Thermodynamic behavior of TiO_2 in $CaO-Al_2O_3-MgO-TiO_2$ slag at high temperatures

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ABSTRACT

High-Cr and Ti-bearing ferritic stainless steel (FSS) has superior corrosion resistance compared to other steels. The Ti-bearing FSS requires not only high corrosion resistance and formability, but also high cleanliness of the cold rolled sheet. Specifically, the cleanliness of Ti-bearing FSS has been improved through the vacuum oxygen decarburization (VOD) and the ladle treatment (LT) processes. Nevertheless, there are still unsolved problems such as large fluctuations in Ti yield due to various factors including Al deoxidation practice and slag-metal reactions after Ti alloying. The activity of TiO_2 in the CaO-Al_2O_3–based slag must be measured to determine the equilibrium of the reaction between Ti and O in the molten steel and TiO_2 in the slag. Moreover, in continuous casting tundish, the internal cleanliness of molten steel is significantly affected by the reoxidation due to the reaction with the atmosphere as well as tundish flux and insulation cover powder. Therefore, the present study aims to provide a systematic understanding the reaction between Ti-bearing FSS melt and the slag, and to investigate the thermodynamic behavior of TiO_2 in the CaO-Al_2O_3-MgO-TiO_2 slag.

INTRODUCTION

In the vacuum oxygen decarburization (VOD) and the ladle treatment (LT) processes, a systematic understanding the slag-metal reaction is required to control the Ti yield and cleanliness of high-Cr and Ti-bearing FSS melt. Therefore, it is important to investigate the thermodynamic behavior of TiO_2 in the CaO-Al_2O_3–based slag.

Several studies have been performed to investigate the activity coefficient of TiO_2 in the slag. Park et al. (2008) reported the thermodynamic behavior of TiO_2 in the CaO-SiO_2-Al_2O_3–based slag in equilibrium with Fe-11%Cr melt using MgO crucible. The activity coefficient of TiO_2 decreases with increasing basicity when the modified basicity (=(%CaO+%MgO)/(%SiO_2)) was above 0.7. Sun et al. (2018) reported the activity coefficient of TiO_2 in the CaO-SiO_2-Al_2O_3–based slag in equilibrium with C-saturated molten iron. The activity coefficient of TiO_2 decreases with increasing basicity (=(%CaO)/(%SiO_2)) from 1.0 to 1.3.

However, because there are few experimental data for the thermodynamic behavior of TiO_2 in the CaO-Al_2O_3–based slags, the activity of TiO_2 in the CaO-Al_2O_3-MgO-TiO_2 slag in equilibrium with molten silver as well as molten Fe-Cr melts was measured at 1823 K using MgO crucible.

EXPERIMENTAL PROCEDURE

A super-kanthal electric resistance furnace, shown in FIG 1 was used for equilibrium experiments between slag and metal at 1823 K. The temperature was controlled within ±2K using a B-type thermocouple. The slag samples were prepared using reagent grade Al_2O_3, MgO, TiO_2 and CaO calcined from $CaCO_3$ at 1273 K.

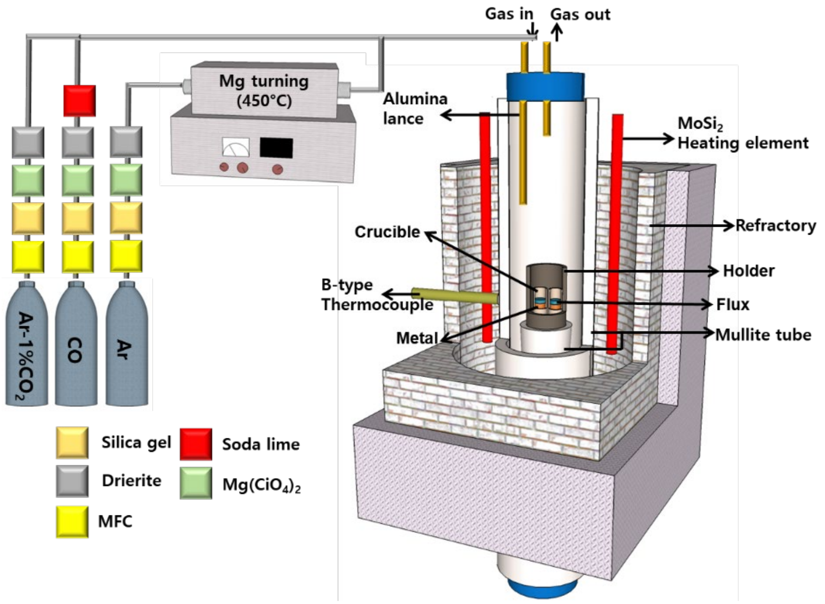
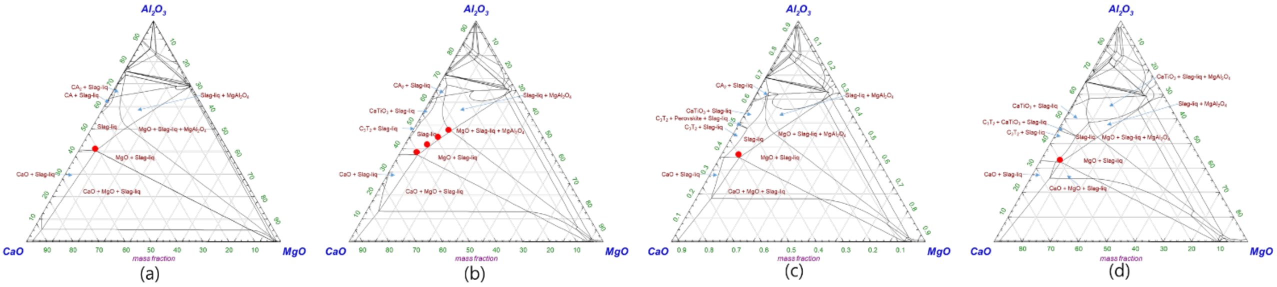


FIG 1 – Schematic diagram of the experimental apparatus.

In order to perform the equilibrium experiment between pure silver and Ti_3O_5 phase, Ti_3O_5 pellet was prepared by inserting TiO_2 pellet in a graphite crucible at 1573 K under CO atmosphere for 4 days in a vertical tube furnace (FIG 1) based on the Ti-O phase diagram (Kang and Lee, 2005).

First experiments were performed with 0.3g Ti_3O_5 pellet and 10g pure silver to measure the Henrian activity coefficient of Ti in silver using Al_2O_3 crucible. The equilibration time was 24 hrs under $p_{O_2} = 10^{-13} atm$ using CO and Ar-1%CO_2 gas mixture.

Second experiments were performed with 3g slag and 5g pure silver to measure the activity coefficient of TiO_2 in the CaO-Al_2O_3-MgO-TiO_2 slag using a graphite crucible under CO atmosphere $(p_{O_2} = 10^{-16} atm)$ at 1823 K. The compositions of slags are shown in FIG 2.



(a) (b) (c) (d)

FIG 2 – Composition of slags in different TiO_2 content, (a) 2wt%, (b) 5wt%, (c) 7wt%, and (d) 10wt% in the CaO-Al_2O_3-MgO-TiO_2 system for the silver-slag equilibrium experiments at 1823 K.

After equilibrium, all samples were quenched by Ar flushing and water. The components in the slags and silver samples were determined using the ICP-AES (ACROS II, Spectro). The N/O combustion analyser (ONH-p, ELTRA Co.) was used to determine oxygen content in metal samples. The ionic speciation of titanium oxide in the slag was confirmed by employing an XPS (Nexsa G2 Co.) analysis with quenched slag samples.

RESULTS AND DISCUSSION

In Ag-Ti_3O_5 equilibrium experiment, Ti_3O_5 pellet was in equilibrium with [Ti] and [O] in pure silver by Eq. [1]. Henrian activity coefficient of Ti in silver can be calculated by Eq. [2]. The oxygen partial pressure $(p_{O_2} = 10^{-13} atm)$ at 1823 K was set by controlling CO and Ar-1%CO_2 gas flow rate according to Eqs. [3] and [4] (Stull, 1965; Turkdogan, 1980).

$$Ti_3O_{5(s)} = 3Ti_{(s)} + \frac{5}{2}O_{2(g)}, \quad \Delta G^{\circ}_{[1]} = 2435{,}100 - 420.5\,T\ (J/mol) \qquad [1]$$

$$K_{[1]} = \frac{(\gamma^{\circ}_{Ti(Ag)} \cdot X_{Ti(Ag)})^3 \cdot p_{O_2}^{5/2}}{a_{Ti_3O_5}(=1.0)} \qquad [2]$$

$$CO_{(g)} + \frac{1}{2}O_{2(g)} = CO_{2(g)}, \quad \Delta G^{\circ}_{[2]} = -281{,}900 - 87.3\,T\ (J/mol) \qquad [3]$$

$$K_{[3]} = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{1/2}} \qquad [4]$$

FIG 3 shows the temperature dependency of the Henrian activity coefficient of Ti in molten silver and the linearly fitted data are given in Eq. [5].

$$\ln \gamma^{\circ}_{Ti(Ag)} = -\frac{91{,}180(\pm 230)}{T} + 48.1(\pm 0.1) \qquad [5]$$

From XPS spectra for Ti 2p shown in FIG 4, it was confirmed that the oxidation state of Ti was Ti^{4+} in the present CaO-Al_2O_3-MgO-TiO_2 slag system from the observation of Ti^{4+} peaks (458.5 eV) in TABLE 1 (Rotole et al., 2001; Yang and Park, 2017; Cho et al., 2021).

In Ag-slag equilibrium experiment, the activity of TiO_2 in the slag can be calculated by Eqs. [6] and [7] using Henrian activity coefficient of Ti in molten silver given in Eq [5]. The oxygen partial pressure ($p_{O_2} = 10^{-16} atm$) at 1823 K was controlled by Eqs. [8] and [9] (Stull, 1965; Turkdogan, 1980).

$$TiO_{2(s)} = Ti_{(s)} + O_{2(g)}, \quad \Delta G^{\circ}_{[6]} = 941{,}000 - 177.6\,T\ (J/mol) \qquad [6]$$

$$K_{[6]} = \frac{\overset{\circ}{\gamma}_{Ti(Ag)} \cdot X_{Ti} \cdot p_{O_2}}{\gamma_{TiO_2} \cdot X_{TiO_2}} \qquad [7]$$

$$C_{(s)} + \frac{1}{2} O_{2(g)} = CO_{(g)}, \quad \Delta G^{\circ}_{[8]} = -112{,}900 - 86.5\,T\ (J/mol) \qquad [8]$$

$$K_{[8]} = \frac{p_{CO}}{a_C \cdot p_{O_2}^{1/2}} \qquad [9]$$

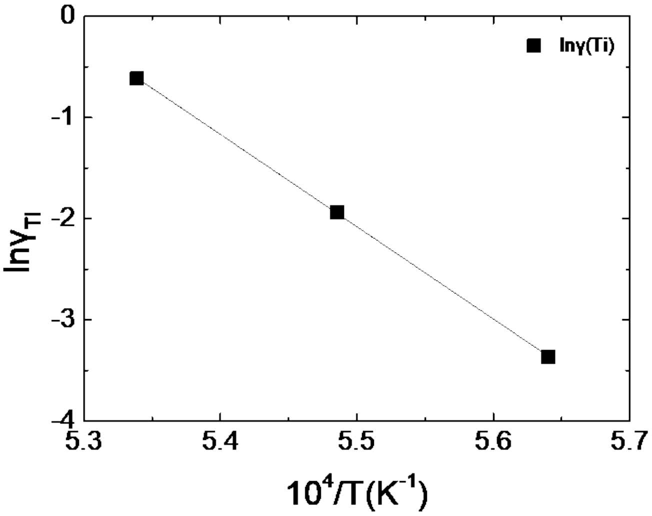
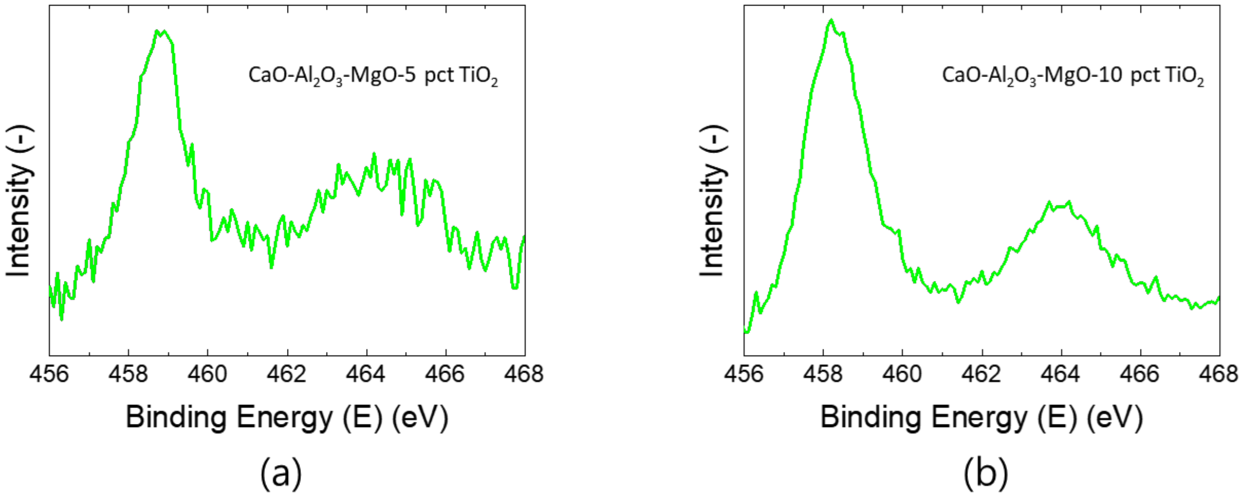


FIG 3 – Dependence of logarithmic form of the activity coefficient of Ti in silver on the reciprocal temperature.



(a) (b)

FIG 4 – X-ray photoelectron spectroscopy spectra of quenched slag samples with different content of titanium oxide; (a) 5 wt% and (b) 10 wt%.

TABLE 1 – Binding energy of titanium oxides at different valances.

	Ti^{2+}	**Ti^{3+}**	**Ti^{4+}**
Binding Energy	455.0 eV	457.0 eV	458.5 eV

The activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-5\%TiO_2$ slag decreases with increasing slag basicity (=%CaO/%Al_2O_3) shown in FIG 5(a), and FactSage calculation shows similar tendency (but less sensitive) to the present work. The activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-TiO_2$ slag close to the CaO-MgO double saturation condition sharply decreases with increasing TiO_2 content as shown in FIG 5(b), while the calculated result from FactSage software exhibits nearly constant value irrespective of TiO_2 content.

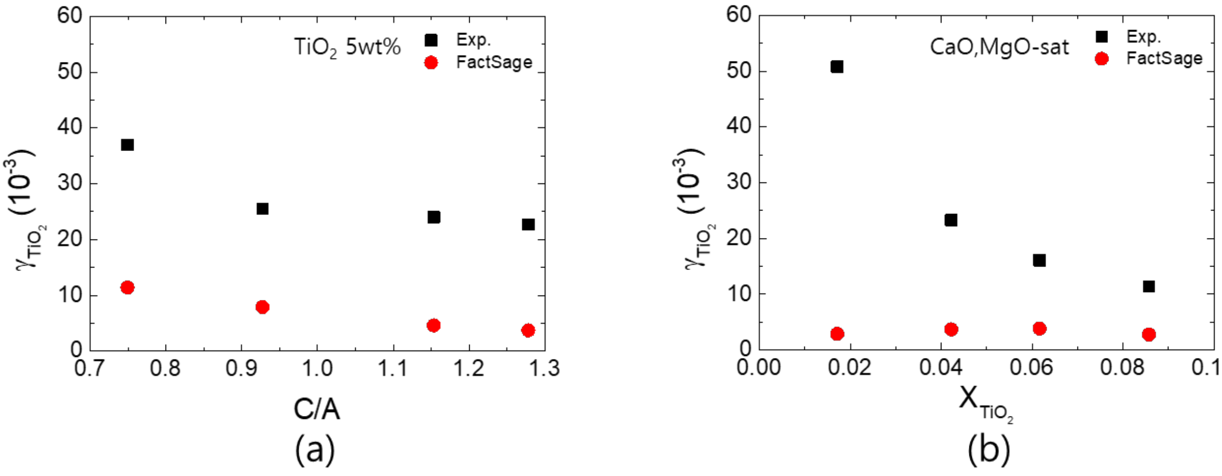


FIG 5 – Effect of (a) basicity and (b) TiO_2 content on the activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-TiO_2$ slag measured in the present study, and comparison with the values calculated by FactSage (ver.8.2).

CONCLUSIONS

The activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-TiO_2$ slag was measured and compared with FactSage calculations at 1823K. The major findings of present study can be summarized as follows.

1. The Henrian activity coefficient of Ti in silver ($\overset{\circ}{\gamma}_{Ti(Ag)}$) can be expressed as a function of the reciprocal temperature.

2. It was found that Ti was stabilized as TiO_2 (Ti^{4+}) in the present slag system, which was confirmed by XPS analysis.

3. The activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-5\%TiO_2$ system decreases with increasing C/A ratio at C/A>0.7 and FactSage shows similar tendency. Especially, there is a little change in activity of TiO_2 in the range of C/A ratio greater than 0.9.

4. The activity coefficient of TiO_2 in the $CaO-Al_2O_3-MgO-TiO_2$ system close to the CaO-MgO double saturation condition sharply decreases with increasing TiO_2 content, while calculated result from FactSage software exhibits nearly constant value irrespective of TiO_2 content.

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