

INFLUENCE OF LIMESTONE CONTAINING REFRACTORIES ON THE ELEMENT CONTENT AND TOTAL OXYGEN CONTENT OF MANGANESE STEEL AT 1873K

Yaowu Wei, Nan Li, Yanlong Wang, Changsong Ye, Zhiqiang Liu

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan, China

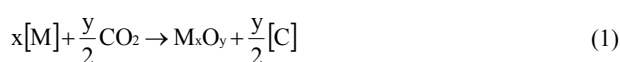
ABSTRACT:

Reactions between CO₂ gas from limestone containing refractories and [Mn], [C] in molten steel and its influence on carbon content, manganese content and total oxygen content of steel are investigated via vacuum medium frequency induction furnace. Limestone containing MgO-CaO refractory crucibles and manganese steel are used in this study. The interesting result shows that the total oxygen content of steel did not increase with the increment of limestone content in refractory crucible always, the latter continues release CO₂ gas under high temperature, but the carbon content of steel is continue increased. It can be concluded that the elements in steel were consumed by the reaction with CO₂ gas and the oxidation products were absorbed by refractory lining.

Key words: CO₂ gas; steel ; refractories; carbon content

INTRODUCTION

Free CaO is expected to exist in working lining of vessels for clean steelmaking, which can purify the steel liquid. Free CaO has the most superior high temperature stability among refractory oxides with extremely low oxygen potential index in liquid steel^[1], the fabrication of MgO-CaO refractories and its reaction with molten steel has been paid great attentions in recent years^[2-3]. But it is very difficult to fabricate refractories with free CaO aggregates directly because CaO aggregate is hydrated easily in the air. Limestone (namely CaCO₃) can be used as the CaO resource during refractories manufacturing process that used for tundish since last century and got satisfied results^[4]. However, due to the effects of thickness and structure of refractory lining on heat transfer and decomposition kinetics of limestone, limestone in refractories does not thoroughly decompose during preheating before application and even can be detected after casting sequence in the lining of tundish. It is possible that CO₂ gas from decomposition of the residual limestone would result in carbon pick up of steel in steelmaking via the reactions between CO₂ gas and elements in steel^[5] which is shown in equation (1).



Where, M represents the elements in steel, such as Mn, Si, Ti, Al.

The reactions between CO₂ gas from five different limestone containing refractories and main elements of steel liquid such as [C], [Mn] is studied. The purpose of this research is to investigate the influence of limestone containing refractories on the element content and total oxygen content of manganese steel, especially the carbon content of steel.

EXPERIMENTAL

Raw materials

The raw materials used in this study were fused magnesite [w(MgO), 96.85%] and limestone [w(CaO), 55.65%, w(ignition loss), 41.67%]. Elkem 968 Microsilica was used as the binder. The chemical composition of manganese steel was 1.424Mn-0.146C-0.364Si-0.040Al (wt %). The total oxygen content of manganese steel was 18ppm. The chemical composition of refining slag was 39.93SiO₂-10.21Al₂O₃- 10.58MgO- 32.31CaO - 1.12MnO- 0.63TiO₂-2.42FeO (wt %).

Experimental procedure

The raw materials were mixed according to the compounding that was shown in Table 1 and then it was fabricated in crucible shape (the inner size of crucible is Ø82mm×Ø90mm×160mm, the weight of refractory crucible is 9.8 kg).

Table 1 Formulations of crucible for experiments (wt %)

Number	A	B	C	D	E
Fused MgO	100	90	80	70	60
Limestone	0	10	20	30	40
Microsilica (in addition)	2	2	2	2	2

A: MgO crucible; B,C,D,E: MgO-CaO crucible

The crucibles were dried at 383K for 24hours and then the refractory crucible with 5.5kg manganese steel specimen was placed in vacuum induction furnace. Finally, the crucible with steel was heated under 1873K with flowing argon atmosphere.

100g refining slag was added into the crucible sooner after the steel was melt via a manually operation under Ar atmosphere . The illustration of the experiment is shown in Figure 1. The steel were sampled via quartz tube at regular intervals (The first sampling time was marked as zero minute and melting time was also marked as zero at this moment). The Mn and C content of steel samples was determined using ICP method (SHIMAZU ICP-1015, Japan), total oxygen content (hereinafter called TOC) of steel was determined via oxygen determinator (RO-416DR, USA). The steel samples were analyzed by SEM and EDS (XL30TMP Philips, Phoenix EDAS) .

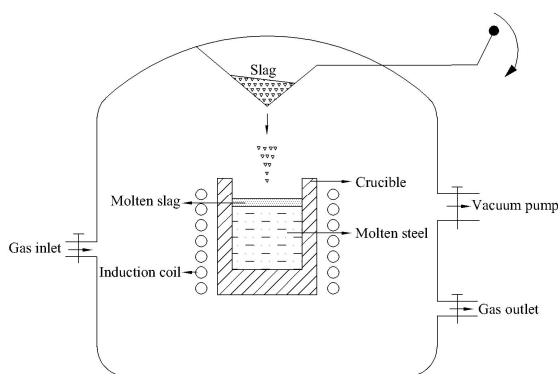


Fig.1 Illustration of experiment

RESULTS AND DISCUSSION

Total oxygen content of steel

Figure 2 shows the relationship between TOC of steel and sampling time. It can be seen from Figure 2 that TOC of steel increases quickly with the increment of sampling time for the first 30 minutes and then increases slightly. The TOC of steel that got from different limestone containing crucible did not differ from each so much at the end of experiment. TOC of steel that got from no limestone containing crucible was lower than that got from limestone containing crucible.

MnO was formed during the reaction between CO₂ gas and Mn in steel result in TOC of steel increase^[5]. On the other hand, oxides in the refractories such as MgO would dissolve into molten steel under such experiment condition and increase TOC of steel a little^[6]. This experiment was conducted in induction furnace, the liquid steel was kept stirring in the experiment that intensified the dissolving process of refractory oxides into steel.

Deoxidation and reoxidation process is co-existed in steel during the experiment. For example, Slag and refractory lining absorb oxide inclusions to decrease TOC of molten steel. Liquid phase formed in the matrix of refractories play an important role on the mass transfer between refractories and molten steel. This

liquid layer would separate molten steel from refractories and direct dissolution of refractory oxides into molten steel was stopped^[6]. The adsorption of refractories on inclusions of steel was not obviously at earlier stage of experiment and oxygen content was increased apparently for the steel sample got from limestone containing crucible. Reoxidation and deoxidation process reached equilibrium later and TOC of steel becomes stable because CaO in refractories plays an important role on inclusion adsorption due to its good adsorption capacity on oxide inclusions in steel^[7]. Yet the TOC of steel was increased rapidly with the increment of soaking time for the steel sample got from MgO crucible with non limestone containing although the TOC value was lower than that got from limestone containing crucible. The dissolution of MgO from MgO crucible in the steel result in TOC of steel increase a little, and the adsorption ability of MgO based refractories on oxide inclusions in steel was lower than that of CaO based refractories^[6] result in the increment of TOC of steel that got from no limestone containing MgO crucible continuously.

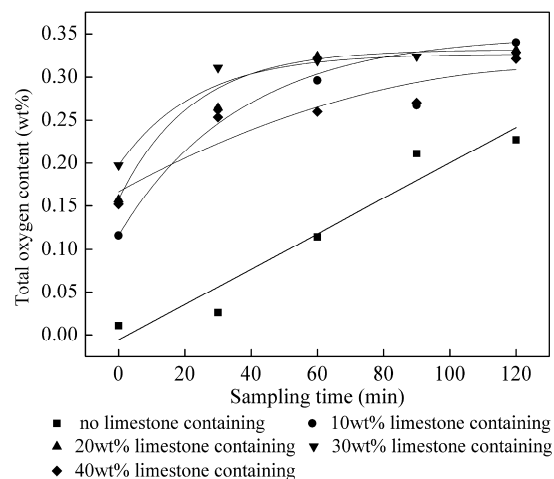
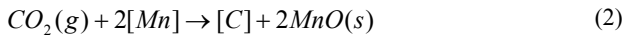


Fig.2 Relationship between TOC of steel and sampling time

Manganese content and carbon content of steel

Figure 3 shows the relationship between Mn content of steel and sampling time. Mn content of steel samples was decreased with the increment of sampling time, including samples from non limestone containing MgO crucible. But the Mn content of samples from limestone containing MgO-CaO crucible was much lower than that from non limestone containing MgO crucible.

[Mn] was consumed by the reaction between CO₂ gas and [Mn]. The related reaction is shown bellow and the calculation on Gibbs free energy was shown in reference 5 already.



$$\Delta G_{(2)}^0 = -393970 + 206.14T$$

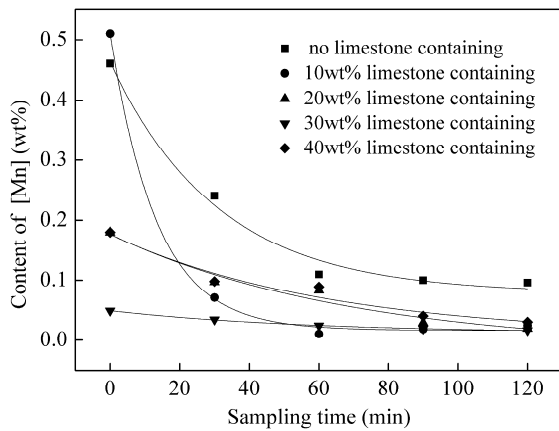


Fig.3 Relationship between [Mn] content and sampling time

Chemical composition of reacted layer and unreacted layer of refractories was shown in Table 2. Reacted layer of refractories is the hot face of refractories which contact with molten steel during experiment. Unreacted layer is the part of refractories in the cold face which does not contact with steel. It can be seen from Table 2 that MnO was found in the reacted layer of refractories, yet there was almost no MnO in refractory crucible before it contacted with steel. That implies Mn in reacted layer of refractories was come from steel which means the oxidation product MnO was adsorbed by refractory lining.

Table 2 Chemical composition of crucible (20% CaCO₃), wt%

	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	MnO	IL
UL	2.67	0.57	15.12	77.38	0.72	0.05	2.55
RL	3.14	1.80	11.03	76.08	1.65	0.57	4.86

UL:unreacted layer; RL: Reacted layer; IL:Ignition loss

Figure 4 shows the relationship between carbon content of steel and sampling time. It can be seen that carbon content in molten steel which smelted in MgO crucible decreased with the increment of sampling time. But carbon content of molten steel got from limestone containing MgO-CaO crucible was increased with the increment of sampling time, and it was much higher than that of MgO crucible.

The carbon content of steel got from MgO crucible was decreased due to carbon reacted with oxygen produced by refractory oxides. The carbon content of steel got from limestone containing MgO-CaO crucible was increased with

increment of sampling time was due to the reaction between CO₂ gas and [Mn] that was shown in Equation (2) and other similar reactions. The related oxidation products such as Al₂O₃, SiO₂, Fe₂O₃, MnO et al were absorbed by refractory lining as shown in Table 2. Figure 5 and Table 3 shows an typical analysis (SEM and EDS) results on steel sample taken from limestone containing crucible, from which it can be seen that inclusions has high carbon content and that comes from the decomposition of CO₂ because CO₂ is the only one carbon resource in this experiment.

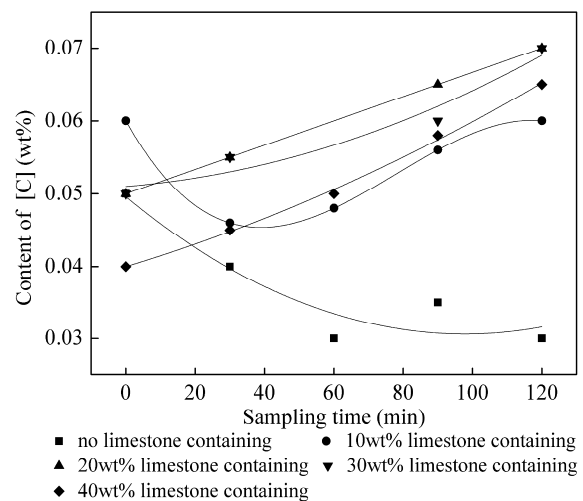


Fig.4 Relationship between [C] content and sampling time

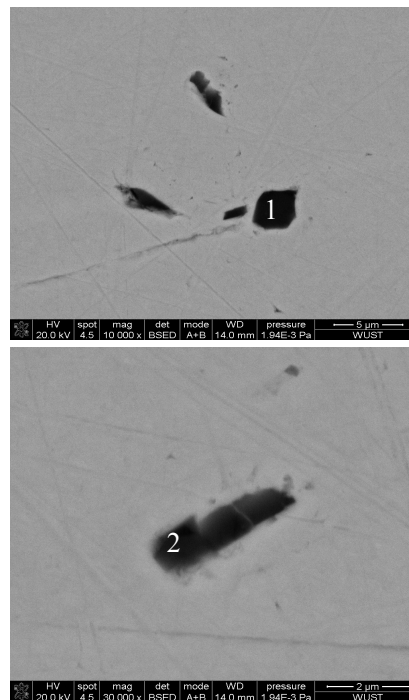


Fig.5 SEM photo on steel taken from limestone containing crucible (mass content in %, atomic mass fraction in %)

Table 3 EDS result of points in Fig.5

Point	C/O/Fe/Si	
	Mass	Atomic
1	39.68/1.54/9.19/49.59	61.98/1.81/3.09/33.13
2	32.93/11.56/42.39/13.12	62.01/15.65/17.17/5.18

The mechanism of reactions between CO₂ gas and the elements in molten steel and its effects on manganese, carbon and TOC of steel can be described as follows: CO₂ gas from refractories reacts with [Mn] and [C] in the steel until the reaction reaches equilibrium. The Mn in steel was oxidized by increasing oxygen potential due to CO₂ dissolved from refractory. The deoxidized products as MnO inclusions floated to the slag phase or directly absorbed by refractories. At the same time, carbon content was increased due to the reaction between CO₂ and elements of steel. The related oxidation products caused by CO₂ were absorbed by refractories (MgO-CaO lining). TOC and Mn content of steel got from different limestone containing crucible during experiment are getting closer at the end of experiment respectively. The inclusion amount was decreased with the increment of CaO content of crucible.

Crucible with 40wt% limestone shows best adsorption on inclusions among limestone containing crucibles. Reoxidation of steel was a result from oxides dissolution when experiment was done with MgO crucible and it was a slowly process.

It is important to point out that the weight ratio of "refractory crucible/steel" in the lab research was much higher than that in steelmaking plant, so the values such as TOC got from experiment was higher.

CONCLUSION

CO₂ gas from decomposition of limestone in refractories react with element of manganese steel such as Mn and C, which result in Mn content of manganese steel decrease. At the same time, total oxygen content and carbon content of manganese steel was increased. Total oxygen content of steel did not continuously increase with the increment of limestone amount in refractories always, and Mn content of steel got from crucible with different limestone amount was proximate after 2 hours. It can be concluded that the influence of CO₂ gas on total oxygen

content of steel was not increased with the increment of limestone amount in refractories always due to the good adsorption capacity of CaO in refractories on oxide inclusions.

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