Desulfurization of CaO–Al₂O₃–SiO₂–TiO₂ Slag System

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(Received on April 4, 2014; accepted on June 30, 2014)

The desulfurization ability of CaO–Al₂O₃–SiO₂–TiO₂ slag at 1873 K was studied through the slag-metal desulfurization experiment by using a 10 kg inductive furnace and through theoretical calculation by using thermodynamic software FactSage. The experimental index considered were the sulfur distribution coefficient of the slag (LS) and the desulphurization ratio (η). The effect factors were binary basicity, the mass percentage of Al₂O₃ and TiO₂. Research results are as follows. The effect of binary basicity is significant, compared with the mass percentage factors of Al₂O₃ and TiO₂. Under the optimal experimental conditions, with the binary basicity is 7, the mass percentage of Al₂O₃ is 30% and TiO₂ is 3%, the corresponding highest sulfur distribution coefficient for the slag are 58.14. While the content of TiO₂ in the CaO–Al₂O₃–SiO₂–TiO₂ slag is in a range lower than 3–4%, the desulfurization ability of the CaO–Al₂O₃–SiO₂–TiO₂ slag is equal to that of the CaO–Al₂O₃–SiO₂ slag. The slag system with TiO₂ can meet the desulfurization requirements of steelmaking, which is a good way for resource utilization of solid waster containing titanium.

KEY WORDS: desulfurization; refining slag; TiO₂; FactSage.

1. Introduction

The commonly used refining slags in steelmaking processes include the CaO–Al₂O₃ slag, the CaO–SiO₂ slag, the CaO–Ca₂F slag, and the BaO-based slag. At present, the practically used slag for industry production is CaO–Al₂O₃-based multi-component slag, for example, the CaO–Al₂O₃–SiO₂ and CaO–Al₂O₃–CaF₂ ternary slags. There is abundant work on the knowledge of the commonly used slags in literature.¹–⁴)

Research on Titanium containing slag usually focused on its desulfurization effect in the blast furnace (BF) process,⁵ only a few application of Titanium bearing slag as refining slag has been reported. Considering the melting performance of CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system, the meltability temperature of the slag can be greatly increased when the mass content of TiO₂ higher than 1%.⁶,⁷) Studies on the influence of TiO₂ on the viscosity of the CaO–Al₂O₃–CaF₂ slag system find that when the mass content of TiO₂ is lower than 15%, the increment of TiO₂ content is beneficial to reduce the viscosity of the slag system.⁸,⁹) Research finds that the BF slag tailings containing 1.86 wt.% Titanium can be prepared for refining desulfurization agent.¹⁰,¹¹) In the study of the CaO–Al₂O₃–SiO₂–MgO–TiO₂ slag system, results showed that the sulfide capacities decreased with increasing of TiO₂ content in the temperature range 1773–1873 K.¹²,¹³) However, the slag system of CaO–Al₂O₃–SiO₂–TiO₂ applied to steelmaking desulfurization has not been systematically studied.

In this paper, on the basis of a commonly used steelmaking refining slag, CaO–Al₂O₃–SiO₂ system, certain amount of TiO₂ is added into the slag. Desulfurization experiment was conducted between the newly formed CaO–Al₂O₃–SiO₂–TiO₂ slag systems and deformed steel bar at 1873 K in the first place. Later on, thermodynamic software FactSage was used to calculate the desulfurizing ability of concerned slags. The research work is to find the feasibility of the CaO–Al₂O₃–SiO₂–TiO₂ slag applied as desulfurization slag in steelmaking process. To some extent, this work will promote the recycling of the waste containing titanium.

2. Experiment Design

2.1. Experimental Method and Procedures

2.1.1. Material and Equipment

A) Steel preparation: HRB 400 grade of deformed steel bar is selected as the raw material of the steelmaking experiment. The composition of the steel is shown in Table 1. The amount of steel consumption in each heat is about 5 kg.

B) Slag preparation: Slags were mixed with CaO, SiO₂, Al₂O₃, and TiO₂ powder in analytical pure. The well mixed slags were dried at 673 K for 3 h in muffle furnace in order

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<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
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<tr>
<td>0.25</td>
<td>0.65</td>
<td>1.55</td>
<td>0.025</td>
<td>0.026</td>
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DOI: http://dx.doi.org/10.2355/isijinternational.54.2248
to remove the water of crystallization. The composition of the slag is matched with the experimental scheme in Table 3. The content of the slag is 8% of the steel consumption, which is about 400 g in each heat.

C) The experimental equipment used is a covered 10 kg high temperature inductive furnace (ZG-0.01) in normal atmosphere condition. A schematic diagram of the experimental set-up is shown in Fig. 1. A charger, a sample spoon, a quartz tube with a rubber suction bulb, and a thermocouple were fitted on the furnace lid to allow slag addition, sampling of slag and liquid steel, and temperature measurements. Thermocouple of Pt-6% Rh/Pt-30% Rh was used to measure the temperature of the system. An experiment was carried out to determine the system temperature. The prepared deformed steel bar was charged into the furnace and melted down. After that, the temperature of the liquid steel was recorded every 5 minutes at certain power input into the furnace by thermocouple. If the temperature of the liquid steel kept unchanged at 1873 K at certain power input for 30 minutes, the power input figure will be wrote down and used in the desulfurization experiment.

D) High purity magnesia crucible (98% purity of MgO) was selected for the experiment. The influence of MgO content on sulfur capacity at 1873 K are calculated as Fig. 2 shown,14) when the MgO content is below 5 mass%, the desulfurization ability is low, and the influence of the MgO content on the desulfurization should be negligible.

2.1.2. Experimental Procedures
The experimental procedures are taken according to the scheme as shown in Fig. 3. The refining time for deformed steel bars metallurgy in LF process is about 15–20 minutes in the researched steel plant. For this reason, the reaction time of desulfurization chosen in this paper is 20 minutes. The time for MgO in crucible dissolving into the liquid slag is shorter than the reaction time, and the concentration of MgO in the final slag should be low.

A) Charging: firstly, the prepared deformed steel bar is charged into the furnace, after melting down of the steel at 1873 K, the first batch of slag about 200 g is added into the liquid steel, 10 minutes later, the second batch about 200 g is added into the melt, and after 10 minutes, the whole process of steelmaking ends.

B) Sampling: When the liquid steel smelts down, the first specimen (liquid steel) is sampled before the first batch of slag added; after 10 minutes, the second specimen (liquid steel) is sampled before the second batch of slag added; the third specimen (liquid steel and slag) is sampled at tapping point.

2.2. Experimental Scheme
The sulfur distribution coefficient of the slag ($L_S$) and the desulphurization ratio ($\eta_S$) are considered in this experiment. The sulfur distribution coefficient of the slag ($L_S$) is defined as: $L_S = \frac{[\%S]}{[\%S]}$, where $[\%S]$ is the sulfur content in the slag in mass percentage; $[\%S]$ represents the sulfur content in the steel in mass percentage. The desulphurization ratio ($\eta_S$) is defined as: $\eta_S = \frac{[\%S]_0 - [\%S]_{100}}{[\%S]_0} \times 100$, $[\%S]_0$ and $[\%S]_{100}$ represent the mass content of sulfur in the initial sample before slag adding and the sulfur content in the final sample at the tapping point respectively. The inductive furnace experiment takes three factors into consideration, which are binary basicity (the mass ratio between CaO and SiO$_2$ in the slag), the mass percentage of Al$_2$O$_3$ and TiO$_2$ respectively. The effect of three considered factors on the desulfurization ability of the CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ system is studied in this article. Experimental factors and levels can

![Fig. 1. Schematic diagram of the experimental set-up.](image)

![Fig. 2. Influence of MgO content on sulfur capacity at 1873 K according to the theoretical calculation.](image)

![Fig. 3. Schematic diagram of the experimental procedure.](image)
be seen in Table 2. Binary basicity, the mass percentage of Al₂O₃ and TiO₂ are set as factor A, B, and C. No. 1, 2, 3 in the first column represent levels of each factor. Experiment is arranged to the L₉(3⁴) proposed level of orthogonal matrix.¹⁵)

3. Experimental Results and Validation

3.1. Experimental Results

During the experiment, each batch of slag added into the liquid steel was melted down in about 3–5 minutes, and with excellent fluidity. In each heat, specimens were sampled with experimental scheme in Fig. 3. The sulfur content in the specimen is analyzed by GB/T20123-2006 standard in National Analysis Center for Iron & Steel in China. Experimental results are shown in Table 3. The sampling steps were taken according to Fig. 3.

3.2. Analysis of the Experimental Data

Table 4 lists the result of variance analysis.¹⁶) As seen in Table 4, the changes of binary basicity have significant effect on $L_S$ and $\eta_S$, while the change of Al₂O₃ and TiO₂ content on the result of $L_S$ and $\eta_S$ are not so obvious.

From main effect analysis on the experimental factors in Fig. 4,¹⁵,¹⁶) it can be concluded that:

A) Both $L_S$ and $\eta_S$ increase rapidly as binary basicity increases. $L_S$ are the highest when binary basicity is 7 in the present work. This value is higher than the $L_S$ figure when binary basicity is 3 by 29.49. At lower basicity, the CaO content in the slag is less, so that only a few free O²⁻ ions exist. This results in low $L_S$ and low $\eta_S$ of slags. As the basic oxide contents increase, the SiO₂ networks are broken into smaller anion groups and the proportion of free oxygen ions increases.¹²) Consequently, the $L_S$ and $\eta_S$ of slag are expect-
ed to increase.

B) \( L_S \) and \( \eta_S \) fall down as the mass content of \( \text{Al}_2\text{O}_3 \) rises. \( L_S \) decreased by 10.51 when the mass content of \( \text{Al}_2\text{O}_3 \) in the slag system rises from 30 to 35%. When the concentration of \( \text{Al}_2\text{O}_3 \) is from 25 to 30 mass\%, both \( L_S \) and \( \eta_S \) have no obvious variation. Higher content of \( \text{Al}_2\text{O}_3 \) will reduce the meltability temperature of the slag under a high basicity condition without much influence on the value of \( L_S \) and \( \eta_S \). In this point, the optimum concentration of \( \text{Al}_2\text{O}_3 \) is selected as 30 mass\% under present experimental conditions.

C) There is no substantial change of \( L_S \) and \( \eta_S \) when the \( \text{TiO}_2 \) content increases from 1 to 5 mass\%. Although \( L_S \) is highest when the \( \text{TiO}_2 \) content is 1 mass\%, while \( \eta_S \) is highest when the \( \text{TiO}_2 \) content is 3 mass\%. Both the \( L_S \) and \( \eta_S \) have a tendency of decreasing as the content of \( \text{TiO}_2 \) increases. The best level of factor C is obtained from the result of \( \eta_S \), i.e. the optimum concentration of \( \text{TiO}_2 \) is selected as 3 mass\%. This is partially due to \( \eta_S \) is a more direct experimental index in industry production compared with \( L_S \) and partly to slightly changes of both \( L_S \) and \( \eta_S \) in the experimental ranges of \( \text{TiO}_2 \). The main interest of this work is to study the effect of titania on the sulfide ability of concerned liquid slags. It has been confirmed by Sommerville et al.\textsuperscript{17)} that in high basicity, \( \text{TiO}_2 \) exists as \( \text{TiO}_6^{8-} \) ions in the slags. Therefore, \( \text{TiO}_2 \) in slags forms the anions which make the free \( \text{O}^2^- \) ions decrease. In other words, \( \text{TiO}_2 \) acts as acidic oxide in basic slags. Higher content of \( \text{TiO}_2 \) will have a tendency to reduce the activity of CaO which is not good for desulfurization reaction and decrease \( L_S \) and \( \eta_S \).

According to the result from Fig. 4 and above discussion, the optimal combination of experimental condition with the best desulfurization ability of the slag can be derived as \( \text{CaO} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{TiO}_2 = 58.62 : 30 : 8.38 : 3 \). The main composition of the slag system used in the steel plant is the \( \text{CaO} \) 50\%, \( \text{Al}_2\text{O}_3 \) 45\%, and \( \text{SiO}_2 \) 5\%. The test procedure is the same as Section 1.1. During the experiment, both the two types of slag showed excellent melting performance which melted down in about 3–4 minutes after adding.

The initial sulfur content in the steel is 0.0200\%. Results showed that after the desulfurization process with the optimal refining slag and the commonly used refining slag, the sulfur content in the steel reduced to 0.0043% and 0.0057% respectively. The corresponding values of \( \eta_S \) are 78.15\% and 71.5\%. The optimal refining slag is better than the commonly used refining slag in the steel plant with respect to the desulfurization ability.

4. Calculation on the Desulfurization Ability of the \( \text{CaO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{TiO}_2 \) Slag System

FactSage, one of the largest fully integrated database computing systems in chemical thermodynamics in the world, is the fusion of the \( \text{FToxid, FTsalt, FThall, etc.} \) databases of thermodynamic data for thousands of compounds. It contains six calculate modules, which are Reaction, Predom, PhaseDiagram, Equilib, etc. Some literature\textsuperscript{18,19)} calculated the conditions for multi-component phase diagram and the liquid phase zone with PhaseDiagram module. In this paper, the FactSage 6.2 and \( \text{FToxid} \) data base were selected. Melting property and desulfurization ability of the \( \text{CaO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{TiO}_2 \) slag systems under different conditions were calculated with PhaseDiagram and Equilib modules.

4.1. Melting Property of \( \text{CaO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{TiO}_2 \) System

The phase diagrams and liquidus of the \( \text{CaO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{TiO}_2 \) slags containing 0–7% \( \text{TiO}_2 \) at 1 773 K and 1 873 K were plotted by PhaseDiagram module with FactSage software in Fig. 5. In Fig. 5, at different temperatures of 1 773 K and 1 873 K, the content of \( \text{TiO}_2 \) increased from 0 to 7%, the liquid phase zone is enlarged. The melting property of the system doesn’t change much with the \( \text{TiO}_2 \) addition. The \( \text{TiO}_2 \) contained slag system can satisfy the melting requirement for desulfurization in steelmaking.

![Fig. 5. Liquid phase areas of \( \text{CaO}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{TiO}_2 \) slag under different \( \text{TiO}_2 \) content at 1 773 K and 1 873 K.](image-url)
4.2. Simulation on the Desulfurization of CaO–Al₂O₃–SiO₂–TiO₂ System

The Sosinsky regression model²⁰,²¹ and KTH (Kungliga Tekniska Högskolan) model²²–²⁴ were used for calculating the sulfur capacities to research the desulfurization ability of certain slags in some references. In the current study, the desulfurization reaction process was simulated by FactSage software in order to further research the effect of TiO₂ composition on the desulfurization ability of the CaO–Al₂O₃–SiO₂–TiO₂ slag system at 1 873 K.

The composition of simulated steel is the same as that of the HRB400 grade deformed steel bar used in this experiment (see Fig. 3). The composition of the CaO–Al₂O₃–SiO₂–TiO₂ slag system in the simulation is in the position of the liquid phase zone where the content of SiO₂ is under 35% at 1 873 K.

The sulfur content in molten steel and in the liquid slag under thermodynamic equilibrium can be obtained through FactSage calculation. Then, the sulfur distribution coefficient can be calculated. According to the composition data corresponded in the dot of the phase diagram, iso-sulphide distribution ratio line can be plotted with the help of Surfer software²⁵ using Kriging interpolation calculation method. Iso-sulphide distribution ratio lines are depicted in Fig. 6 with different TiO₂ composition in the CaO–Al₂O₃–SiO₂–TiO₂ systems. Related experimental heat number of certain slag system is marked in Fig. 6. Position C in Fig. 6(a) and position R in Fig. 6(c) represent the composition positions of the commonly used refining slag and the optimal refining slag from this experiment respectively.

It can be concluded from Figs. 5 and 6 that:

(1) With 0 to 3 mass% TiO₂, the sulfur distribution coefficient of the CaO–Al₂O₃–SiO₂–TiO₂ system changes slightly, which is quite near to that of the CaO–Al₂O₃–SiO₂ system. With the TiO₂ content up to 5 mass%, the regime with low sulfur distribution coefficient enlarged, which shows the desulfurization ability of the slag system is reduced.

(2) With higher binary basicity, there is stronger desulfurization ability of the slag system. Higher binary basicity means a relative higher content of CaO and lower content of SiO₂, which will result in higher sulfur distribution coefficient and finally a better desulfurization ability of the slag.

(3) Position C in Fig. 5(a) is the position of commonly used refining slag where \( L_s \) are 200. The values of \( L_s \) in the corresponding position with the optimal refining slag (position R in Fig. 6(c)) are 400, which are higher than that of commonly used refining slag in position C. Andersson...
et al.\textsuperscript{26} indicated that \( L_S \) increases with the decrement of \( \text{Al}_2\text{O}_3/\text{CaO} \). The \( \text{Al}_2\text{O}_3/\text{CaO} \) in commonly used slag is 0.9 while the \( \text{Al}_2\text{O}_3/\text{CaO} \) in the optimal slag is 0.5. This can explain the differences on \( L_S \) of the two refining slags. The main reason for this may be explained as the following. First, increased \( \text{Al}_2\text{O}_3/\text{CaO} \) would decrease sulphur capacity of refining slags. Based on the following equation: 
\[ \lg L_S = \frac{-935}{T} + 1.375 + \lg C_S + \lg f_S - \lg a_O. \]
Where \( C_S \) represents the sulphur capacity, \( f_S \) represents the activity coefficient of sulphur in metal phase, and \( a_O \) represents the activity of oxygen. From the above expression, it is known that a decrement of \( C_S \) leads to direct drop of \( L_S \). Second, the increment of \( \text{Al}_2\text{O}_3/\text{CaO} \) means higher content of \( \text{Al}_2\text{O}_3 \) in slags, which increases the activity of oxygen, and finally decreases \( L_S \).\textsuperscript{26} Zhao et al.\textsuperscript{27} and Gao et al.\textsuperscript{28} also observed this result.

(4) Compared the sulfur distribution coefficient result from the experiment and Fig. 6, it is easy to find that the experimental result is lower than that from FactSage calculation. However, the variation trend of the result is the same. Theoretical calculation only takes the thermodynamic conditions into consideration. In fact, the desulfurization in real conditions is also affected by dynamic factors. This may explain the reason for the difference between theoretical calculation and experimental result.

Figure 7 shows the influence of \( \text{TiO}_2 \) content on \( L_S \) under different basicity. \( L_S \) decreases with the increase of \( \text{TiO}_2 \) content. At a given basicity of slag, when the \( \text{TiO}_2 \) content increases to 3–4%, \( L_S \) slightly decreases, however, when the \( \text{TiO}_2 \) content is higher than 4%, \( L_S \) decreases appreciably as the \( \text{TiO}_2 \) content increases.

This effect is more clearly seen in Fig. 8(a) where the percent decrease of sulfur distribution ratio (\( \Delta L_S \)) are drawn against \( \text{TiO}_2 \) concentration. \( \Delta L_S \) is expressed by 
\[ \Delta L_S = \frac{L_{S0} - L_S}{L_{S0}} \times 100. \]
Where \( L_S \) is sulfur distribution ratio at given \( \text{TiO}_2 \) concentration, \( L_{S0} \) is sulfur distribution ratio without \( \text{TiO}_2 \). This occurs because effective basicity decreases with the increase in \( \text{TiO}_2 \) content, and this decrease in basicity is significant above 4% \( \text{TiO}_2 \). Figure 8(b) shows the effect of basicity on sulfur distribution ratio. It is evident from Fig. 8(b) that, at a given \( \text{TiO}_2 \) concentration of a slag, the higher the basicity of the slag is, the less the percent decrease of \( L_S \). This is because higher basicity means higher concentration of free oxygen ions exist in the slag, at this time, the effect of \( \text{TiO}_2 \) on decreasing the concentration of free oxygen ions is limited than lower basicity conditions. That is to say that in a low \( \text{TiO}_2 \) concentration range, the changes of \( \text{TiO}_2 \) concentration has limited effect on \( L_S \) which has been confirmed by experimental work in Section 2.2. For this reason, the content of \( \text{TiO}_2 \) should be controlled under 3–4 mass%.

The content of \( \text{CaO} \) greatly influences the desulfurization reaction in the slag, with binary basicity increases, the activity of \( \text{CaO} \) increases, which will promote the desulfurization reaction. The existence of \( \text{Al}_2\text{O}_3 \) in the slag can keeps a relatively lower melting point of the slag at higher basicity which will satisfy the requirement of steelmaking. However, the \( \text{Al}_2\text{O}_3 \) in the slag doesn’t much affect the desulfurization ability, hence, the content changes of \( \text{Al}_2\text{O}_3 \) in the range of...
25–35% doesn’t have obvious effect on the sulfur distribution coefficient. TiO$_2$ is usually considered as acid oxide, the increase of the TiO$_2$ content will decrease the activity of CaO which is not good for desulfurization reaction. When the content of TiO$_2$ is higher than 4%, the desulfurization ability of the slag will be greatly decreased.

The results from the experiments and the calculations above all show that, when the content of TiO$_2$ is under 3–4%, the desulfurization ability of the CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ slag system is quite close to that of the CaO–Al$_2$O$_3$–SiO$_2$ slag system; as a result, the TiO$_2$ contained slag system can be further studied for steelmaking desulfurization. This research will promote the recycling of the waste containing titanium.

5. Conclusions

(1) The best combination of the experimental condition by orthogonal analysis is $A_2B_1C_3$. This condition means the binary basicity of the optimal slag is 7, the content of Al$_2$O$_3$ in the slag is 30%, and the content of TiO$_2$ is 3%. Experimental results showed that the sulfur distribution coefficient of the optimal refining slag was 58.14, which is higher than the commonly observed refining slag.

(2) Higher binary basicity of the slag will greatly improve the desulfurization ability of the CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ slag system. Compared with the content of the Al$_2$O$_3$ and TiO$_2$, the change of the binary basicity is the main influencing factor on the sulfur distribution coefficient.

(3) The addition of TiO$_2$ will retard the desulfurization reaction. The results from the experiments and the calculations above all show that, when the content of TiO$_2$ is in a lower range (lower than 3–4%), the desulfurization ability of the CaO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ slag system is quite approach to that of the CaO–Al$_2$O$_3$–SiO$_2$ system. The lower TiO$_2$ containing slag system can be applied to steelmaking desulfurization, which will promote the recycling of the waste containing titanium.

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