\text{O}_3)/(\text{mass}\% \text{TiO}_x) \approx 0.43$. Oxygen content was assumed to be 30 mass ppm in the steel and Eq. (13) was solved about contents of aluminum, silicon and titanium by trial and error. Relationship between the composition of the oxide and the steel is shown

Table 8. Interaction parameters between Al, Si, Ti and O in molten iron at 1873 K.¹⁵⁾

e_i^j ($j \rightarrow$)	Al	Si	Ti	O
Al	0.043	0.056	0.004 ¹⁴⁾	-1.98
Si	0.058	0.103	1.23	-0.119
Ti	0.0037 ¹⁴⁾	2.1	0.042	-3.4
O	-1.17	-0.066	-1.12	-0.17

Fig. 13. Relationship between the steel compositions equilibrated with the Al_2O_3 – SiO_2 – TiO_x oxide and SiO_2 content in the oxide at 1873 K. $[(\text{mass}\% \text{Al}_2\text{O}_3)/(\text{mass}\% \text{TiO}_x) \approx 0.43]$

in Fig. 13.

Figure 13 shows a considerable change in titanium content of the steel with the change in Al_2O_3 and SiO_2 contents of the oxide although activity of Ti_2O_3 slightly changes. Titanium content in the steel changes from 0.024 mass ppm to 44.6 mass ppm while silicon content from 2.2 mass% to 0.57 mass% when SiO_2 content of the oxide increases from 47 mass% to 78 mass%. It is considered that the remarkably large value of the interaction parameter between silicon and titanium in the steel has caused such estimation. Therefore, these parameters must be examined intensively. On the other hand, aluminum content is in the range from 7 mass ppm to 10 mass ppm when the steel is in equilibrium with the melting oxide. An effect of complex deoxidation of the Al–Si–Ti is hardly recognized compared with value for single deoxidation of Al, 10 mass ppm.¹⁵⁾

4. Conclusions

Thermodynamic properties of the Al_2O_3 – SiO_2 – TiO_x sys-

tem at 1 873 K have been investigated in order to optimize the process related to the oxide inclusions.

- Reciprocal solid solubility for the Al_2O_3 – Ti_2O_3 binary system was investigated by X-ray diffraction. Al_2O_3 and Ti_2O_3 coexist with solid solubility of 3.6 mass% Al_2O_3 into Ti_2O_3 and that of 6.2 mass% Ti_2O_3 into Al_2O_3 .
- Phase relations of the oxide system were measured by the chemical equilibrium between the oxide and the tablet of the saturating oxide. Liquidus area is narrower than that of the Al_2O_3 – SiO_2 – TiO_2 system in the region of lower SiO_2 content.
- Liquidus for the Al_2O_3 – SiO_2 – TiO_2 –5mass%MnO system was investigated. Liquidus changes wider with addition of MnO.
- Behavior of tetravalent and trivalent titanium was investigated about relationship between the ratio of $\text{Ti}^{4+}/\text{Ti}^{3+}$ and SiO_2 content. Phenomenon that TiO_2 is more stable than $\text{TiO}_{1.5}$ in high SiO_2 content is explained by the structural model of the Si–Ti–O in the oxide melt.
- Activities of $\text{AlO}_{1.5}$ and SiO_2 were measured by the chemical equilibrium between the oxide and the Fe–Si–C alloy and Knudsen effusion method. Activities of SiO_2 obtained by the both methods have good agreement with each other.
- Activities of TiO_2 and $\text{TiO}_{1.5}$ were calculated from the activity of the Si–Al–Ti alloy estimated from the composition by Toop's method.
- Steel composition in equilibrium with the oxide was calculated with the interaction parameter in the steel and the activities of $\text{AlO}_{1.5}$, SiO_2 and $\text{TiO}_{1.5}$. Though activity of $\text{TiO}_{1.5}$ changes slightly, titanium content changes remarkably with the change of content of Al_2O_3 and SiO_2 .

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