ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 21, No. 4. 2015

Thermodynamic Study on Production of Fe-Si-Ca Master Alloy Using Modified Molten Converter Slag

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http://dx.doi.org/10.5755/j01.ms.21.4.9559

Received 23 January 2015; accepted 19 June 2015

The thermodynamic behavior and the effects of energy saving in the production of Fe-Si-Ca master alloy from modified molten converter slag using SiO_2 as a modifier were investigated by thermodynamic analysis with different additions of the modifier and reductant at various temperatures to fully recycle the physical sensible heat and valuable elements in the metallurgical slag. The results showed that the activity of SiO_2 in the slag increased rapidly with the $w(SiO_2)$ increase from 40 wt.% to 60 wt.%, but the activity of CaO was low and decreased slightly with the $w(SiO_2)$ increase. When the $w(SiO_2)$ in the slag was 60 wt.% with an external addition of 35 wt.% of reductant at 1800 °C, the reduction ratios of silicon and calcium reached 90.05 mass % and 52.87 mass %, respectively, and the $w[Si]$ and $w[Ca]$ in the master alloy were 51.60 wt.% and 17.67 wt.%, respectively, resulting in an energy saving of 805.6 kWh per ton of produced ferroalloys.

Keywords: converter slag, Fe-Si-Ca alloy, molten modification, energy consumption.

1. INTRODUCTION

In recent years, the diminution and recycling of large amounts of steel slag generated during the steelmaking process has been extensively carried out for both environmental and economical benefits including less slag melting and the secondary utilization of slag. For example, it is recycled as metallurgical materials, agricultural fertilizers, construction materials, and other uses [1 – 3].

In general, the current utilization of steel slag based on low-value products, and the physical sensible heat carried by the molten slag cannot be well utilized.

Fortunately, several studies have been carried out by taking the valuable elements and physical sensible heat into account for the direct utilization of the molten slag to obtain higher-value products, such as the enrichment of the phosphorus from the slag and the production of Fe-Mn alloy from the slag generated in the Mn-removal treatment of the molten cast iron [4, 5].

However, most of the other valuable elements cannot be recycled.

Furthermore, the production of ferroalloys is an energy-consuming and high-pollution industry. Considering that there are plenty of Ca and Si elements in molten steel slag as well as their massive physical heat, the present work investigated a novel treatment method for molten steel slag using deep reduction to produce Fe-Si-Ca master alloy according to the selective reduction principle to cut down on the energy consumption of traditional ferroalloy production [6].

Using the commercial thermodynamic software FactSage 6.2, the thermodynamic behaviors of the components in molten slag during the reduction process and the energy consumption were discussed.

2. RAW MATERIALS AND PROCEDURES

The molten converter slag at 1400 °C with 17.66 wt.% $w(SiO_2)$ shown in Table 1 was used as the raw material, and SiO_2 was used as a modifier to adjust the alkalinity of the molten slag [6]. Additionally, carbon powder was selected as a reductant by external addition. Considering that the solution of SiO_2 in the converter slag increased from 57.8 wt.% at 1450 °C to 78.2 wt.% at 1750 °C and the liquidus temperature of the modified slag was below 1600 °C from 30 wt.% $w(SiO_2)$ to 60 wt.% $w(SiO_2)$, the physical properties of the slag were good with 40 – 60 mass % $w(SiO_2)$ at temperatures over 1600 °C [6, 7]. Therefore, the properties of the modified molten slag and the thermodynamic behaviors were calculated at 1700 ~ 1900 °C with different amounts of reductant using the Equilib module, Reaction module and Phase Diagram module of FactSage 6.2. The materials balance and heat balance corresponding to 100 g slag with 60 wt.% $w(SiO_2)$ shown in Table 1 were calculated using the View Date module and the Equilib module [8].

3. RESULTS AND DISCUSSION

3.1. Relations between the activity of components and SiO_2 content in the slag

Fig. 1 shows the activity changes of the components in the slag with the SiO_2 content at different temperatures under an equilibrium oxygen partial pressure of 21.15 kPa. In Fig. 1 a, it can be observed that the activity of the SiO_2 was low when its content was small. It started to increase rapidly while the content was over 40 wt.%, and then increased gradually once it was more than 60 wt.%. This result could be due to the fact that while the SiO_2 content was lower, it was mainly in the form of $2CaO{\cdot}SiO_2$ in the slag. When the content increased, the $2CaO{\cdot}SiO_2$

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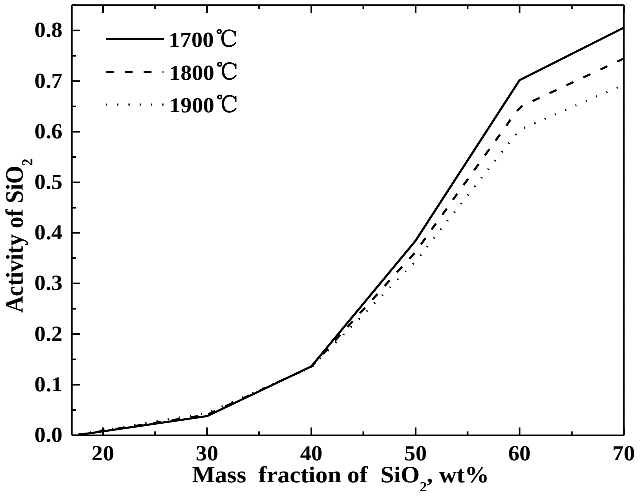
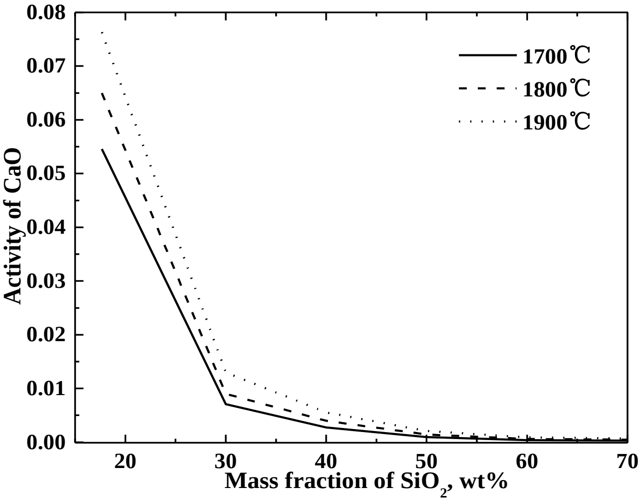
transformed into the form of $CaO\cdot(1+x)SiO_2$ and the amount of free SiO_2 in the molten slag increased [9, 10].



a $a(SiO_2)$



b $a(CaO)$

Fig. 1. Relations between activity of components and SiO_2 content in the slag at P_{O_2}= 21.15 kPa

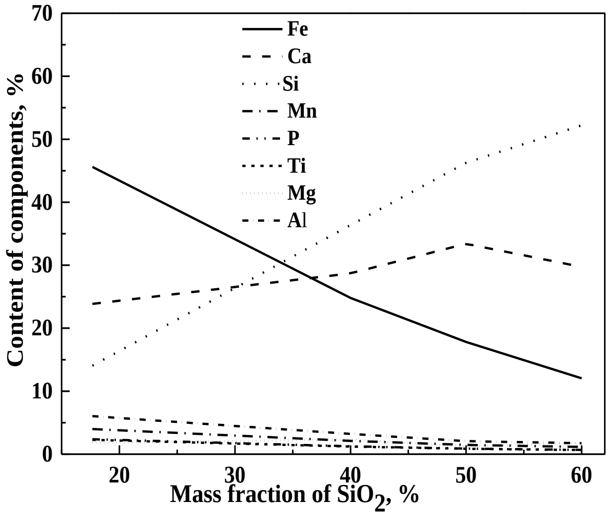
In addition, it can also be observed in Fig. 1 a that the activity of the SiO_2 decreased slightly once the $w(SiO_2)$ was over 40 wt.% when the temperature increased from 1700 °C to 1900 °C due to the occurrence of Reaction (1) to reduce the content of silica in the slag.

$$(SiO_2) = SiO(g) + 1/2O_2(g). \quad (1)$$

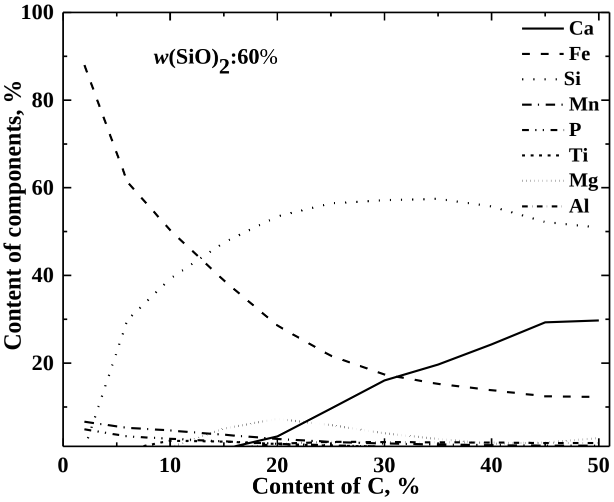
Fig. 1 b shows the change of activity of the CaO with the SiO_2 content at different temperatures. The activity of the CaO was very low when the SiO_2 content was more than 30 wt.%. This was considered to be due to the large amounts of silica added leading to the dilution of the concentration of calcia and the formation of calcium silicate ($CaO\cdot(1 + x)SiO_2$) in the slag. Moreover, when the SiO_2 content was over 30 wt.%, the free calcia almost completely turned into complex oxides, and thus its activity was slightly decreased. However, according to the ionic theory [9], silica is an acidic oxide that can strongly attract surrounding O^{2-} to form covalent silicate anions as a variety of complex silicon-oxygen anions in the slag. At the same time, silicon-oxygen anions further polymerize to form more complex silicon-oxygen compound oxides when the $w(SiO_2)$ increases. In general, Ca^{2+} and other cations are located in the cavity among ions, and are in mutual coordination with the non-bridging oxygen to affect the activity of the CaO in the slag [10, 11]. When the alkalinity was decreased by increasing the $w(SiO_2)$, the silicone-oxygen compound oxides further polymerized to consume large amounts of O^{2-}, which increased the Si-O-Si bond, and simultaneously decreased the free Ca^{2+}-O^{2-} and the activity of the CaO in the slag. In addition, contrary to the activity of the SiO_2, the activity of the CaO also slightly increased with temperature increases.

3.2. Metallurgical properties of the modified slag during the reduction process

Fig. 2 a shows the influence of the SiO_2 content on the alloy composition at 1800 °C with sufficient reductant under the equilibrium carbon monoxide partial pressure of 93.08 kPa.



a $w(SiO_2)$ at 1800 °C



b $w(C)$ at 1800 °C

Fig. 2. Influence of the factors on the alloy composition

It was observed that the content of Si and Ca in the alloy increased simultaneously with the increase of the content of SiO_2 to 50 wt.% due to increase of the activity of the SiO_2 (as shown in Fig. 1 a) and the occurrence of Reaction (2) and (3) in the modified slag as the main of reaction in the production of Fe-Si-Ca ally at high temprature to increase the content of Si and Ca in the metal pool [12]. But a further increase of silica content diluted the concentration of CaO in the slag and the activity of CaO was decreased; as a result, the content of Ca in the alloy was decreased and the content of Si was further increased gradually when the content of the SiO_2 in the modified molten slag was more than 50 wt.%. Therefore, in order to obtain Fe-Si-Ca master alloy with higher levels of silicon and calcium, the content of the SiO_2 should be more than 50 wt.% in the modified slag.

$$1/4SiC(s) + 3/8(SiO_2) + 1/4(CaO) + 3/4C(s) = \\ = 1/4CaSi(l) + 3/8Si(l) + CO(g) \qquad (2)$$

$$CaC_2 + 2(SiO_2) – 2[C] = [CaSi] + [Si] + 4CO(g) \qquad (3)$$

Fig. 2 b shows the change of the composition of the master alloy with different amounts of the added reductant wen the SiO_2 content was 60 wt.%. It is known from the thermodynamics analysis that the reduction order of the components in the slag was FeO, P_2O_5, MnO, SiO_2, TiO_2, MgO, Al_2O_3 and CaO [3, 6]. As a result, the content of Fe in the alloy was maximal while the amount of the added reductant was insufficient, and it decreased gradually with the increase of Si content in the alloy after the SiO_2 in the slag was reduced when the added reductant was more than 2.5 wt.%. With a further increase of the amount of reductant more than 16 wt.%, the CaO conten in the slag began to be reduced, resulting in the increase of the Ca content and decrease of the content of Fe and Si in the alloy. But the content of Ca did not further increased after the amount of reducing agent was more than 45 wt.%. To put it simply, during the reduction process of the modified converter slag, Fe-Si alloy was formed firstly, and then subsequently transformed into Fe-Si-Ca master alloy. To obtain Fe-Si-Ca master alloy, the proper amount of the reductant should be from 30 wt.% to 45 wt.% by external addition.

Fig. 3 shows the influence of temperature on the reduction ratios of the CaO and SiO_2 in the modified slag with various SiO_2 contents. Here, the reduction ratio is defined as the mass percentage of the reduced oxides to its original mass in the molten slag. From Fig. 3 a it can be observed that the reduction ratio of the SiO_2 climbed quickly with increments of the temperature up to 1800 °C due to the increase of the SiO_2 activity, and it increased slowly with further temperature increasing. For the same reason, as the activity of the SiO_2 was dependent on its content, the reduction ratio of the SiO_2 was also increased with increments of its content. Similar to the case of the SiO_2 reduced, as shown in Fig. 3 b, it was observed that the reduction ratio of the CaO also increased obviously with increasing temperatures up to 1800 °C and then increased subtly. In addition, though the activity of the CaO decreased with the increase of $w(SiO_2)$ in the slag, as shown in Fig. 1 b, the reduction ratio also obviously increased with the increase of $w(SiO_2)$ up to 60 wt.% due to the formation of CaSi in the alloy by the occurrence of Reaction (2) and (3). A further increase of $w(SiO_2)$ in the slag showed a smaller effect on the CaO reduction ratio. From this result, it was also believed that the proper content of SiO_2 in the modified converter slag should be up to 60 wt.% in order to obtain the Fe-Si-Ca master alloy, and the temperature should reach up to 1800 °C at higher reduction ratios of CaO and SiO_2 in the modified slag.

Fig. 2 b shows the change of the composition of the master alloy with different amounts of the added reductant wen the SiO_2 content was 60 wt.%.

3.3. The materials balance and the energy consumption

Table 2 shows the materials balance of the main elements of the modified converter slag with 60 wt.% SiO_2 (see Table 1) after reduced at 1800 °C by the external addition of appropriate 35 wt.% carbon under the equilibrium carbon monoxide partial pressure of 93.08 kPa.

As shown in Table 2, according to the analysis on the composition of the reaction products (including the alloy phase, the slag phase, and the gas phase), the reduction ratios of CaO, SiO_2, and FeO were 52.87 %, 90.05 %, and 100 %, respectively. And at the same time, 45 g ferroalloy per 100 g modified slag with contents of Ca 19.16 wt.% and Si 55.94 wt.% was obtained. Calcia and silicon compounds (SiO_2, SiC) accounted for 73.04 wt.% and 26.20 wt.%, respectively, in the final slag. CO with a content of more than 90 wt.% was the main gas phase.

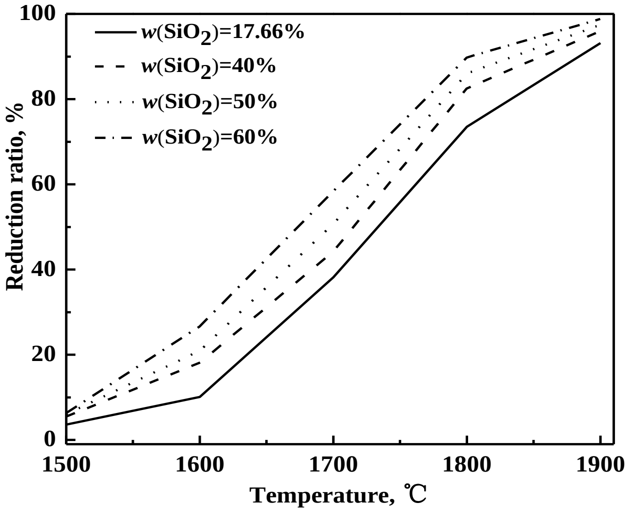
In order to analyze further energy consumption, Table 3 shows the heat balance of 100 g of the modified converter slag and the pure compounds with 60 wt.% SiO_2 (as shown in Table 1) at 1800 °C by the external addition of the appropriate 35 wt.% carbon under the equilibrium carbon monoxide partial pressure of 93.08 kPa slag.

On the bases of actual production conditions and convenient calculation, the reduction ratios of silica, calcia, and ferrous oxide were 90.05 %, 52.87 %, 100 %, respectively, by the traditional technology using the pure compounds [12]. It could be seen that the heat income included the physical sensible heat of the slag, chemical heat by the formation of CaSi and FeSi in the metal, and the slag forming heat from the formation of $CaO{\cdot}(1+x)SiO_2$.

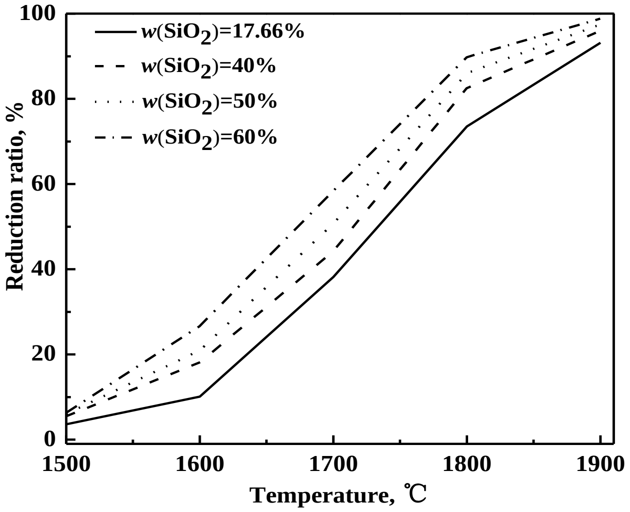
Heat expenditure also included the oxide chemical heat for the reduction of the oxides in the slag, the physical heat for heating the carbon, modifier (silica) from room temperature to 1800 °C, the physical heat for heating the molten slag from 1400 °C to 1800 °C, and the physical heat carried by the formed gas phase, alloy phase, and slag phase.

Compared to the modified slag and the pure compounds, there was not physical sensible heat carried by the molten slag in the mixed pure oxides reduced in the same conditions, as shown in Table 3. Meanwhile, the energy consumption was 1228.1 kJ for the reduction of the modified slag, and 1283.0 kJ for the reduction of the mixed pure oxides. In addition, the heat income was 123.4 kJ for the reduction of the modified slag, and it was 48.4 kJ for the mixed pure oxides reduced. The results indicated that energy consumption was 1104.7 kJ under 100 g modified slag condition, which was lower than 1234.6 kJ under 100 g pure compounds condition.

Table 2 and Table 3 illustrate that 0.13×10^7 kJ energy could be saved in the production of 0.45 ton ferroalloy using 1 ton modified steel slag with 60 wt.% SiO_2 compared to that of the mixed oxides, corresponding to save 0.29×10^7 kJ energy in the production of per ton ferroalloy, amounting to 805.6 kWh per ton ferroalloy. Thus, it is considered that the modification treatment and deep reduction of converter slag is an effective method to recycle valuable elements in the metallurgical slag.



a SiO_2



b CaO

Fig. 3. Reduction ratios of CaO and SiO_2 at various temperatures

4. CONCLUSIONS

A thermodynamic study on physical sensible heat and valuable elements recycling from the molten converter slag using SiO_2 as a modifier by deep reduction was carried out on the production of Fe-Si-Ca master alloy, and the following conclusions could be drawn.

1. The activity of SiO_2 in the slag system increased rapidly when its content increased from 40 wt.% to 60 wt.%, and then increased gradually with additional increments of $w(SiO_2)$. Meanwhile, the activity of CaO was low and decreased slightly with the increase of $w(SiO_2)$.
2. The reduction order of the components in the modified slag was FeO, P_2O_5, MnO, SiO_2, TiO_2, MgO, Al_2O_3 and CaO. In a word, during the reduction process of the modified converter slag, Fe-Si master alloy was formed initially, and was subsequently transformed into Fe-Si-Ca master alloy.
3. The reduction ratios of the SiO_2 and CaO climbed quickly with increments of temperature up to 1800 °C, and then increased subtly with further increase of temperature. The contents of Si and Ca in the alloy began to increase when the amount of the reducing agent was more than 2.5 wt.% and 16 wt.% respectively, but it did not further increase after the amount of the reducing agent was more than 45 wt.%.
4. When the $w(SiO_2)$ in the modified slag was 60 wt.% with 35 wt.% reductant added at 1800 °C, the reduction ratios of the CaO and SiO_2 reached 52.87 wt.% and 90.05 wt.%, respectively, which could save approximately 805.6 kWh of energy per ton of ferroalloy produced compared to using mixed pure oxides.

Acknowledgement

The authors gratefully acknowledge the National Natural Science Foundation of China (No. 51174049, 51174052, 51374057, 51374062) and the Fundamental Research Funds for the Central Universities of China (No.120402005) which has made this research possible.

Table 2. Materials allocation sheet after reaction for 60 % SiO_2 at 1800 °C (P_{CO} = 93.08 kPa)

Component ingredient	The metal phase		The slag phase		The gas phase		Total
	Mass, g	Percentage, wt.%	Mass, g	Percentage, wt.%	Mass, g	Percentage, wt.%	Mass, g
SiO_2	54.081	90.048	1.521	2.533			60.058
SiC			2.398	3.990			
SiO					2.058	3.427	
CaO	12.102	52.873	10.329	45.127	0.459	2.005	22.889
FeO	8.583	100.000	0.000	0.000	0.000	0.000	8.583
C	1.006	2.877					34.972
CO					33.246	95.065	
SiC			0.719	2.059			

Table 3. Energy balance sheet of heat at 1800 °C (P_{CO} = 93.08 kPa)

Income items			Expenditure items		
Item	Modified slag, J	Pure compounds, J	Item	Modified slag, J	Pure compounds, J
Physical sensible heat of the slag	84828.4	0	Oxides chemical heat for reduction of oxides	715891.8	675896.6
Chemical heat by the formation of CaSi and FeSi in the metal	28489.6	28259.6	Physical heat for heating reactants	209748.8	294577.2
The slag forming heat by formation Of $CaO(1+x)SiO_2$	10032.2	20122.2	Physical heat carried by the formed the reaction products	302497.5	312507.5
Total	123350.2	48381.8	Total	1228138.1	1282981.3

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