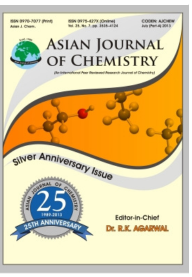
Asian Journal of Chemistry; Vol. 25, No. 7 (2013), 3897-3901

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13838



Thermodynamic and Experimental Analysis on Vacuum Silicothermic Reduction of MgO in Molten Slags

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(*Received*: 4 April 2012; *Accepted*: 16 January 2013) AJC-12719

Smelting reduction, a new magnesium production process, has been investigated. At high temperature, appropriate mixture of Al_2O_3 and SiO_2 with calcined dolomite can make charge to form molten slag and reduction reaction take place between liquid MgO and liquid ferrosilicon. Smelting reduction on molten slag of the compositon 55 % calcined dolomite (32 % CaO and 23 % MgO), 35 % Al_2O_3, 10 % SiO_2 reacted with ferrosilicon was studied. By thermodynamic analysing, the semlting reduction could react at 1873 K under atmosphere. The experiments of semlting reduction were carried out under vacuum for avoiding re-oxidation of Mg vapour and the results showed that reduction extent of MgO was achieved up to 97 % with 1X silicon stoichiometry at 1873 K for 2 h.

Key Words: Slag, Calcined dolomite, Smelting reduction, Thermodynamic analysis, Silicothermic reduction.

INTRODUCTION

Magnesium production by Pidgeon process uses ferrosilicon to reduce MgO from calcined dolomite and China becomes the largest primary magnesium producer in the world because of having abundant dolomite resources[1,2]. Reaction in Pidgeon process takes place in solid state, so the duration of completely-reduced MgO is quite long because of too slow reaction rate. Due to such disadvantages of Pidgeon process, it is necessary to develop new magnesium production technologys with low pollution and energy cost.

Smelting reduction technology is a new metallurgical process in which oxides in liquid slag state are reduced to liquid or gaseous metals. Smelting reduction takes place in liquid state, which can accelerate reaction rate and improve productivity. In recent years, smelting reduction has gained increasing importance to produce metal, such as Fe, Mn, Zn, Cr[3-6]. Most literatures on the Mg production from dolomite or Magnesite focused on solid phase reduction[7-11]. The studies on smelting reduction of MgO have seldomly published except for the patents. The reduction of MgO in molten slag with the composition of 5.6 % MgO, 48.1 % Al_2O_3 and 46.3 % CaO reacting with ferroaluminium (80 % Al and 35 % Al) had been reported by Capocchi and Rajakumar[12]. The content of MgO in slag was low and the composition of slag was not applied to smelting reduction of MgO from dolomite.

The aim of this work was to study silicothermic smelting reduction of MgO from calcined dolomite in molten slags though thermodynamic and experimental analysis. This research was expected to widen the understanding of the extraction for Mg from dolomite by smelting reduction.

Thermodynamic analysis: Calcined dolomite mainly composed of CaO and MgO(n_{CaO}/n_{MgO} = 1), together with a small amount of other oxide impurities(less 2 %). CaO and MgO are alkaline earth oxides and have very high melting temperatures. In order to get molten slag between 1773 and 1873 K, it is required to mix appropriate Al_2O_3 and/or SiO_2 with calcined dolomite.

At high temperature, MgO is liquid state in slag and reacts with liquid ferrosilicon as reducing agent. The overall reaction that occurs in this process can be expressed by the equation:

$$2MgO_{(l)} + Si_{(l)} = 2Mg_{(g)} + SiO_{2(l)} \qquad (1)$$

Because reactant MgO and resultant SiO_2 are liquid states in smelting reduction, before analyze thermodynamics of eqn. 1, it is necessary to calculate the standard enthalpy and entropy of these two liquid oxides under 1 atm and 298 K. As status function, enthalpy and entropy just lie on the first and finally status. So the melting process of solid oxides at 1873 K was shown in Fig. 1. The results of thermodynamic calculation were as follows: $\Delta H^{\circ}_{298(MGO)(l)} = -545.345$ kJ/mol,

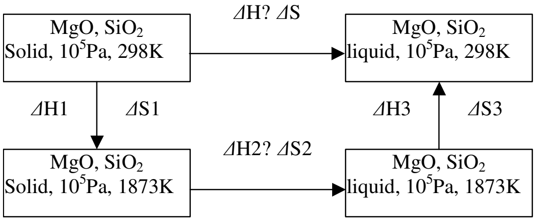

Fig. 1. Melting process of solid oxides

$\Delta S^o{}_{298(MgO)(l)} = 27.004$ J/(mol K), $\Delta H^o{}_{298(SiO_2)(l)} = -896.796$ kJ/mol, $\Delta S^o{}_{298(SiO_2)(l)} = 50.829$ J/(mol K).

Based on formula $\Delta G^o = \Delta H^o - T \times \Delta S^o$, the standard Gibbs free energy of eqn. 1 is depicted as follow:

$$\Delta G^o = 388745 - 176.84\ T \qquad (2)$$

By calculating eqn. 2, the starting temperature of silicothermic reduction of MgO in molten slag was above 2198 K under atmosphere. This temperature was higher than the maximum operating temperature of experimental furnace. Vacuum was used to decrease the starting temperature of silicothermic reduction and avoid re-oxygenation of Mg vapour. Moreover, activities of MgO and SiO_2 in slag and Si in ferrosilicon also affected smelting reduction process. From the above analyses, the reaction could not be processed under standard status in real reduction. The possibility of smetling reduction of MgO must be decided by the real Gibbs free energy (ΔG) and ΔG is given by the eqn. 3:

$$\Delta G = \Delta G^o + RT \ln K \qquad (3)$$

where R is gas constant and K is equilibrium constant.

The equilibrium constant K is defined as follow:

$$K = (P_{Mg}{}^2 \cdot a_{SiO_2})/(a_{MgO}{}^2 \cdot aSi) \qquad (4)$$

where P_{Mg} = magnesium vapour pressure at the slag metal interface, a_{SiO_2} = activity of SiO_2 in salg, a_{MgO} = activity of MgO in salg, a_{Si} = activity of silicon in the ferrosilicon alloy.

Simultaneous eqns. 2-4, relationship of ΔG to equilibrium temperature and pressure of system in different slag can be acquired.

In previous work, slag containing 55 % calcined dolomite and 45 % additive (Al_2O_3 and SiO_2) can be molten at 1873 K[13]. In this study,the chemical composition of experimental slag and activity of reactant and resultant were given in Table-1. By calculation, relationship of ΔG to equilibrium temperature and pressure of system in this slag were given in Table-2.

TABLE-1
CHEMICAL COMPOSITION OF EXPERIMENTAL SLAG [wt. %] AND ACTIVITY OF REACTANT AND RESULTANT

Chemical composition of experimental slag			Activity of reactant and resultant		
Calcined dolomite (CaO·MgO)	Al_2O_3	SiO_2	a_{Si} (75 % SiFe)	a_{MgO}	a_{SiO_2}
55	35	10	0.9	0.14	3.6×10^{-4}

It was well known from Table-2 that reduction of MgO in slag can react at 1873 K under atmosphere and higher temperature and/or lower system pressure can make smelting reduction process easier. During the smelting reduction, activity of SiO_2 will increase and activity of MgO and Si will decrease because of composition changes in slag and ferrosilicon. For avoiding re-oxidation of Mg vapour, vacuum will continue to be used in smelting reduction of MgO.

TABLE-2
RELATIONSHIP OF ΔG TO TEMPERATURE AND PRESSURE OF SYSTEM IN SLAG

T (K)	ΔG			
	P = 10^5 (Pa)	P = 10^4 (Pa)	P = 10^3 (Pa)	P = 10^2 (Pa)
1723	28138	-37831	-103800	-169769
1773	17674	-50210	-118093	-185977
1823	7209	-62589	-132387	-202185
1873	-3255	-74968	-146680	-218392
1923	-13720	-87346	-160973	-234600
1973	-24184	-99725	-175266	-250807

EXPERIMENTAL

Raw materials: The experimental dolomite ores were supplied by the Chongqing Haibo magnesium smelting Co., Ltd. The chemical composition of the dolomite sample was given in Table-3. The dolomite ores were calcined at 1273 K for 1 h and pulverized to powder which passed through the 200-mesh sieve.

TABLE-3
CHEMICAL COMPOSITION OF DOLOMITE [wt. %]

CaO	MgO	SiO_2	Burning loss
29.46	20.97	1.60	46.40

Pure grade Al_2O_3 and SiO_2 were used as slagging agents and CaF_2 of reagent grade was used as catalyst in this study. The chemical composition of experimental primary slag mixed by calcined dolomite and additive was given in Table-4.

TABLE-4
CHEMICAL COMPOSITION OF EXPERIMENTAL PRIMARY SLAG [wt. %]

CaO	MgO	SiO_2	Al_2O_3	CaF_2
33.08	22.92	9.45	32.55	3.00

The experimental ferrosilicon ores were used as reductant provided by the Chongqing Haibo magnesium smelting Co., Ltd. The chemical composition of the ferrosilicon sample contains in weight percentage: 76.4 % Si, 23.1 % Fe and others impurities. The ferrosilicon ores were ground with agate mortar and pestle. All of the powder passed through the 200-mesh sieve.

Equipment: The reduction process was carried out in the high-temperature vacuum furnace. The furnace was internally heated by using a regulated graphite resistance and had a maximum temperature of 1873 K and a limit vacuum 0.01 Pa. Chemical compositions of the slags were measured using X-ray fluorescence (XRF-1800).

Mineralogical investigation was analyzed by XRD (D/max 1200 X-ray diffractometer). The experimental conditions were as follows: 45 kV, 40 mA, no filter, $2\theta = 10$-80^o, continuous scan with rate 3 °/min and step size of 0.03°.

Experimental procedure: Charges consisting of calcined dolomite, Al_2O_3, SiO_2, CaF_2 and ferrosilicon were compacted into 10 mm-diameter and 30 mm-height pellets. The charged graphite crucible with 150 g mixture was laid in the furnace at room temperature. In order to help reduction processing, the system pressure was controled under 4-40 Pa. The experimental temperature was controled at 1773-1873 K due to the limitation of the maximum operating temperature of the furnace. After reduction processing under different experimental condition, the slag in graphite crucible was cooled to room temperature. The chemical composition and mineralogical investigation of the residue obtained were analyzed by XRF and XRD.

RESULTS AND DISCUSSION

Reduction extent of MgO was measured for the smelting reaction which takes place between MgO in molten CaO-MgO-Al_2O_3-SiO_2-CaF_2 slag and ferrosilicon under high-temperature and vacuum condition. The effect of temperature, CaF_2, reduction time and ferrosilicon stoichiometry were studied. The reduction extent of MgO in slag was defined by the eqn. 5:

$$\eta = \left[\frac{1 - W_{(MgO)t}}{W_{(MgO)0}} \times 100\ \%\right] \tag{5}$$

where $W_{(MgO)t}$ is the weight of MgO in the slag at any time t and $W_{(MgO)0}$ is the weight of MgO in the slag at t = 0, respectively.

Effect of reduction temperature: The variation of the reduction extent of MgO in slag at different temperatures is given in Fig. 2. The reduction experiments were carried out under vacuum for 1 h and n(Si)/n(2MgO) ratio of 1.0. The increase of reduction temperature from 1773 to 1873 K enhanced the reduction extent of MgO from 73.1 to 91.4 %, respectively.

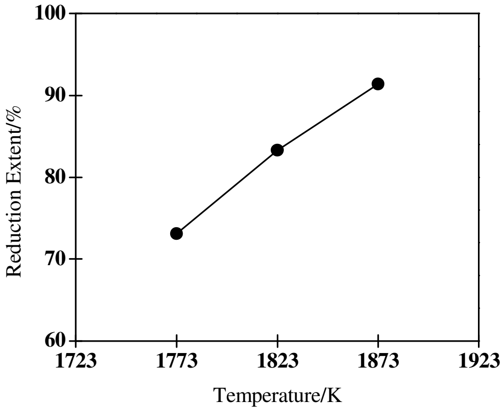

Fig. 2. Effect of temperature on the reduction extent of MgO in slag

From macroscopical pictures in Fig. 3, it is clearly observed that most of the charges didn't melt at 1773 K and reduction reaction took place mainly between solid oxide and liquid metal. When reduction temperature was above 1823 K, the charges formed melting slag and reduction became liquid-liquid reaction, so reaction rate accelerated with the increase of reduction extent of MgO.

The X-ray diffraction patterns of the primary slag in the absence of reductant and the residue after reaction with ferrosilicon at 1823 K for 1 h were shown in Fig. 4. The XRD analysis of the primary slag without reductant at high temperature revealed the formation of the phases $Ca_{12}Al_{14}F_2O_{32}$, Ca_2SiO_4 and $MgAlO_4$ as well as MgO. After the reaction of the primary slag and ferrosilicon at a constant temperature of 1823 K for 1 h, the main phase in residue slag was $Ca_2Al_2SiO_7$. The results indicated that the disappearance of the phases $MgAlO_4$ and MgO and the formation of $Ca_2Al_2SiO_7$ were due to the reduction of MgO by Si in molten slag.

Fig. 3. Macroscopical pictures for residue at different redution tempeture

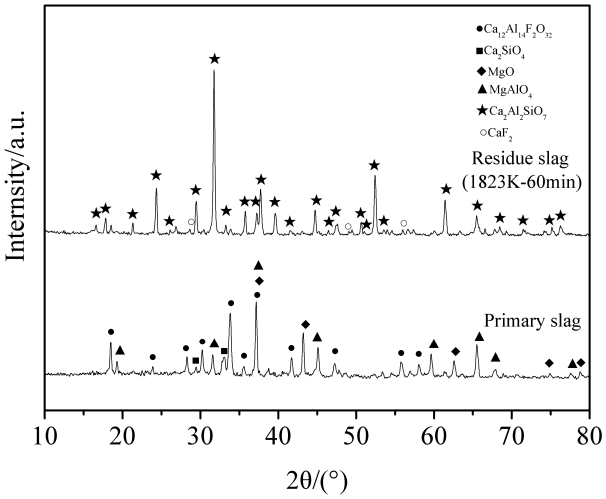

Fig. 4. XRD patterns of the slags in the absence of reductant and after reaction with ferrosilicon at 1823 K for 1 h

Effect of reduction time: The variation of the reduction extent of MgO in slag at different time was given in Fig. 5 and reduction experiments were carried out at 1823 and 1873 K for n(Si)/n(2MgO) ratio of 1.0. The reduction extent of MgO increased from 80.3 to 91.7 % when the reation time prolonged from 30 to 120 min at 1823 K. The reduction extent of MgO increased from 81.7 to 97.0 % as the reation time prolonged from 30 to 120 min at 1873 K, respectively.

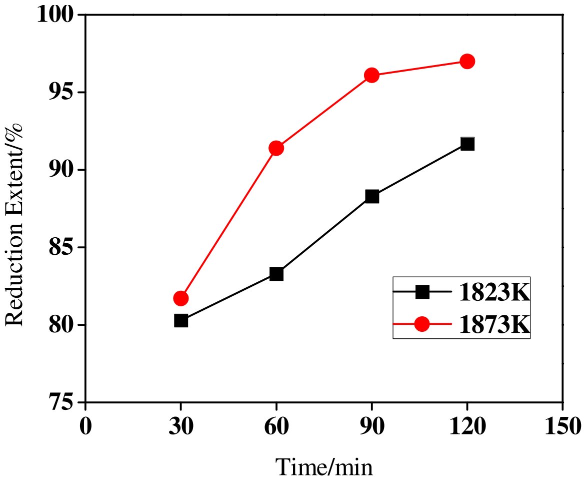

Fig. 5. Effect of time on the reduction extent of MgO in slag

The XRD patterns of the residues after smelting reduction process between the experimental slag and ferrosilicon at 1823 K for 30 min and 120 min were shown in Fig. 6. It was noticed that the phases of $MgAlO_4$ and $Ca_2Al_2SiO_7$ were both present with lower intensity in the residue slag for a shorter reduction time of 0.5 h while $MgAlO_4$ phase disappeared and $Ca_2Al_2SiO_7$ phase was present with higher intensity in the residue slag for a longer reduction time of 2 h. Based on the analysis results of the reduction extent of MgO in Fig. 5 and XRD patterns in Fig. 6, it is suggested that reduction reaction is not complete and the residue slag contains a small amount of $MgAlO_4$ at 1823 K for 0.5 h. With prolonging reaction time, the rest of the $MgAlO_4$ in slag was reduced continuously and more $Ca_2Al_2SiO_7$ was generated, so the diffraction peaks of the $MgAlO_4$ disappeared while the peaks of the $Ca_2Al_2SiO_7$ became higher when smelting reduction process was carried out at 1823 K for 2 h.

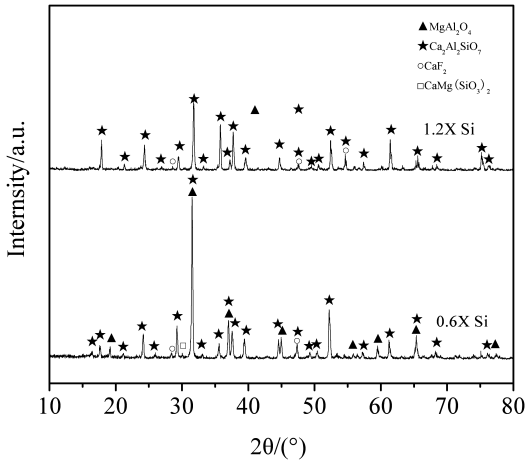

Fig. 6. XRD patterns of the residues after smelting reduction process at 1823 K for 30 min and 120 min

Effect of silicon stoichiometry: The variation of the reduction extent of MgO in slag added as a fuction of silicon stoichiometry to charge was given in Fig. 7. The reduction experiments were carried out at 1823 K for 30 min and 120 min. The silicon stoichiometry in the mixture was calculated according to eqn. 1. At a short reduction time of 0.5 h, the reduction extent of MgO increased from 49.3 to 83.5 % as silicon stoichiometry increased from 0.6 to 1.2 X. When reduction time prolonged 2 h, the reduction extent of MgO increased from 58.4 to 91.9 % while silicon stoichiometry increased correspondingly from 0.6-1.2 X.

The XRD patterns of the reduction residues for different silicon stoichiometry added to charge at 1823 K for 2 h is shown in Fig. 8. It was found that the main phases, identified as $MgAlO_4$ and $Ca_2Al_2SiO_7$ in the residues for the charge containing 0.6XSi and $Ca_2Al_2SiO_7$ in the sample of 1.2XSi The presence of $MgAlO_4$ in the residues for the charge containing 0.6XSi was due to lack of sufficient reductant. With the increase in silicon stoichiometry, more and more $MgAlO_4$ in slag was reduced by Si. The absence of $MgAl_2O_4$ phase and stronger characteristic peaks of $Ca_2Al_2SiO_7$ phase in the 1.2XSi sample are due to sufficient active Si, an excess of which can promote the reduction of residual $MgAlO_4$ and the formation of more $Ca_2Al_2SiO_7$ in the slag.

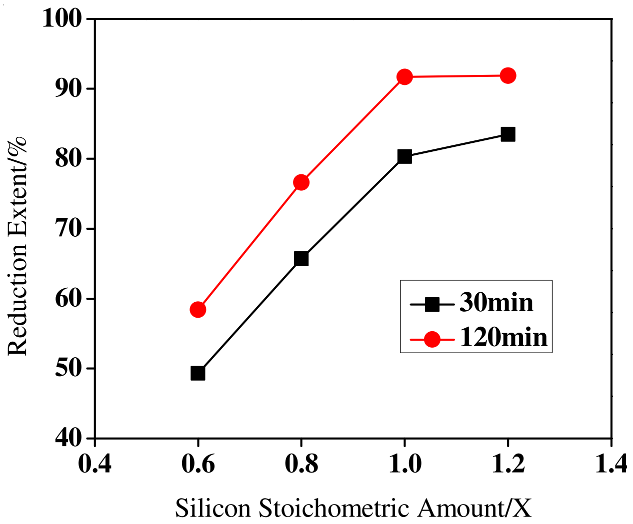

Fig. 7. Effect of silicon amount on the reduction extent of MgO in slag

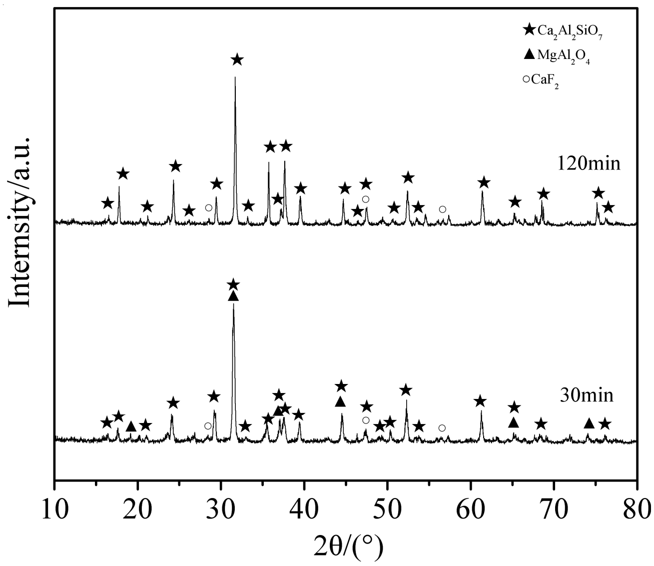

Fig. 8. XRD patterns of the reduction residues for different silicon stoichiometry added to charge at 1823 K for 2 h

Conclusion

- The thermodynamics analysis of smelting reduction of MgO by ferrosilicon indicated that the molten slag of the compositon 55 % calcined dolomite (32 % CaO and 23 % MgO), 35 % Al_2O_3 and 10 % SiO_2 could reduced by ferrosilicon at 1873 K under atmosphere.
- The smelting reduction experiments were carrid out under vacuum for avoiding re-oxidation of Mg vapour and protecting carbon tube furnace. With the increase in the reduction temperature as well as reduction time and silicon stoichiometry, reduction extent of MgO improved. Reduction extent of MgO was achieved up to 97.0 % when using the optional parameters of reaction temperature of 1873 K, n(Si)/n(2MgO) ratio of 1.2 and reduction time of 2 h.

ACKNOWLEDGEMENTS

The work was sponsored by Chongqing Science and Technology Commission under contract No. CSTC2009AB4109.

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