

Effect of slag composition on titanium distribution ratio between ferrosilicon melt and CaO-SiO₂-Al₂O₃ slag at 1773 K

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ABSTRACT

Because the environmental problems are occurred by greenhouse gases such as CO₂, the industries have tried to increase electric motor efficiency to reduce CO₂ emissions. A core material of electric motor is high-silicon electrical steel. The ferrosilicon (FeSi) alloy, a raw material for the production of electrical steel, affects the electric properties of silicon steel. The main impurities such as Ca, Al, and Ti make inclusions or precipitates that causes core loss. The slag treatment has been widely used to remove impurity elements. Thermodynamic principles for the refining of several impurities, specifically Ca and Al, have been investigated, whereas thermodynamic behaviour of Ti has not been fully understood yet. Therefore, in the present study, the titanium distribution ratio (L_{Ti}) between ferrosilicon and CaO-SiO₂-Al₂O₃ slag system at 1773 K was investigated.

The results show that L_{Ti} is influenced by both the basicity and stability of titanium ion in the slag. Specifically, L_{Ti} exhibits a minimum value at about C/S=0.7 indicating a shift in the titanate structure unit from [TiO₅]-square pyramid to [TiO₄]-tetrahedron because of lack of Ca²⁺ ions in a C/S<0.8 region, contributing to an increase in titanate capacity and L_{Ti} .

INTRODUCTION

The electric vehicle market is growing quickly, and study of electric motor efficiency is in progress to reduce CO₂ emission and air pollutants. The raw material for production of high-silicon electrical steel, i.e., ferrosilicon (FeSi) alloy, affects the electric properties of silicon steel. The common impurities of Ca, Al, Ti, C, and B form inclusions or precipitates that result in core loss by decreasing grain size (Nakayama and Tanaka, 1997; Nakayama and Honjou, 2000; Steiner Petrovič et al., 2010). These impurities in electrical steel are generally originated from FeSi alloy which have an adverse effect on the magnetic properties. Unfortunately, Ti equilibrium distribution data between silicon and slag are very limited. Moreover, the thermodynamics of the Ti distribution behavior between FeSi melt and CaO-based slags has not been investigated. Therefore, in the present study, we measured the Ti distribution ratio between FeSi melt and the CaO-SiO₂-Al₂O₃ slag at 1773 K. Additionally, a structural analysis using Raman spectroscopy was performed to understand the stabilization mechanism of titanium in aluminosilicate melts.

EXPERIMENTAL PROCEDURE

The slag-metal equilibrium experiments were performed using an electric resistance furnace with a MoSi₂ heating element. A schematic diagram of the experimental apparatus is shown in FIG 1. The temperature was controlled within ± 2 K. A mixture of 5g commercial low-carbon FeSi alloy (0.013 wt% Ti) and 3g slag were loaded in a graphite crucible placed in an alumina porous holder at 1773 K. The furnace was filled with purified Ar gas controlled by a mass flow controller at a flow rate 500 ml/min. After the equilibration for 24 hours, the sample was extracted from the furnace and quenched in water. The compositions of metal and slag samples were determined by XRF and ICP-OES.

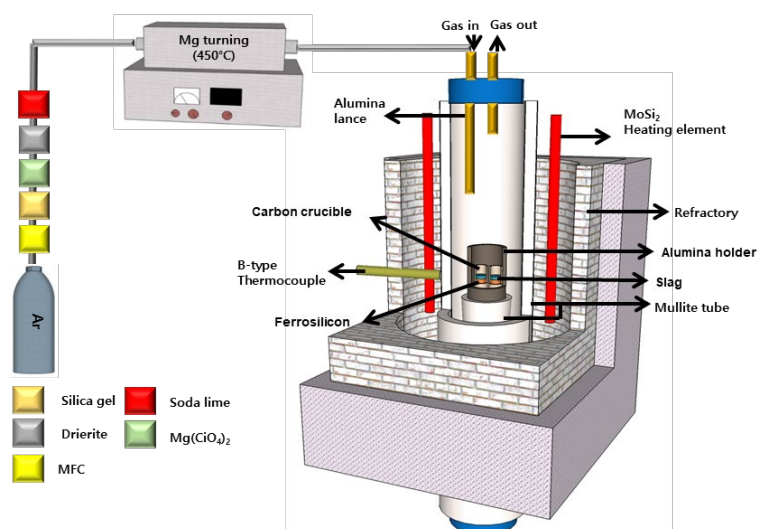


FIG 1. Schematic diagram of the experimental apparatus.

RESULTS AND DISCUSSION

- Influence of basicity on Ti distribution ratio between FeSi melt and CaO-SiO₂-Al₂O₃ slag

The distribution ratio of Ti (L_{Ti}) between FeSi and slags at 1773 K as a function of CaO/SiO₂ (=C/S) ratio is depicted in FIG 2. The distribution ratio of Ti is defined by the following equation.

$$L_{Ti} = \frac{(\text{wt}\% \text{TiO}_2)_{\text{slag}}}{[\text{wt}\% \text{Ti}]_{\text{metal}}} \quad (1)$$

As shown in FIG 2, the V-shaped Ti distribution behavior is observed in entire slags. In the 20% Al₂O₃ system, the distribution ratio of Ti in a logarithmic scale is consistently greater than zero, i.e., $L_{Ti} > 1.0$, except for the C/S=0.8 system. This result suggests that the distribution ratio of Ti is significantly affected by the C/S ratio and Al₂O₃ content.

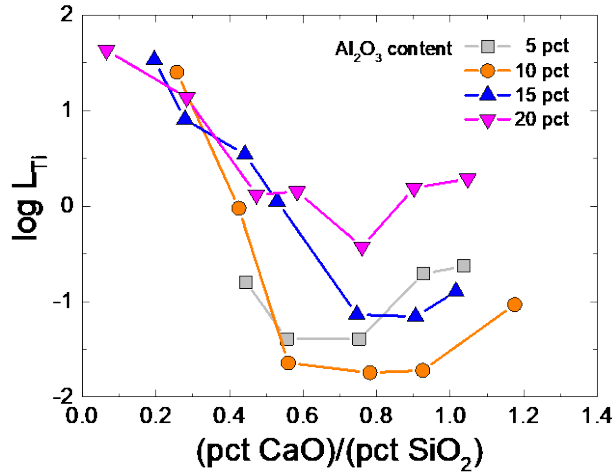


FIG 2. Distribution ratio of Ti between CaO-SiO₂-Al₂O₃ slags and FeSi melts at 1773 K.

- Effect of basicity and Al₂O₃ on titanate capacity and stability of titanium in slag

In the present study, it was assumed that the valence state of titanium is 4, i.e., Ti⁴⁺ is preferentially stable and the coordination number of titanium with oxygen is 5, i.e., [TiO₅] square-based pyramid structure mainly exists in the present CaO-SiO₂-Al₂O₃ system (Romano et al., 2000; Le Cornec et al., 2021). Based on this assumption, the titanium refining reaction and titanate capacity of molten slag are represented as given in Eqs. (2) and (3), respectively. Here, the titanate capacity is the ability of a slag to absorb titanium as a function of slag basicity, stability of titanate ion in the slag, and temperature. To our knowledge, few study have reported titanate capacity, C_{TiO_x} , of molten slag. Hence, in the present study, we propose the application of titanate capacity to understand the thermodynamic behavior of titanium oxide in the slag.



$$C_{\text{TiO}_5^{6-}} = \frac{K_{(2)} \cdot a_{\text{O}_2}^3}{f_{\text{TiO}_5^{6-}}} = \frac{(\text{wt}\% \text{TiO}_5^{6-})}{f_{\text{Ti}}[\text{wt}\% \text{Ti}] \cdot p_{\text{O}_2}} = \frac{L_{\text{Ti}}}{f_{\text{Ti}} p_{\text{O}_2}} \quad (3)$$

where $K_{(2)}$ is the equilibrium constant of Eq. (2), a_{O_2} and f_{Ti} represent the activity of free oxygen ion in slag and the Henrian activity coefficient of titanium in FeSi melt, respectively. In the present study, f_{Ti} was assumed to be unity because the concentration of Ti in FeSi melt is not more than 0.4 wt%. Here, $f_{\text{TiO}_5^{6-}}$ is the activity coefficient of titanate ion in slag, and p_{O_2} is the oxygen partial pressure, calculated from the following equilibrium (Turkdogan, 1980).



$$\Delta G_{[4]}^0 = -907,130 + 175.7 T \text{ (J/mol)} \quad (5)$$

On the other hand, it is suggested that CaO behaves as a basic oxide by contributing free oxygen ion in the slag as shown below (Sano, 1997).



$$a_{O^{2-}} = \frac{K_{(6)} \cdot a_{CaO}}{a_{Ca^{2+}}} \quad (7)$$

Therefore, the titanate capacity is a function of the basicity ($a_{O^{2-}}$) and the stability of titanate ion ($f_{TiO_5^{6-}}$) at fixed temperature and it can be calculated using L_{Ti} and p_{O_2} . The activity of CaO in the slag system at 1773 K was calculated using Factsage software. By combining Eqs. (3) and (7), the relationship between CaO activity and titanate capacity can be described as follows:

$$\log C_{TiO_5^{6-}} = 3 \log a_{CaO} - 3 \log a_{Ca^{2+}} - \log f_{TiO_5^{6-}} + Const. \quad (8)$$

Based on Eq. (8), the titanate capacity is expected to exhibit a linear relationship with the activity of CaO by assuming that $a_{Ca^{2+}}$ and $f_{TiO_5^{6-}}$ terms are not significantly affected by slag compositions. As shown in FIG 3, the titanate capacity linearly increases with increasing activity of CaO in a logarithmic scale at $\log a_{CaO} > -2.2$, indicating that titanium oxide primarily acts as an acidic component in the relatively basic slag. The fitted lines have slopes of 2.7~3.0, indicating that $a_{Ca^{2+}}$ and $f_{TiO_5^{6-}}$ terms would be constant with increasing CaO activity. Therefore, in the basic slag system (i.e., $\log a_{CaO} > -2.2$), it is confirmed that titanate ion forms $[TiO_5]$ -square pyramid based on Eq. (2).

However, in the acidic slag system ($\log a_{CaO} < -2.3$), the titanate capacity increases with decreasing activity of CaO, suggesting that Ti dissolution reaction given in Eq. (2) does not simply applicable in the relatively acidic region. Under the same activity of CaO condition, titanate capacity varies with Al_2O_3 content. This also implies that the Al_2O_3 concentration influences the $f_{TiO_5^{6-}}$ term in the slag. Overall, the titanate capacity of the slag is significantly influenced by the activity of CaO and Al_2O_3 under the experimental conditions.

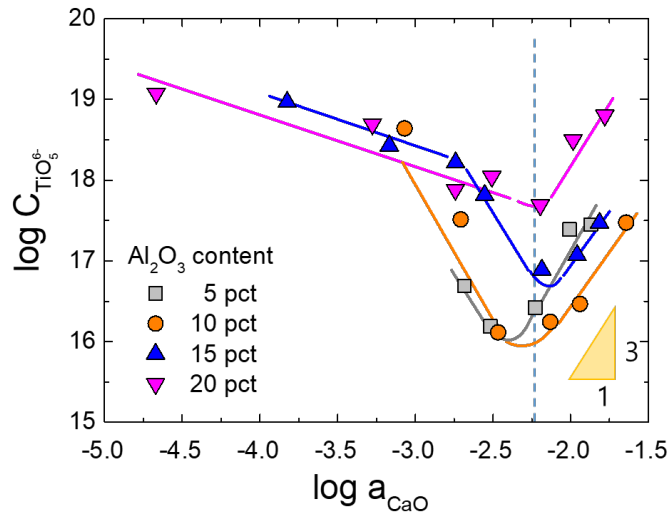


FIG 3. Titanate capacity as a function of activity of CaO in the CaO-SiO₂-Al₂O₃ slags at 1773 K.

- Effect of aluminosilicate structure on titanate stability

From the literature, titanium ion in aluminosilicate glasses have been studied and found that it is mainly Ti⁴⁺ and has five-fold coordination by Ti K-edge XAFS and thermodynamic analysis (Romano et al., 2000; Le Cornec et al., 2021). The five-coordinated Ti incorporated into the silicate framework through the Ti–O–Si bonds including the non-bonding oxygen of the short Ti=O titanyl bond requires a local charge compensation by Ca²⁺ ion. A distribution of titanium coordination region in the CaO-SiO₂-Al₂O₃ system is illustrated in FIG 4. The four-fold coordinated Al, i.e., $[AlO_4]$ tetrahedral unit also requires Ca²⁺ ion for charge balancing. When the Al_2O_3 is relatively low at C/S>0.8 region (Region A in FIG 4), the Ca²⁺ ion interacts with $[AlO_4]$ unit to keep the charge balance, and thus the activity coefficient of TiO₂ is increased by increasing the Al_2O_3 concentration due to deficiency of Ca²⁺ ion. Over the 10% Al_2O_3 at C/S>0.8 (Region B in FIG 4), Ca²⁺ ion is mainly consumed for charge balance

of $[\text{AlO}_4]$ structure, and thus some Ti in five-fold coordination is forced to transform to four-fold coordination (Romano et al., 2000). Transformation of titanium coordination from five to four also occurred in $C/S < 0.8$ region (Region C in FIG 4) due to the lack of Ca^{2+} ion. Because $[\text{TiO}_4]$ group can be incorporated into the aluminosilicate network by replacing $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedrons (Duan et al., 1998), the activity coefficient of TiO_2 is decreased by decreasing the C/S ratio and increasing Al_2O_3 concentration.

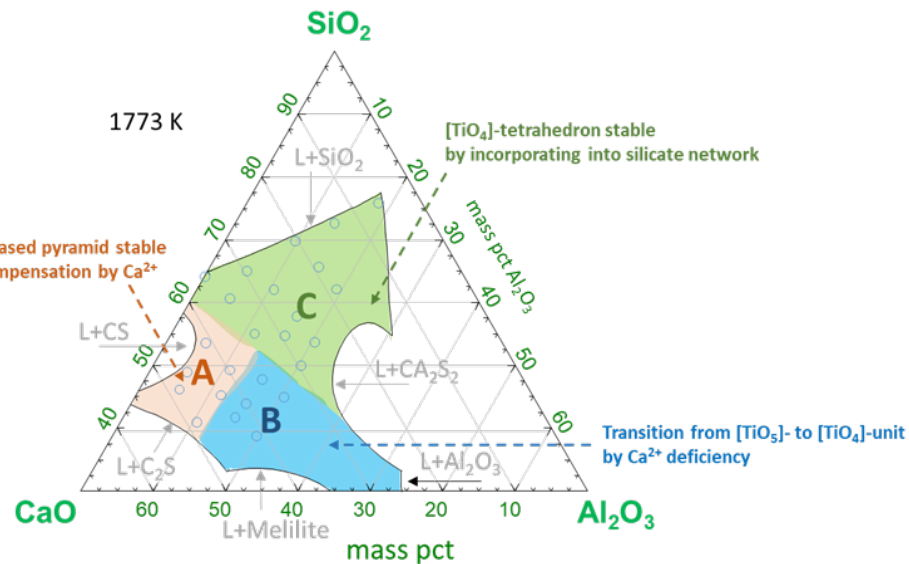


FIG 4. Titanium coordinations in different regimes in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system at 1773 K

CONCLUSIONS

The distribution behavior of titanium between FeSi and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ slag was investigated at 1773 K. The major results of present study can be summarized as follows:

1. The distribution behavior of Ti is strongly influenced by slag basicity. The activity coefficient of TiO_2 decreases with an increase in C/S ratio at $C/S > 0.8$, whereas it significantly decreases by decreasing the C/S ratio at $C/S < 0.8$ system.
2. At $C/S > 0.8$ basic system, the addition of CaO stabilizes five-fold coordinated Ti, but addition of Al_2O_3 depletes free Ca^{2+} ion due to charge balancing of $[\text{AlO}_4]$. Beyond 10% Al_2O_3 , Ti coordination partly shifts from five to four, resulting in a stabilization of TiO_2 in slag.
3. At $C/S < 0.8$ acidic system, Ti in five-fold coordination is forced to transform to four-fold coordination because of Ca^{2+} depletion. The $[\text{TiO}_4]$ group incorporates into the aluminosilicate network by replacing $[\text{SiO}_4]$ and $[\text{AlO}_4]$ structure, which increases the stability of TiO_2 .

REFERENCES

- Duan, R. G. et al. 1998. The effect of Ti^{4+} on the site of Al^{3+} in the structure of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system glass. *Materials Science and Engineering: A*, 249, 217-222.
- Le Cornec, D. et al. 2021. Structural role of titanium on slag properties. *Journal of the American Ceramic Society*, 104, 105-113.
- Nakayama, T., Honjou, N. 2000. Effect of aluminum and nitrogen on the magnetic properties of non-oriented semi-processed electrical steel sheet. *Journal of Magnetism and Magnetic Materials*, 213, 87-94.
- Nakayama, T., Tanaka, T. 1997. Effects of titanium on magnetic properties of semi-processed non-oriented electrical steel sheets. *Journal of Materials Science*, 32, 1055-1059.
- Romano, C. et al. 2000. Effect of aluminum on Ti-coordination in silicate glasses: A XANES study. *American Mineralogist*, 85, 108-117.
- Sano, N. 1997. *Advanced Physical Chemistry for Process Metallurgy*, New York, Academic Press.
- Steiner Petrovič, D. et al. 2010. Correlation of titanium content and core loss in non-oriented electrical steel sheets. *Metallurgija*, 49, 37-40.
- Turkdogan, E. T. 1980. *Physical Chemistry of High Temperature Technology*, New York, Academic Press.

