

Activities of the Constituents in Spinel Solid Solution and Free Energies of Formation of MgO, MgO·Al₂O₃

Katsumori FUJII, Tetsuya NAGASAKA¹⁾ and Mitsutaka HINO¹⁾

Formerly graduate student at Tohoku University, now at Aishin AW Co. Ltd., Anjo 444-1192 Japan.

1) Department of Metallurgy, Graduate School of Engineering, Tohoku University, 02 Aoba-yama, Sendai 980-8579 Japan.

E-mail: takahino@material.tohoku.ac.jp

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Spinel (MgO·Al₂O₃) is known as one of the most harmful non-metallic inclusions in steel. However, the technology to avoid spinel formation has not yet been established due to lack of thermodynamic information on the spinel itself. In the present work, the free energies of formation of MgO and MgO·Al₂O₃, and the activities of the constituents in spinel solid solution have been directly measured by the chemical equilibrium technique. The free energies of formation of MgO and MgO·Al₂O₃ determined in the present work are expressed by the following equation:



The activity of stoichiometric MgO·Al₂O₃ exhibits negative deviation from ideality in the spinel solid solution. Phase stability diagram of spinel formation in liquid steel was assessed as a function of aluminum, magnesium and oxygen contents in iron at 1873 K. The predicted phase boundaries of MgO·Al₂O₃, MgO and Al₂O₃ agreed well with previous observations by one of the present authors.

KEY WORDS: Spinel; non-metallic inclusion; free energy of formation; steelmaking; activity.

1. Introduction

Spinel (MgO·Al₂O₃) has a high melting point, and forms as an undeformed C-type inclusion in steel in extremely low oxygen contents. Therefore, it is very important to avoid the formation of spinel in the deoxidation process of high-grade wire and bearing steels. However, the mechanism and phase stability of spinel formation in liquid steel are not clarified due to the lack of reliable thermodynamic information on spinel formation.

Itoh *et al.*¹⁻⁵⁾ have assessed thermodynamic deoxidation equilibria of magnesium, calcium and aluminum in liquid iron and conducted thermodynamic studies on the phase stability of spinel inclusion in molten steel. As will be seen in some of their results to be presented in later sections, they have predicted the stable formation region of spinel inclusions in liquid steel as a function of oxygen, aluminum and magnesium contents.^{4,5)} As they have also pointed out in their paper, however, two problems should be solved for a precise description of spinel stability. The one is the uncertainty of the free energy of formation of spinel at steelmaking temperatures, and the other is the lack of activity data of the constituents in the solid solution range of spinel.

Some free energy data are available in the literature on the formation of spinel.⁶⁻¹³⁾ However, the agreement of free energy of formation among them is poor, and only four researches¹⁰⁻¹³⁾ have been conducted for direct measurement of the free energy of formation of MgO·Al₂O₃ while all of

them were conducted at lower temperatures than 1673 K except for the one by Rein and Chipman,¹¹⁾ who determined the free energy at 1873 K from the estimated activities of MgO and Al₂O₃ in MgO–SiO₂–Al₂O₃ slags and the liquidus line of spinel. Phase equilibria in MgO–spinel, Al₂O₃–spinel or the MgO–Al₂O₃ system near steelmaking temperatures have been studied by some researchers.¹⁴⁻²²⁾ Recently, a thermodynamic assessment for the MgO–Al₂O₃ system was conducted by Hallstedt.²³⁾ Spinel has a wide solid solution range, over 50 to 65 mol% of Al₂O₃, so that the activity of stoichiometric spinel, MgO·Al₂O₃, should change as a function of composition in the homogeneous solid solution range. However, there exists no report on the activity-composition diagram of spinel in the solid solution range. Due to the lack of such information, Itoh *et al.*^{4,5)} assumed the behavior of an ideal solid solution of spinel. Though Itoh *et al.* assessed the related deoxidation thermodynamics of liquid steel and predicted the phase stability of spinel, the thermodynamic information on spinel itself is still insufficient. Hallstedt²³⁾ also pointed out that there is a surprising lack of reliable thermodynamic data on spinel.

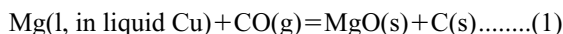
The present work focused on the direct measurement of the Gibbs free energy of formation of spinel from each component oxide, $\Delta G_{f, \text{MgO} \cdot \text{Al}_2\text{O}_3}^\circ$, and the change of activities of constituents in the homogeneous solid solution region of the spinel phase. The chemical equilibrium technique previously employed for the measurement of the activities of

constituents in steelmaking slags²⁴⁾ was used. MgO and Al₂O₃ are the component oxides of spinel, and their free energies of formation are necessary to determine $\Delta G_{f, MgO \cdot Al_2O_3}^\circ$ and the activity in the spinel solid solution. Reliable data on the free energy of Al₂O₃ formation have been reported in the literature.^{6-9,24)} On the other hand, the reported value of $\Delta G_{f, MgO}^\circ$ shows discrepancy with the order among ΔG_f° of other alkaline earth oxides such as CaO, SrO and BaO.^{25,26)} Therefore, $\Delta G_{f, MgO}^\circ$ is also directly measured in the present work.

2. Experimental Principle

2.1. Free Energy of Formation of MgO

For the measurement of $\Delta G_{f, MgO}^\circ$, experiments were conducted by equilibrating liquid copper containing graphite in a MgO crucible with CO–Ar atmosphere. The following equilibrium reaction should be established:



The free energy change of Eq. (1), ΔG_1° , can be related to its equilibrium constant, K_1 :

$$\Delta G_1^\circ = -RT \ln K_1 = -RT \ln \frac{a_{MgO} \cdot a_C}{a_{Mg} \cdot P_{CO}} \dots\dots\dots(2)$$

Where, a is the activity of each component relative to the pure substance, and P_{CO} denotes the partial pressure of CO (atm). Since the activities of MgO and carbon are unity due to the use of a pure MgO crucible and a pure graphite block, Eq. (3) can be simply derived from Eq. (2):

$$K_1 = \frac{1}{a_{Mg} \cdot P_{CO}} = \frac{1}{\gamma_{Mg} \cdot X_{Mg} \cdot P_{CO}} \dots\dots\dots(3)$$

Where, γ_{Mg} and X_{Mg} are the activity coefficient of Mg relative to its pure liquid and the mole fraction of Mg in liquid copper, respectively.

The activity coefficient of Mg in liquid copper has been reported by Sieben and Schmahl,²⁷⁾ Garg *et al.*,²⁸⁾ Juneja *et al.*,²⁹⁾ Hultgren *et al.*³⁰⁾ and Nayeb-Hashemi and Clark.³¹⁾ The literature data on γ_{Mg} are summarized in Fig. 1(A). The agreement of the activity coefficient among literature values at the high concentration range of Mg seems to be excellent. On the other hand, there are some discrepancies in the low concentration range of Mg. Since the accuracy of γ_{Mg} at low concentration range is the most important for the precise determination of ΔG_1° , the present authors³²⁾ have assessed the thermodynamic properties of liquid Cu–Mg alloy with mass spectrometry. Their values are also plotted in Fig. 1(A). It is seen from Fig. 1(A) that the values of $RT \ln \gamma_{Mg}$ evaluated by the authors agree well with the values observed by Garg *et al.* and recommended by Hultgren *et al.* Therefore, the values of $RT \ln \gamma_{Mg}$ given by the authors have been employed in the present work. It has also been reported that the temperature dependence of $RT \ln \gamma_{Mg}$ is very small as shown in Fig. 1(A).³²⁾

Therefore, the value of K_1 can be determined from the equilibrium concentration of Mg in liquid copper, P_{CO} , and temperature. Finally, the free energy change of formation of MgO, $\Delta G_{f, MgO}^\circ$, is obtained by the combination of Eq. (6)

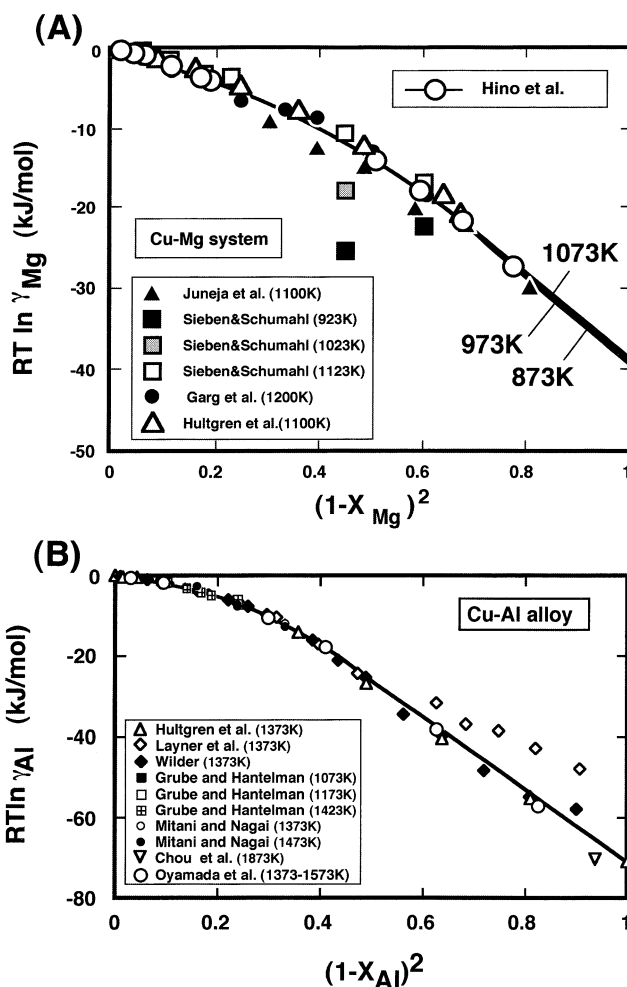


Fig. 1. Activity coefficients of Mg and Al in liquid Cu.

with ΔG_1° :



$$\Delta G_5^\circ = -116\,560 - 84.8T^8 \quad (J/mol) \dots\dots\dots(6)$$

2.2. Free Energy of Formation of MgO·Al₂O₃

The reaction of the stoichiometric spinel formation from the respective pure oxides:



$$\Delta G_{f, MgO \cdot Al_2O_3}^\circ = -RT \ln K_7 = -RT \ln \frac{a_{MgO \cdot Al_2O_3}}{a_{MgO} \cdot a_{Al_2O_3}} \dots\dots\dots(8)$$

If the standard state of the activity of spinel is taken as a stoichiometric composition of spinel, MgO·Al₂O₃, Eq. (9) can be obtained under the presence of pure MgO·Al₂O₃:

$$\Delta G_{f, MgO \cdot Al_2O_3}^\circ = -RT \ln \frac{1}{a_{MgO} \cdot a_{Al_2O_3}} \dots\dots\dots(9)$$

Therefore, if we could determine the activities of MgO and Al₂O₃ in equilibrium with pure MgO·Al₂O₃, K_7 and, thus, $\Delta G_{f, MgO \cdot Al_2O_3}^\circ$ can be determined. For the measurement of $\Delta G_{f, MgO \cdot Al_2O_3}^\circ$, pure stoichiometric MgO·Al₂O₃ was in equilibrium with liquid copper in a graphite crucible under a fixed ratio of CO–Ar gas mixture in the present work.

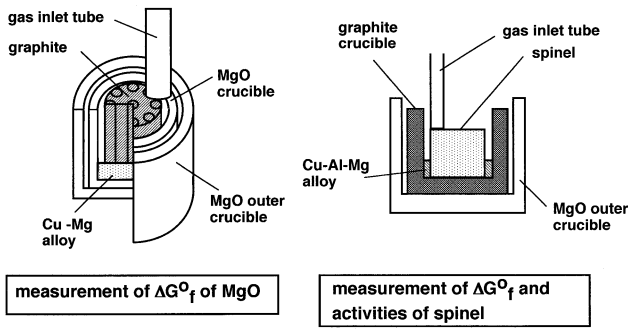
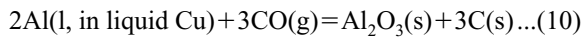


Fig. 2. Schematic diagram of the crucible assemblies for the chemical equilibrium technique.

The equilibrium reaction of Eq. (10) should be also established together with Eq. (1) on such condition:



$$\Delta G_{10}^\circ = -RT \ln K_{10} = -RT \ln \frac{a_{Al_2O_3} \cdot a_C^3}{a_{Al}^2 \cdot P_{CO}^3} \dots (11)$$

Since the activity of carbon is unity because of the use of a graphite crucible, the activity of Al_2O_3 can be expressed by Eq. (12):

$$a_{Al_2O_3} = K_{10} \cdot a_{Al}^2 \cdot P_{CO}^3 = K_{10} \cdot \gamma_{Al}^2 \cdot X_{Al}^2 \cdot P_{CO}^3 \dots (12)$$

Where, γ_{Al} and X_{Al} denote the Raoultian activity coefficient and mole fraction of Al in liquid copper, respectively. The value of K_{10} can be known from the well-established value of ΔG_{10}° in the JANAF thermochemical tables.⁸⁾ The value of γ_{Al} in liquid copper has been accurately determined by the authors³³⁾ as shown in Fig. 1(B). Therefore, the activity of Al_2O_3 in the stoichiometric compound $MgO \cdot Al_2O_3$ can be determined from the equilibrium Al content in liquid copper.

The activity of MgO can also be determined from the following equation and ΔG_1° , which is determined in the present work as mentioned before:

$$a_{MgO} = K_1 \cdot a_{MgO} \cdot P_{CO} \dots (13)$$

Finally, the free energy of Eq. (7) can be determined from Eq. (9) by substituting each activity.

2.3. Activities of the Constituents in Spinel Solid Solution Region

In the measurement of activities of constituents in the spinel phase, spinel solid solution which has a non-stoichiometric composition was in equilibrium with liquid copper in a graphite crucible under a constant gas ratio of CO–Ar. The activities of MgO and Al_2O_3 in the spinel solid solution can be determined from Eqs. (12) and (13) according to the same experimental principle. Then, the activity of stoichiometric spinel in the solid solution can be obtained according to the following equation:

$$a_{MgO \cdot Al_2O_3} = K_7 \cdot a_{MgO} \cdot a_{Al_2O_3} \dots (14)$$

3. Experimental

The experimental apparatus and procedure are essentially the same as described elsewhere.²⁴⁾ A vertical electric resistance furnace with $LaCrO_4$ heating elements was used in

the present work. **Figure 2** shows a schematic diagram of the crucible assembly. For measurements of the free energy of MgO formation, 5 gr of Cu–0.1mass%Mg master alloy was charged in a MgO crucible with a cylindrical graphite block, where 7 or 8 holes were drilled to allow the direct contact of the CO–Ar gas mixture with the surface of the molten copper. In the measurement of free energy of spinel formation and activities of the constituents in the spinel solid solution, 5 gr of Cu–(0.005–0.03mass%)Mg–(0.1–1.1mass%)Al master alloy was charged in a graphite crucible with a tablet-shaped stoichiometric spinel. The appropriate initial Mg and Al contents in the master alloy were selected based on preliminary experiments in order to minimize the amount of Mg and Al transfer between the liquid copper and the spinel. The spinel specimen was made by sintering an equimolar powder mixture of MgO and Al_2O_3 for 24 hr in air at 1 873 K. The formation of spinel was confirmed by X-ray diffraction technique, the wavelength dispersion type Electron Probe Micro-Analyzer (EPMA) and wet chemical analysis. Standard materials for EPMA analysis were high purity MgO and Al_2O_3 polycrystals. The graphite block or spinel tablet was dipped into the molten copper bath by pushing them with a gas inlet nozzle for better contact. After setting the crucible assembly in the hot zone of the resistance furnace which was already at the desired temperature, the reaction tube was sealed and the atmosphere was quickly changed from air to purified Ar. Subsequently, the atmosphere was changed to a CO–Ar stream and the crucible assembly was held for 8 hr to attain equilibrium. The holding time was confirmed in preliminary experiments. After the equilibrium was attained, the crucible assembly was quickly withdrawn from the upper end of the reaction tube by a Mo wire and was quenched by flushing He gas. The copper phase was separated from the crucible and was used in the chemical analysis. The equilibrium contents of Al and Mg in the copper were determined by Induction Coupled Plasma Spectroscopy (ICP). In the experiment for the activity measurements of the constituents in the spinel solid solution at MgO or Al_2O_3 saturation, an excess amount of MgO or Al_2O_3 was added to the predicted compositions of spinel phase boundaries in the published phase diagram.^{14–23)}

Some additional experiments were also conducted to determine exactly the phase boundaries of the spinel phase. The diffusion couple technique was employed for this purpose. A cylinder-shaped Al_2O_3 sample was tightly connected with MgO plate. Each contact surface was previously polished. This diffusion couple was held for 24 hr at 1 700, 1 800, 1 873 and 1 900 K under a purified Ar stream and then was withdrawn from the furnace. This quenched sample was mounted in a mold and was cut in the longitudinal direction. The concentration profile of Mg and Al in the sample was detected by the wavelength dispersion type EPMA. Thickness of spinel layer formed between MgO and Al_2O_3 was found to be from 300 to 500 μm depending on the temperature.

4. Results and Discussion

4.1. Free Energy of Formation of MgO

Experimental results on the free energy of formation of

Table 1. Experimental results on the free energy of MgO formation.

Heat No.	Temp. (K)	P _{CO} (atm)	X _{Mg} in Cu(l)	a _{Mg} in Cu(l)	ΔG ₁ ^o (kJ/mol)
172	1700	0.516	1.22E-04	8.411E-06	-174.52
173	1700	0.367	1.41E-04	9.710E-06	-177.31
174	1700	0.247	2.05E-04	1.407E-05	-177.68
175	1700	0.296	1.28E-04	8.813E-06	-181.74
177	1800	0.984	2.74E-04	2.184E-05	-160.85
178	1600	0.098	3.95E-05	2.293E-06	-203.59
180	1700	0.975	7.23E-05	4.966E-06	-172.97
182	1750	0.990	1.09E-04	8.032E-06	-170.84

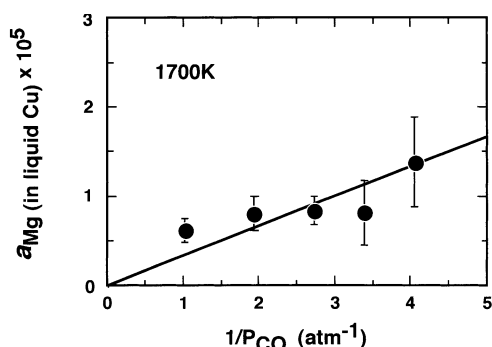


Fig. 3. Variation of the activity of Mg in liquid Cu with the reciprocal of the partial pressure of CO at 1700 K.

MgO are summarized in **Table 1**. **Figure 3** shows the relation between the partial pressure of CO in the atmosphere and the activity of Mg in liquid copper at 1700 K. Error bar of each data point denotes the scattering range of Mg contents in liquid Cu determined by chemical analysis. The activity of Mg was calculated from the concentration of Mg in liquid copper and the activity coefficient of Mg shown in Fig. 1(A). The linear relation passing through the origin can be expected from Eq. (15) which can be obtained by the rearrangement of Eq. (3):

$$a_{Mg} = \frac{1}{K_1 \cdot P_{CO}} \dots\dots\dots(15)$$

Though the scatter in the experimental data is relatively large, there exists an almost linear relation between a_{Mg} and the reciprocal of P_{CO}. Therefore, it can be concluded that the equilibrium among graphite, CO, MgO and liquid copper was established in the present experiment. The slope of a linear line in Fig. 3 corresponds to 1/K₁, and therefore, ΔG₁^o can be derived. Then, Gibbs free energy of Eq. (4), ΔG_{f,MgO}^o, was determined from ΔG₁^o and ΔG_S^o, as a function of temperature.

$$\Delta G_1^o = 552\,790 - 220.0T \quad (\text{J/mol}) \dots\dots\dots(16)$$

$$\Delta G_{f,MgO}^o = -669\,350 + 135.0T \quad (\text{J/mol}) \dots\dots\dots(17)$$

Very similar values have been reported in the literatures^(6-9,24,25) on the entropy term in the free energy of formation of alkaline-earth metal oxide as -100 to -140 kJ/mol·K. It is deduced that there should be a regularity between the entropy term and atomic number of alkaline-

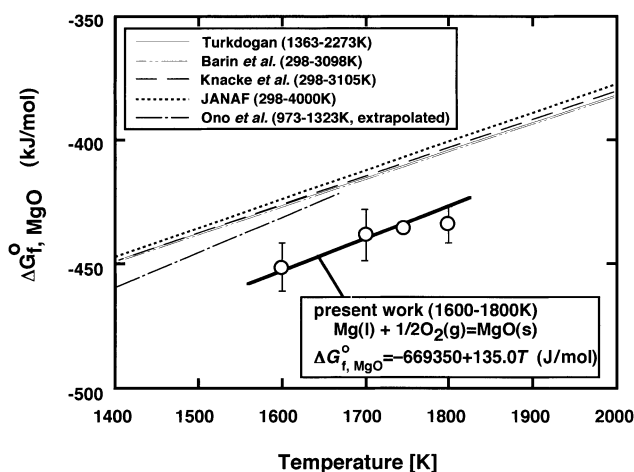


Fig. 4. Gibbs free energy of formation of MgO.

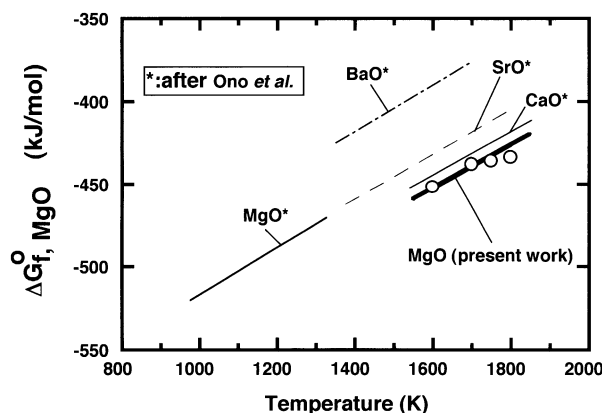


Fig. 5. Comparison of the free energy of formation of alkaline earth metal oxides.

earth metal. According to such considerations, the entropy terms of Eqs. (16) and (17) have been determined in the present work. ΔG_{f,MgO}^o determined in the present work is shown in **Fig. 4** together with other literature values^(6-9,25) for comparison. The present result is approximately 20 to 30 kJ/mol more negative than other free energy data, but the temperature dependence of ΔG_{f,MgO}^o seems to be almost the same as others, especially as the value proposed by Ono *et al.*⁽²⁵⁾ ΔG_{f,MgO}^o determined in the present work is shown in **Fig. 5** with free energies of formation of alkaline-earth metal oxides measured by Ono *et al.*^(25,26) The order of ΔG_f^o of BaO, SrO and CaO by Ono *et al.* and ΔG_{f,MgO}^o by the present work is in consistent with the order of alkaline earth metal in the periodic table as Ba, Sr, Ca and Mg.

4.2. Free Energy of Formation of MgO·Al₂O₃

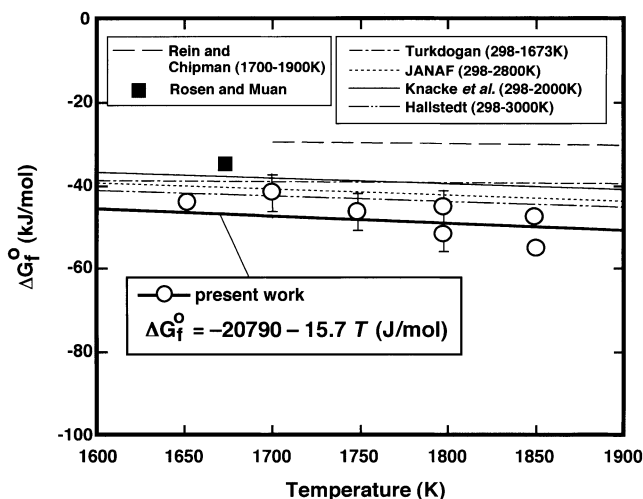
Experimental results on the free energy of formation of MgO·Al₂O₃ are summarized in **Table 2**. The free energy of formation of MgO·Al₂O₃ from each oxide, ΔG_{f,MgO·Al₂O₃}^o, determined in the present work is expressed as a function of temperature as follows:

$$\Delta G_{f,MgO \cdot Al_2O_3}^o = -20\,790 - 15.7T \quad (\text{J/mol}) \dots\dots\dots(18)$$

Figure 6 shows the free energy of formation of stoichiometric MgO·Al₂O₃ from each pure oxide determined in the present work. Error bar in Fig. 6 denotes the uncertain range of each data point which is mainly caused by the

Table 2. Experimental results on the free energy of MgO·Al₂O₃ formation.

Heat No.	Temp. (K)	P _{CO} (atm)	X _{Al} in Cu(l)	X _{Mg} in Cu(l)	a _{Al₂O₃}	a _{MgO}	ΔG _{f, MgO·Al₂O₃} ^o (kJ/mol)
1	1700	0.250	3.40E-03	2.34E-05	0.422	0.124	-41.68
2	1651	0.100	4.50E-03	1.31E-05	0.519	0.079	-43.91
5	1850	0.970	9.50E-03	1.03E-04	0.248	0.111	-55.35
6	1850	0.990	9.80E-03	1.38E-04	0.296	0.154	-47.52
8	1749	0.200	1.42E-02	6.05E-05	0.447	0.092	-46.34
13	1798	0.700	7.10E-03	5.10E-05	0.472	0.105	-44.86
14	1798	0.500	1.13E-02	4.76E-05	0.474	0.070	-50.86


Fig. 6. Gibbs free energy of formation of MgO·Al₂O₃ from MgO and Al₂O₃.

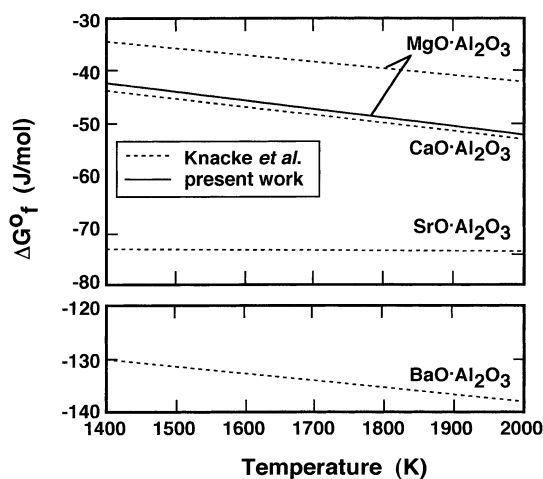
scattering of analytical value of Mg contents in liquid Cu. Since only a very small amount of Al and Mg transferred between the spinel and liquid copper in the present experimental conditions, the composition of spinel was kept constant as stoichiometric MgO·Al₂O₃. This was also confirmed by EPMA after the experiment. **Table 3** and **Fig. 7** show the literature values⁹⁾ on the free energy of formation of spinel structure compounds containing alkaline-earth metal oxide from their oxide components. Very similar values have been reported on the entropy term in each free energy of formation as 13.4 to 16.1 kJ/mol·K except for SrO·Al₂O₃ which has unusual small entropy term as 0.813 kJ/mol·K. By taking into account the entropy terms in ΔG_{f, CaO·Al₂O₃}^o and ΔG_{f, BaO·Al₂O₃}^o, the entropy term in Eq. (18) have been determined as 15.7 kJ/mol·K in the present work.

The literature values^{7-13,23)} are also compared in Fig. 6. Among these free energy values, direct measurement has been conducted by Taylor and Schmalzried,¹⁰⁾ Rein and Chipman,¹¹⁾ Tretjakow and Schmalzried,¹²⁾ Rosen and Muan¹³⁾ and the present work at high temperature. The value of ΔG_{f, MgO·Al₂O₃}^o determined in the present work is approximately 5 to 20 kJ/mol lower than the other literature data.

Rein and Chipman¹¹⁾ measured the activity of SiO₂ in a SiO₂-Al₂O₃-MgO slag by the distribution of Si between the slag and liquid iron. They determined ΔG_{f, MgO·Al₂O₃}^o from the activities of MgO and Al₂O₃ which were estimated from the activity of SiO₂ by Gibbs-Duhem integration and the liquidus line of spinel in the SiO₂-Al₂O₃-MgO slag. Their free energy is 10 to 20 kJ/mol higher than that of other researchers. Generally, accuracy of the activity is not high enough when it is determined by the Gibbs-Duhem integra-

Table 3. Gibbs free energies of formation of some spinel structure compounds from alkaline-earth metal oxide and Al₂O₃.

MO(s) + Al ₂ O ₃ (s) = MgO·Al ₂ O ₃ (s) (M: Mg, Ca, Sr, Ba)	ΔG _f ^o (J/mol)	Ref.
MgO·Al ₂ O ₃	-15734-13.42T	9)
	-20790-15.7T	present work
CaO·Al ₂ O ₃	-21324-16.04T	9)
SrO·Al ₂ O ₃	-72015-0.813T	9)
BaO·Al ₂ O ₃	-110860-13.59T	9)


Fig. 7. Gibbs free energies of formation of MO·Al₂O₃ (M=Mg, Ca, Sr, Ba) spinel structure compounds from MO and Al₂O₃.

tion from one component in a ternary system. This may be a reason of their higher value of the free energy. Taylor and Schmalzried¹⁰⁾ and Tretjakow and Schmalzried¹²⁾ determined the free energy by EMF measurement using an oxygen solid electrolyte. Tretjakow and Schmalzried reported the value of ΔG_{f, MgO·Al₂O₃}^o at 1273 K as -35.1 kJ/mol which is approximately 5.7 kJ higher than the extrapolated value of Eq. (18), while Taylor and Schmalzried obtained -10 kJ/mol at 803 K which is much higher than the extrapolated value of Eq. (18) to 803 K (-33.4 kJ). The result by Rosen and Muan¹³⁾ with the chemical equilibrium technique is plotted in Fig. 6. Their value is approximately 10 kJ/mol higher than the present work.

4.3. Phase Boundary of Spinel Solid Solution

It is known that MgO·Al₂O₃ has a relatively wide solid solution range at high temperature. **Table 4** and **Figure 8** are the experimental results on the phase boundary lines of the spinel solid solution determined in the present work by the diffusion-couple technique. A homogeneous solid solution range of spinel was found from 48.4 to 57.5 mol% Al₂O₃ at 1700 K and from 46.5 to 64.2 mol% Al₂O₃ at 1900 K, respectively. Some experimental results are avail-

able in the literature¹⁴⁻²³⁾ on the phase diagram of the MgO–Al₂O₃ system. The solvus of the spinel with MgO observed in the present work was in good agreement with the predicted by Hallstedt.²³⁾ The Al₂O₃ content at the solvus of the spinel phase with Al₂O₃ in the present work was observed to be in good accord with that reported by Lejus.¹⁷⁾

It was also found that the solubility of spinel in MgO was less than 1 mol% and that in Al₂O₃ was negligibly small from 1700 to 1900 K. These findings are in good agreement with the literature^{16,18,20,22,23)} and it means that spinel can be in equilibrium with almost pure MgO and Al₂O₃ at steelmaking temperatures.

4.4. Activities of Constituents in Spinel Solid Solution

The activities of MgO and Al₂O₃ measured in the entire composition range of the spinel solid solution at 1800 and 1873 K are represented in Table 5 and Fig. 9. The activities

of MgO and Al₂O₃ at each saturation limit have been reasonably obtained as close to unity. The activity of spinel with respect to the stoichiometric MgO·Al₂O₃ in solid solution was calculated from the activities of MgO and Al₂O₃ and $\Delta G_{f, MgO \cdot Al_2O_3}^0$ (Fig. 10). Fine solid line in Fig. 10 denotes the activity of MgO·Al₂O₃ calculated from Eqs. (19) and (20), where MgO–MgO·Al₂O₃ and MgO·Al₂O₃–Al₂O₃ pseudo-binaries are assumed as ideal solutions.

$$a_{MgO \cdot Al_2O_3} = \frac{X_{Al_2O_3}}{1 - X_{Al_2O_3}} (MgO - MgO \cdot Al_2O_3) \dots\dots\dots(19)$$

$$a_{MgO \cdot Al_2O_3} = \frac{1 - X_{Al_2O_3}}{X_{Al_2O_3}} (MgO \cdot Al_2O_3 - Al_2O_3) \dots\dots\dots(20)$$

Stoichiometric MgO·Al₂O₃ calculated exhibits a negative deviation from ideality in the spinel solid solution. The activities of MgO·Al₂O₃ at MgO and Al₂O₃ saturation are

Table 4. Phase boundaries of spinel solid solution saturated with MgO and Al₂O₃.

Temp. (K)	at%Al ₂ O ₃ at MgO sat.	at%Al ₂ O ₃ at Al ₂ O ₃ sat.
1700	48.4	57.5
1800	47.3	61.1
1873	47.5	62.3
1900	46.5	64.2

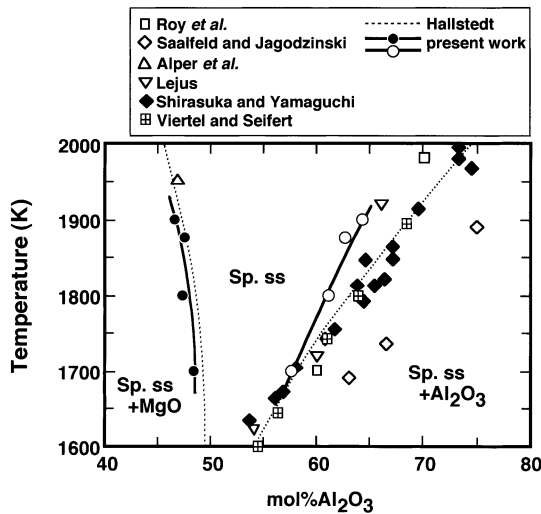


Fig. 8. Phase boundaries of spinel with MgO and Al₂O₃.

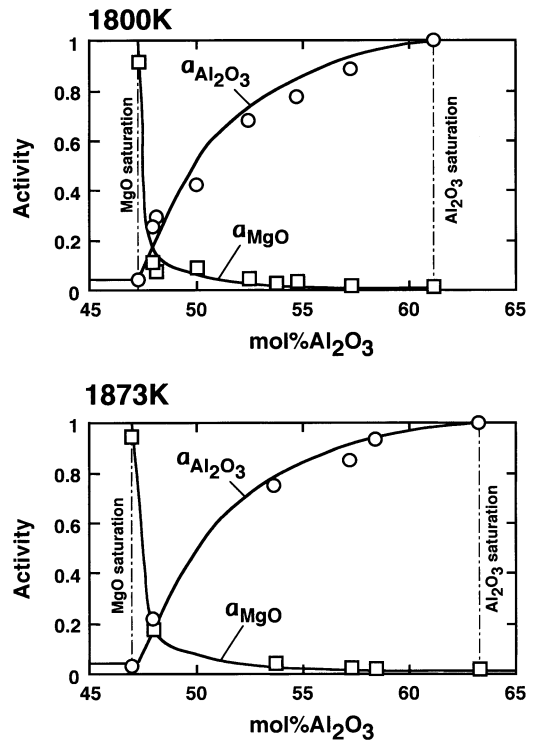


Fig. 9. Activities of MgO and Al₂O₃ in the spinel solid solution at 1800 and 1873 K.

Table 5. Experimental results on the activities of constituents in the spinel solid solution.

Heat No.	Temp. (K)	P _{CO} (atm)	liquid Cu phase		spinel phase			
			X _{Al}	X _{Mg}	X _{Al₂O₃}	a _{Al₂O₃}	a _{MgO}	a _{MgO·Al₂O₃}
SP-3*	1800	0.811	0.0016	3.99E-04	47.300	0.032	0.917	0.781
SP-2	1801	0.383	0.0131	1.03E-04	48.000	0.257	0.109	0.745
SP-7	1801	0.398	0.0132	6.90E-05	48.100	0.293	0.076	0.592
SP-8	1802	0.516	0.0111	6.50E-05	50.000	0.416	0.091	1.006
SP-16	1798	0.499	0.0134	3.55E-05	52.500	0.682	0.052	0.942
SP-10	1799	0.503	0.0144	2.75E-05	54.800	0.786	0.040	0.832
SP-9	1801	0.340	0.0258	2.45E-05	57.300	0.884	0.023	0.541
SP-6**	1800	0.287	0.0327	2.34E-05	61.100	1.020	0.019	0.513
SP-22*	1873	0.993	0.0056	1.29E-03	47.000	0.034	0.954	0.810
SP-24	1874	0.986	0.0136	2.52E-04	47.900	0.218	0.181	0.989
SP-28	1871	0.988	0.0220	6.34E-05	53.800	0.754	0.048	0.910
SP-26	1874	0.986	0.0244	4.77E-05	57.300	0.852	0.034	0.731
SP-25	1875	0.992	0.0256	4.10E-05	58.500	0.937	0.029	0.682
SP-27**	1873	0.990	0.0254	2.57E-05	63.400	0.991	0.019	0.468

* : MgO saturation ** : Al₂O₃ saturation

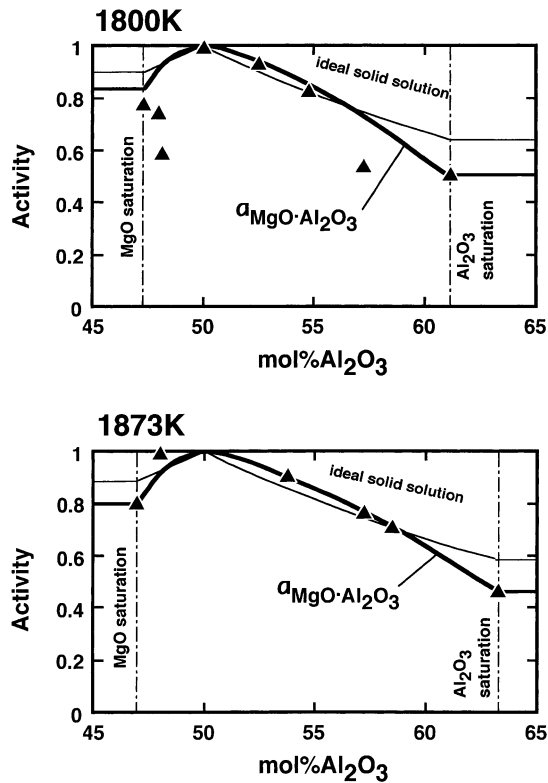


Fig. 10. Activity of $\text{MgO} \cdot \text{Al}_2\text{O}_3$, of which standard state is the stoichiometric compound, in the spinel solid solution at 1 800 and 1 873 K.

evaluated at 1 873 K as 0.8 and 0.47, respectively.

4.5. Assessment of the Stability Diagram of Spinel Formation in Liquid Steel

Itoh *et al.*^{4,5)} evaluated the stable formation region of spinel inclusions in liquid steel by assuming an ideal solid solution behavior of spinel. However, stoichiometric $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel exhibits a negative deviation from ideality, and solubility limits of MgO and Al_2O_3 in the spinel slightly differ from the reported phase diagrams as shown in the former section. Therefore, the stability diagram of spinel formation in liquid steel has been assessed based on the activities of constituents and the free energy of formation of spinel evaluated in the present work. The details for the calculation is described in Refs.^{4,5)} The thermodynamic interaction parameters between dissolved elements in liquid steel used for the present calculation are the same with those used by Itoh *et al.*¹⁻⁵⁾ Figure 11 shows the phase stability diagram of MgO, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 inclusion formation in Ca-free liquid steel at 1 873 K. The lower activity of spinel at saturation limits with MgO and Al_2O_3 and negative free energy of spinel formation make the spinel inclusion region wider than that predicted by Itoh *et al.*, who assumed an ideal behavior of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ in spinel solid solution region. The assessed phase boundary lines in the present work agree with the experimental results,^{4,5,34,35)} and therefore the present assessment on the stability diagram of spinel inclusion formation seems to be more accurate than Itoh *et al.*'s evaluation.

Investigator	Crucible	Deoxidizer	Formed oxide phase		
			$\text{MgO} \cdot \text{Al}_2\text{O}_3$	MgO	Al_2O_3
Itoh, Hino and Ban-ya	MgO	Al	●	○	⊙
	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	Al	▲	△	△
	Al_2O_3	Mg	◆	◇	
Matsuno et al.	$\text{MgO} \cdot \text{Al}_2\text{O}_3$	Al	■		

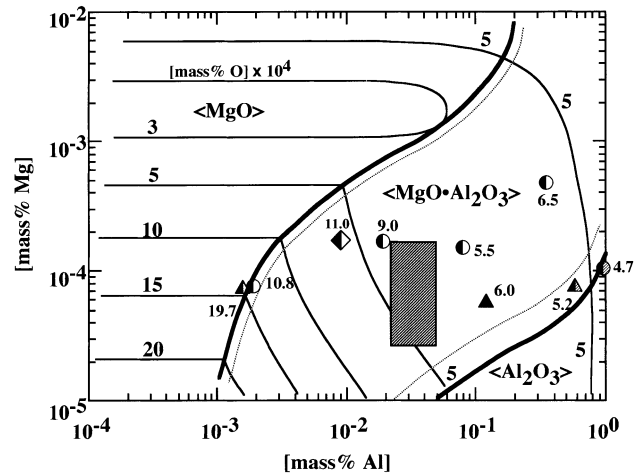
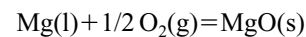


Fig. 11. Phase stability diagram of MgO, $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 inclusion formation in Ca-free liquid steel assessed at 1 873 K based on the present experimental results. Bold solid lines are evaluated in the present work. Fine solid and dotted lines and plots are after Itoh *et al.* Numerical values are the oxygen content in liquid iron.

5. Conclusion

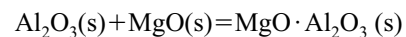
The free energies of formation of MgO and $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and the activities of constituents in spinel solid solution have been determined by the chemical equilibrium technique at 1 800 K and 1 873 K. The following conclusions are obtained:

(1) The free energy of formation of MgO is given by the following equation:



$$\Delta G_{f, \text{MgO}}^\circ = -669\,350 + 135.0T \quad (\text{J/mol})$$

(2) The free energy of formation of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ from MgO and Al_2O_3 is given by the following equation:



$$\Delta G_{f, \text{MgO} \cdot \text{Al}_2\text{O}_3}^\circ = -20\,790 - 15.7T \quad (\text{J/mol})$$

(3) Phase boundary lines of the spinel solid solution saturated with MgO and Al_2O_3 were determined by the diffusion-couple method. There is a negligibly small solubility of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ in MgO and Al_2O_3 at steelmaking temperatures.

(4) $\text{MgO} \cdot \text{Al}_2\text{O}_3$ exhibits negative deviation from ideality in the spinel solid solution region. The activities of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ at MgO and Al_2O_3 saturations at 1 873 K (mol% Al_2O_3 are 47.5 and 62.3) are 0.8 and 0.47, respectively.

(5) The phase stability diagram of spinel formation in liquid steel is assessed based on the present experimental results. The stable formation region of spinel in liquid steel is slightly wider than that predicted by Itoh *et al.* who as-

sumed an ideal behavior of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ in spinel solid solution.

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