Research Article

Validation of FeSiMg Alloy Production Model for the Experimental Process

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This paper investigates the effect of limestone, bauxite, fluorspar, and quartzite additions on the magnesium recovery in FeSiMg production from dolomite. Also, it illustrates the validation of the previous designed model. According to the model, magnesium content in the product alloy is calculated by the equation $[Mg] = (MgO_0)[Si_0][e^{Kt[(MgO_0)-[Si_0]]} - 1] / ((MgO_0)[e^{Kt[(MgO_0)-[Si_0]]} - [Si_0]])$, where $[Mg]$ is the concentration of magnesium metal in ferrosilicon magnesium alloy in mol/L, $[Si_0]$ and (MgO_0) are the initial concentrations of silicon and magnesium oxide in charge in mol/L, t is the time in seconds, and K is the reaction rate constant ($3.26588 \times 10^{-7} \text{ LSec}^{-1} \text{ mol}^{-1}$). The results of the production process are compared with the model results. The deviation between the actual and predicted magnesium content decreases as fluorspar, limestone, and quartzite increase up to 12.8wt.%, 8wt.%, and 8wt.%, respectively, with increase in the amount of the additives, the magnesium content in the produced alloy becomes far from the predicted values. It was found also that the addition of bauxite increases the gap between the actual and predicted values of magnesium content. It was found that the deviation of the actual magnesium content from the predicted depends mainly on the viscosity of the slag.

1. Introduction

Ferrosilicon magnesium alloys are used to produce all types of ductile cast iron. It is added to the molten iron for producing a structure containing graphite in nodular or spheroidal form [1]. This form minimizes the embrittlement effect of graphite on the metal matrix with the result of producing cast iron with better machinability, toughness, and tensile properties. Ferrosilicon magnesium consists mainly of magnesium silicides combined with the silicides of iron, calcium and rare earth metals. The silicothermic process is one of the most attractive techniques for producing FeSiMg alloy. This is attributed to much lower working temperature compared with carbothermic process. Also, it is of much lower cost compared with the alumino-thermic process. The oldest trials to reduce magnesium oxide with silicon were carried out by Kubaschewski and Evans [2] and Misra et al. [3]. Their results [2, 3] showed a low recovery of magnesium under this working conditions. They attributed this phenomenon to the formation of magnesium orthosilicate. Misra et al. [4] have

also found that silicothermic reduction of pure magnesium oxide results in a poor magnesium recovery, due to the fact that a part of the magnesium oxide combines with the silica. Recovery of magnesium can be improved by carrying out the reduction of magnesium oxide in the presence of a metallic oxide that can form silicates more stable than magnesium orthosilicate. According to the thermodynamic data, lime can be considered as a suitable additive for improving the reduction process of magnesium oxide due to the fact that its silicate is more easily formed than magnesium silicate [3, 5, 6]. Thus, better recovery is expected when a mixture of lime and magnesite was used. Calcinated dolomite seems to be a suitable cheap raw material for the production of ferrosilicon magnesium alloy. Using silicothermic reduction process to produce magnesium-bearing alloys, which can be carried out in submerged arc furnace.

At temperature range 1650–1750°C [7–9], silicon will react with the constituents of charge that have lower affinity to oxygen than silicon to form SiO_2 . Then, SiO_2 will react with CaO and MgO to form low-temperature molten

silicates. The product of calcium silicate and magnesium silicate will react with molten silicon metal according to the reactions

The above reactions followed by the fact that calcium oxide has greater affinity to silica, and, therefore, it form more stable suitable silicate than magnesium oxide [10, 11]:

2. Aim and Scope

This paper aims at investigating the influence of bauxite, quartzite, limestone, and fluorspar on the extent of deviation of magnesium content from the predicted values by using the suggested model by Ghali [12]. This model used the following equation to calculate the magnesium content in the produced FeSiMg alloy:

$$[\text{Mg}] = \frac{(\text{MgO}_0)[\text{Si}_0] \left[e^{Kt[(\text{MgO}_0)-[\text{Si}_0]]} - 1 \right]}{(\text{MgO}_0) \left[e^{Kt[(\text{MgO}_0)-[\text{Si}_0]]} \right] - [\text{Si}_0]}, \quad (4)$$

where $[\text{Mg}]$ is the concentration of magnesium metal in ferrosilicon magnesium alloy in mol/L, $[\text{Si}_0]$ and (MgO_0) are the initial contents of silicon and magnesium oxide in charge, respectively, in mol/L, t the time in second, and K the reaction rate constant $3.26588 \times 10^{-7} \text{ L Sec}^{-1} \text{ mol}^{-1}$.

3. Experimental

The FeSiMg production data [13], which are produced by the experimental melting in a submerged arc furnace, are given in Tables 1 and 2. The molar concentrations of SiO_2 , Al_2O_3 , CaF_2 , and CaO were calculated.

The data [13] from the previous study was considered as the main source for the evaluation of the new model. The different production parameters were considered and correlated to predict the different relations and dependences in the product process.

The amount and effect of different additives on the recovery of magnesium and composition of the product alloy were considered. Magnesium content is measured by using wet analysis method [14].

4. Results and Discussion

The data used in this investigation were obtained from El-Faramawy et al. [13] and Ghali [12]. The effect of fluxes (limestone, fluorspar, quartzite, and bauxite) on magnesium content and recovery in FeSiMg production process was

investigated. The differences between the predicted values, by applying Ghali model [12], and the actual magnesium content and recovery in the FeSiMg alloy produced by metallothermic process using silicon as a reducing material [13] were considered. The results of four series of bench scale experiments having constant amount of dolomite with various weight percentages of limestone, quartzite, fluorspar, and bauxite, respectively (Table 1) were selected as the base for theoretical calculation.

Figure 1 shows the influence of weight ratio limestone/dolomite on the difference between the predicted and actual magnesium content. It indicates that the difference decreases by increasing limestone/dolomite mass content ratio up to 8 wt.%. Further increase of limestone wt.% results increases the difference between predicted and actual magnesium mass content. This figure also shows that at optimum limestone mass content the predicted values of magnesium mass content are in good agreement with the actual values. This could be attributed to two opposing effects. The first one is the effect of increasing CaO content in SiO_2 -rich slag leading to the formation of $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, and $\text{CaO} \cdot \text{SiO}_2$ [6, 15–19]. According to the thermodynamic data free energy of formation of pure crystalline silicate from their component oxides as given in (5) and (6) [9], these compounds are formed first and are very stable leading to free MgO to be reduced

The other one is the negative effect of increasing the content of these high melting compounds $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $\text{CaO} \cdot \text{SiO}_2$ with respective melting temperatures of 2070°C , 2130°C , and 1564°C , resulting in increasing the slag viscosity. Furthermore, the presence of CO_2 gas, from the decomposition of limestone, leads to more oxidation of magnesium. The outcome of these two opposite effects leads to an optimum value. In other words, the increase of the CaO content in the charge is accompanied by an increase in the activity of MgO in the slag. This is due to liberation of MgO from $\text{MgO} \cdot \text{SiO}_2$ and formation of $\text{CaO} \cdot \text{SiO}_2$ as shown in (5) and (6). This leads to increasing magnesium recovery and hence the gap between the predicted and actual magnesium content decreases. Further increase of limestone content is accompanied by an increase in slag viscosity. This is due to the formation of $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{SiO}_2$ which have high melting points 2070°C and 2130°C , respectively. This deteriorates the diffusion of reactants to the reaction zone. Thus increasing the difference between the predicted and actual magnesium content in the product alloy.

The effect of fluorspar content in the charge on the deviation of the actual magnesium content, given in Table 1 [13], from the predicted values using Ghali model [12] is illustrated in Figure 2. From this figure it is clear that the difference between the predicted magnesium contents

TABLE 1: Materials balance of the experimental heats.

Heat no.	Input, gm								Output		Predicted Mg mass content in %
	Dolomite	FeSi	Fluorspar	Limestone	Al	Quartzite	Bauxite	CeSo ₄	Metal mass	Mg mass content in %,	
1	1250	750	100	50				25	725	2.25	4.38
2	1250	750	100	70				25	590	2.86	5.30
3	1250	750	100	100				25	550	4.1	5.54
4	1250	750	100	130				25	430	2.0	6.90
5	1250	750	100	150				25	441.5	1.3	6.61
6	1250	600	160		50	50		25	480	1.7	5.48
7	1250	600	160		50	75		25	558	1.8	4.60
8	1250	600	160		50	100		25	622	3.2	4.04
9	1250	600	160		50	150		25	813	1.6	2.96
10	1250	600	40		50			25	750	1.76	4.11
11	1250	600	80		50			25	489	3.5	6.06
12	1250	600	120		50			25	550	3.5	5.19
13	1250	600	160		50			25	575	4.24	4.78
14	1250	600	200		50			25	595	3.25	4.45
15	1250	600	400		50			25	550	3.25	4.05
16	1250	950	160				50	25	983	2.45	3.19
17	1250	950	160				100	25	828	2.84	3.67
18	1250	950	160				150	25	731	3.05	3.99
19	1250	950	160				200	25	805	2.52	3.50
20	1250	950	160				250	25	750	2.63	3.62

FIGURE 1: Effect of limestone/dolomite weight% on the gap between the predicted and actual magnesium content.

FIGURE 2: Influence of fluorspar/dolomite weight% on the difference between the predicted and actual magnesium content.

and actual values decreases by increasing fluorspar/dolomite weight ratios in the charge up to 12.8 weight content in %. Further increase in the fluorspar percentage leads to a large gap between predicted and actual values of magnesium content.

Figure 3 shows the effect of quartzite/dolomite weight ratios on the deviation of the actual magnesium content from the predicted values. It is clear that the gap between the actual and predicted magnesium content decreases by increasing

quartzite/dolomite weight ratio up to 8 weight content in %. Further increase in quartzite/dolomite weight ratio leads to increasing the difference between the actual and predicted magnesium content.

On the other hand, increasing the bauxite content in the charge is accompanied by higher-degree deviation of the actual magnesium content from the predicted values as given in Figure 4.

TABLE 2: Chemical composition of the charge constituents.

Constituents	Chemical composition, mass content in %							
	Calcinated dolomite	Fluorspar	Rare earth metals	Limestone	Quartzite	Bauxite	FeSi	Al
SiO ₂	1.4	12.6		3.88	95	6.43		
Fe ₂ O ₃	1.45	0.35		0.5	0.2			
CaO	62.4		1	51.78				
MgO	33.6		1	0.6	0.3			
L.O.I. at 1000°C	0.43			41.3				
Al ₂ O ₃	1	2.4		0.8	2.5	85		
Na ₂ O			1	1.64				
K ₂ O				0.35				
CaF ₂		82						
CaCO ₃		2.2						
P ₂ O ₃			0.01					
CeO ₂ /ReO			45					
Fe			0.005	0.34	0.14		23.3	
Pb			0.001					
P ₂ O ₅		0.001						
SO ₃			0.03					
FeO						1.8		
C							0.09	
S							0.003	
P							0.031	
Al							1.41	99
Ca							0.31	
Si							74.8

FIGURE 3: Effect of quartzite/dolomite weight% on the difference between the predicted and actual magnesium content.

FIGURE 4: Effect of bauxite/dolomite weight% on the difference between the predicted and actual magnesium content.

Reduction of dolomite by ferrosilicon takes place according to the following sequence: (1) the diffusion of MgO and CaO through the slag layer to the slag/metal interface, (2) chemical reaction between the reactants at the slag/metal interface, (3) the transformation of the metal droplets through slag/metal interface to the molten metal,

(4) diffusion of non-metallic products of reaction through slag/metal interface to the slag layer. The diffusion rate of either the reactants or the products through the slag layer is controlled by the physical properties [20] of the molten slag. So, it is expected that the magnesium content will effectively be influenced by slag viscosity. Increasing viscosity of slag

obstructs the diffusion of reactants and products to and from the reaction zone. Therefore, lower degree of deviation of actual magnesium content from the predicted one—as given in Figure 2—can be a result of increasing the fluorspar content. This phenomenon could be attributed to an increase of the slag fluidity due to high fluorspar content, which results in a higher rate of metallic droplets diffusion. On the other hand, addition of more fluorides to silicate slag results in evolution of silicon tetra fluoride (SiF_4) vapour [21]. Also, there is a diffusion constant of silicon between metal and slag at a given temperature.

Therefore, as the slag is saturated with SiO_2 , the silicon content in the alloy increases also leading to lower deviation in magnesium content between the actual and predicted values as illustrated in Figure 3. With further addition of quartzite, the excess SiO_2 tends to form a less stable compound such as $\text{Ca}_3\text{Mg}(\text{SiO}_2)$ [22, 23]. This compound is dissociated to Ca_2SiO_4 with a high melting point leading to more viscous slag.

The obtained results also showed the negative effect of bauxite addition on the deviation of the actual magnesium content from the predicted values, which could be attributed to the higher viscosity of high alumina slag [24–28].

Figure 4 shows the effect of bauxite (alumina content) on the magnesium content and the difference between the predicted and actual magnesium content. It is clear that the difference between the predicted Mg mass content in % and the actual Mg mass content in % increases as the alumina increase. This behavior can be attributed to the effect of Al_2O_3 on the viscosity of slag. As Al_2O_3 content increases, the slag viscosity becomes higher. The high viscosity has negative significant effect on the diffusion rate. The diffusion rates of either the reactants or products through the slag layer decrease due to the effect of alumina. This leads to decrease in magnesium recovery and hence the gap between the predicted and actual magnesium content increases [13].

5. Conclusions

The following conclusions can be made.

- (i) The deviation between the actual and predicted magnesium content decreases as the magnesium content in the produced alloy increases.
- (ii) The highest magnesium content can be obtained using weight% of limestone/dolomite, quartzite/dolomite and fluorspar/dolomite 8, 8, and 12.8, respectively. This is in good agreement with the theoretically predicted values.
- (iii) The addition of bauxite decreases the magnesium recovery due to high viscosity.
- (iv) The physical properties, mainly the viscosity of the molten charge, play a significant role in the reduction process during the production of ferrosilicon magnesium alloy from dolomite.

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