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Effect of Al_2O_3 Content in Top Slag on Cleanness of Stainless Steel Fe-13Cr

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Abstract

The evolution mechanisms of Al_2O_3-SiO_2 system inclusion in 13Cr stainless steel with CaO-SiO_2-Al_2O_3 top slag were investigated from thermodynamic ,kinetic as well as experimental work.

From theoretical aspect: the stability diagrams of Ca-Si-Al-O and Mg-Al-O were obtained, From experimentally aspect: Increasing Al_2O_3 content in slag would low slag melting temperature and the usage of CaF_2. On the condition of relatively high Al_2O_3 in slag, the top slag would have a good kinetic condition. But excessive high Al_2O_3 in slag would increase total oxygen in stainless steel and cause a more complex series of slag-steel-inclusions reactions. Meanwhile, it is found that high basicity slag has good de-oxidation ability and it also accelerates the transition from high Al_2O_3 inclusions to low melt point CaO-Al_2O_3-SiO_2-MgO system inclusions. But excessive high basicity would have no effect on T.O and leads high content of [Al], [Mg] in liquid iron and which would promote the MgO-Al_2O_3 inclusions.

1 Introduction

The Fe-13Cr stainless steel is one important branch of the martensitic stainless steels. This kind of stainless steel, due to its high strength, high hardness and excellent corrosion resistance, is often used for pump shafts, screw bolts, and so on[1]. The nonmetallic inclusions' size distribution, morphology and chemistry has significantly effect on the stainless steel quality. Though inclusions formed unavoidable in the stainless steel, hard and high melt point inclusions must be reduced.

In stainless steel making, liquid iron-chromium alloys are deoxidized with silicon in many cases, due to the harmful effect of Al_2O_3 and MgO-Al_2O_3 inclusions on corrosion-resisting property of the materials. The ferro-silicon, which is applied in silicon deoxidation, always contains small amount of aluminum as an impurity [2]. SUZUKI[3] calculates Cr13% silicon–aluminum complex deoxidation phase stability diagrams, and points out that Al_2O_3-SiO_2 system inclusions could be easily formed in SiFe killed stainless steel even [Al] content is of quite low level. In fact, Al_2O_3-SiO_2 system inclusions are also hard and have high melt temperature. But little attention has been paid on such kind of inclusions. Much research has aimed at improving the quality of different steel grades by optimizing the composition of top slags[4][5]. Top slag plays important roles on transforming inclusion chemistry by slag-metal-inclusions reaction and also absorbing inclusions in refining process[4]. Thus, it is pretty important to grasp the influence of top slag on the transformation of Al_2O_3-SiO_2 system inclusion in Fe-13Cr stainless steel.

Two kinds of top slag are commonly used in steel production, one is CaO-SiO_2-CaF_2 based slag, and the other is $CaO-Al_2O_3$ based slag. $CaO-SiO_2-CaF_2$ based slag, due to its high basicity, has good deoxidation, good desulfurization and remove inclusions capacity [6][7]. However, high basicity slag has high melt temperature and low fluidity. So certain amount of CaF_2 is benifit to improve slag properties. However, addition of CaF_2 in top slag would enhance refractory erosion, meanwhile cause the environmental pollution. $CaO-Al_2O_3$ based top slag has a low oxidation potential, a low melting temperature, a low viscosity and it can improve steel cleanliness[8]. Although this $CaO-Al_2O_3$-based slag has excellent refining properties in both thermodynamics and kinetics, it hardly used in SiFe killed stainless steel. The reason is slag-steel reaction, high Al_2O_3 in slag cause more [Al] in liquid steel, which would promote Al_2O_3 and $MgAl_2O_4$ inclusions formation. The content of CaF_2 and Al_2O_3 in repoorted top slag are around 15% and 5% , respectively[9-12]. Few of study add further content of Al_2O_3 and reduce the usuage of CaF_2 in $CaO-SiO_2$-based slag.

Therefore, in the current study, the $CaO-SiO_2-Al_2O_3$ based slag equilibrium between the Fe-13Cr stainless steel under SiFe(Al) deoxidation was investigated to understand the effect of basicity and Al_2O_3 contents on the composition of $Al_2O_3-SiO_2$ system inclusions.

2 Experiment

2.1 Materials

The stainless steel was prepared in a vacuum induction furnace and then cast into ingot under a protecting atmosphere. Table 1 shows the chemical composition of the experimental stainless steel.

Top slags were prepared by pure CaO, SiO_2, Al_2O_3, MgO and CaF_2, in which CaO was obtained by calcining $CaCO_3$ (Analytical grade) at 1373 K for 6 h, and the rest oxides were dried at 1273 K for 4h in a muffle furnace. The powders were mixed in an agate mortar and then ready for experiments. In the current study, 5 experiments followed the same procedure except for adjusting CaO, SiO_2, MgO, and Al_2O_3, as shown in Table 1. Experiment No.1, No.2 and No.3, had the same content of Al_2O_3 with different basicity in top slag. Experiment No.2, No.4 and No.5 had the same basiccity with different content of Al_2O_3 in top slag. All Slags had the fixed content of MgO and CaF_2 to reduce disturbing factors.

Table 1 Chemical composition (wt %) of the stainless steel and synthetic slag

	C	Si	Mn	P	S	Cr	Ni	Al	Ca	Mg
Wt%	0.1159	0.557	0.3938	0.0187	0.0019	11.57	0.1195	0.004	0.0005	0.0005

No	CaO	SiO_2	Al_2O_3	MgO	CaF_2
1	0.44	0.24	0.16	0.1	0.05
2	0.48	0.21	0.16	0.1	0.05
3	0.49	0.19	0.16	0.1	0.05
4	0.51	0.22	0.11	0.1	0.05
5	0.44	0.19	0.21	0.1	0.05

2.2 Experimental

In a typical run, 400g of Cr13 stainless steel were contained in an MgO crucible (ID of 50 mm, OD of 55 mm, and height of 115 mm) and placed in a vertical $MoSi_2$ resistance furnace. After the molten steel reached 1873K under high purity Ar atmosphere, 0.2g Fe_2O_3 was added to the molten steel and then followed by 2.5gSiFe(73%Si,2%Al) addition to start deoxidation. 10minutes later, 70g synthetic slag was then added to the molten steel surface. The time when the slag addition completed was defined as the starting time (Time Zero). Thereafter, steel samples were taken at the times of 15, 30, 45, 60, 90minutes and quenched in water.

The concentrations of Ca, Mg and Al in the steel samples were measured by ICP-AAS or ICP-MS. The total oxygen were analyzed by Oxygen/Nitrogen determinator (TCH600). Inclusions were analyzed by SEM with EDS (FEI Quanta 250). Each sample was observed ten view field under 500X(0.034mm^2), and random select 10 inclusions for composition comparison.

3 Results

3.1 Variation chemical composition in Steel

The variations of steel chemical compositions are shown in Figure.1. As shown in Figure 1a, the calcium contents in each heat were varied in the range of 0.0005～0.0015% ,during the reaction process. In addition, the content of [Ca] slightly increased with the increase of slag basicity and Al_2O_3 content. As shown in Fig1b, the content of [Al] in stainless steel is proportional to slag basicity and Al_2O_3 content. The content of [Al] in stainless steel also increase with the reaction time. The content of [Mg] in experiment is shown in Fig1c. From the No.3 experiment and No.5 experiment we can obtain that excessive high basicity and excessive high Al_2O_3 would case the content of [Mg] severe changes in stainless steel. The content of [Mg] in the rest experiment is stable.

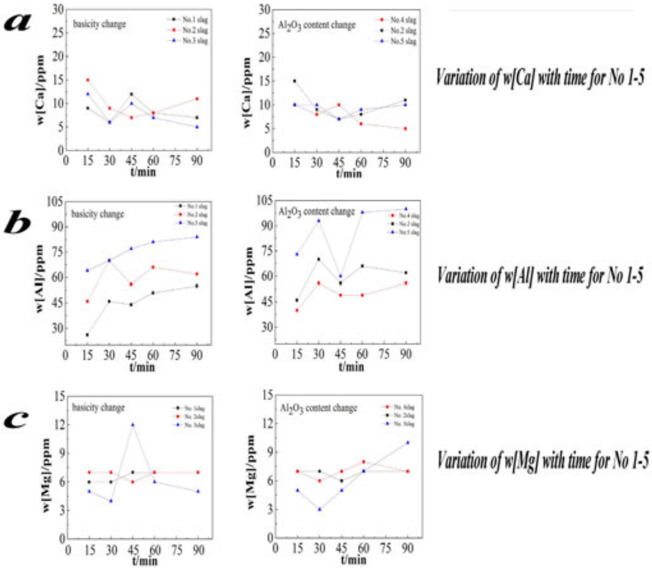

Figure 1. The evolution of [Ca]，[Al] and [Mg] in experiment No.1-5

As shown in Figure 2a, the total oxygen content decreased as the increase of basicity, but when the slag basiccity is over about 2.3, the total oxygen content will tend to be stable. High content of Al_2O_3 in top slag would lead high content of T.O in liquid iron.

The content of [Si] in experiment No.3 is shown in Figure 2b, which is used to characterize the variation of [Si] in all experiments. The content of [Si] had a quickly decrease for the direct deoxidation at the beginning of the reaction process and had a small change after 15min. The content of [Si] was 0.86% at the end of reaction process.

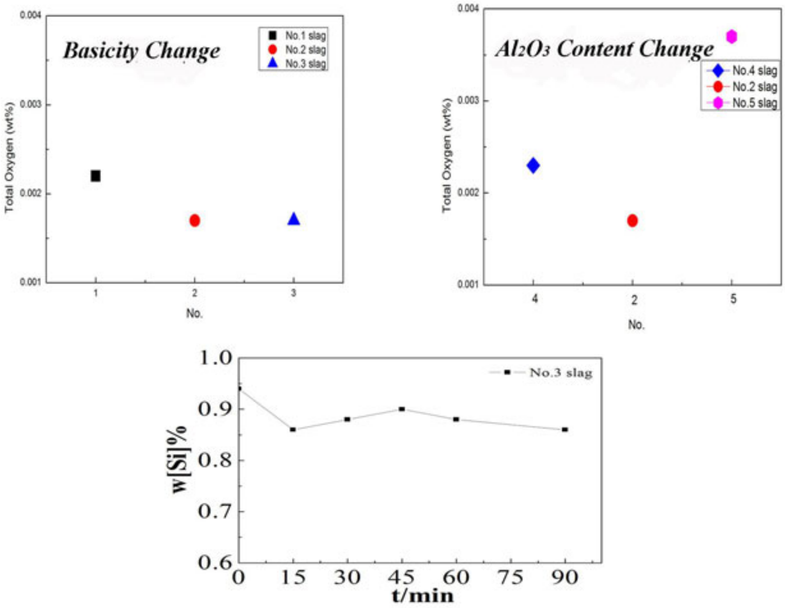

Figure 2. The content of T.O in experiment No.1-5 and the content evolution of [Si] in experiment No. 3

3.2 Variation of inclusions

The morphologies of inclusions in steel sample were observed by SEM and their chemical compositions were analyzed using EDS attached to SEM. The ferro-silicon, which was applied in experiment, contained 2% of aluminum as an impurity. Therefore, the silicon deoxidation changed to complex deoxidation of silicon and aluminum. The Al_2O_3-SiO_2 system inclusion was observed after deoxidation in experiments. Some of these inclusions contained trace of CaO, MgO and MnO. These inclusions consist mainly of spherical or spheroidic shape. The composition mass ratios of Al_2O_3 and SiO_2 in these inclusions were around 3: 2.

Figure3 (a)-(e) give the variations of the inclusion compositions in different experiments. The Al_2O_3-SiO_2 system inclusions serve as deoxidation product were observed in three experiments. In No.1 experiment, inclusions were SiO_2-Al_2O_3-CaO-based inclusion at 15min, and the average content of Al_2O_3 in inclusions increased to 60% at 30 - 60 min. However, inclusions after 90 min reaction were partly low melting temperature CaO-SiO_2-Al_2O_3-MgO-based inclusions although a few high-Al_2O_3-based inclusions existed. In No.2 experiment, inclusions were high-Al_2O_3-based inclusion at 15min and 30min. Inclusions after 45 min reaction, were mainly low melting temperature CaO-SiO_2-Al_2O_3-MgO-based inclusions. However, the average content of MgO in inclusions was increased with reaction time and even pure MgO inclusions were observed. In No.3 experiment, two categories of inclusions were observed, viz $MgO-Al_2O_3$-based inclusions and $Al_2O_3-SiO_2-CaO-MgO$-based inclusions. $MgO-Al_2O_3$ based inclusions refer to high MgO-contained or even pure MgO inclusions. In No.4 experiment, two categories of inclusions were observed, one was $SiO_2-CaO-Al_2O_3-MgO$-based inclusions, and the other was high-Al_2O_3-based inclusion at 15min. There also were two categories of inclusions at 30min, low melting temperature $CaO-SiO_2-Al_2O_3-MgO$-based inclusions and high melting temperature $MgO-Al_2O_3$-based inclusions. The average content of MgO in inclusions was increased with time like experiment No.2. Inclusions were mainly low melting temperature $CaO-SiO_2-Al_2O_3-MgO$-based inclusions at 90min. In No.5 experiment the main part of inclusions at 15 min was high Al_2O_3 inclusion just like No.1 experiment. But $MgAl_2O_4$ wrapped by $CaO-SiO_2-Al_2O_3-MgO$-based inclusions were observed at 30 to 90min. Inclusions after 90 min reaction were partly low melting temperature $CaO-SiO_2-Al_2O_3-MgO$-based inclusions and a few high-MgO-based inclusions were appeared.

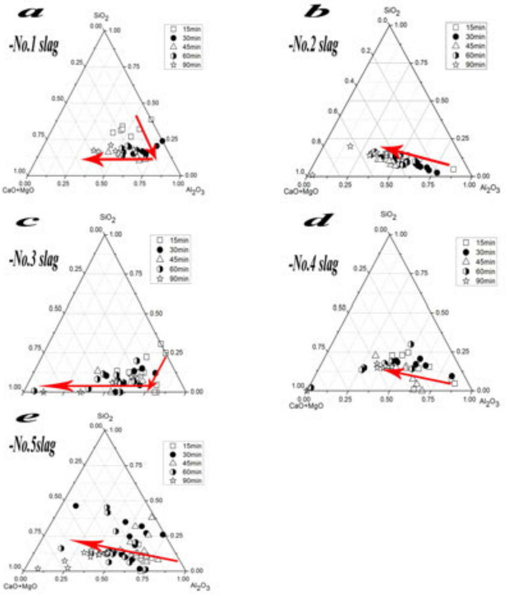

Figure 3. Composition evolution of typical inclusions observed in experiment No. 1-5.

From the Figure 3 we can obtain the inclusions evolution during the treatment. The first, $Al_2O_3-SiO_2$ system inclusions were generated after SiFe(Al) alloy added into liquid steel. The second, $Al_2O_3-SiO_2$ system inclusions change to high Al_2O_3 complex inclusions after the top slag added onto the liquid steel. The third, high Al_2O_3 complex inclusions change to low melting temperature $CaO-SiO_2-Al_2O_3-MgO$-based inclusions or $MgO-Al_2O_3$ system inclusions with reaction time. The forth, two kinds of inclusions would change to high MgO complex inclusions, even pure MgO inclusions at the end of experiment.

4 Discussions

4.1 Formation Mechanism of CaO-SiO_2-Al_2O_3 system inclusions

Thermodynamic calculations were carried out to evaluate evolution of inclusions in Cr13 stainless steel. Formation of CaO-SiO_2-Al_2O_3 system inclusions was calculated.

$2[Ca]+2[Al]+[Si]+7[O]=2CaO \bullet Al_2O_3 \bullet SiO_2(s)$ $\triangle G° = -3190946+861.23T$[13] Equation(5)

$2[Ca]+[Si]+4[O]=2CaO \bullet SiO_2\,(s)$ $\triangle G° = -1964532.7+482.904T$ Equation (6)

$14[Al]+12[Ca]+33[O]=7Al_2O_3 \bullet 12CaO\,(s)$ $\triangle G° = -16229612+4241.48T$[14] Equation (7)

$2[Al]+[Ca]+4[O]=Al_2O_3 \bullet CaO\,(s)$ $\triangle G° = -1867356.4+513.77T$ Equation (8)

$4[Al]+[Ca]+7[O]=2Al_2O_3 \bullet CaO\,(s)$ $\triangle G° = -3066221+892.98T$ Equation (9)

$12[Al]+[Ca]+19[O]=6Al_2O_3 \bullet CaO\,(s)$ $\triangle G° = -7883217.5+2433.46T$ Equation (10)

$2[Al]+3[O]=Al_2O_3\ (s)$ $\triangle G° = -867209.2+222.5T$ Equation (11)

Table 2 Interaction coefficient used in calculation[15]

j	Al	Si	Cr	C	Ni	O	Mn	S
e_{Si}^{j}	0.058	0.103	-0.021	0.18	-0.009	-0.119	0.0042	0.066
e_{Al}^{j}	0.043	0.056	0.012	0.091	-0.029	-1.98	0.035	0.035
e_{Mg}^{j}	-0.12	-0.088	0.047	-0.31	-0.012	-460		
e_{Ca}^{j}	-0.072	-0.097	0.02	-0.34	-0.044	-5600[16]	-0.007	-140

All relevant chemical equations and interaction coefficient are now known from present work and previous data listed in Table 2 and Equation 5-11 by other researchers; the rest of $\triangle G°$ was calculate by using FactSage6.4 software (Datebases:FToxid, FactPS; Reaction module).The a_{Ca}, a_{Al}, a_{Si} and a_O represent Henrian activity of [Al],[Ca],[Si]and [O] based on infinitely dilute solution in liquid iron and $a2CaO \bullet Al_2O_3 \bullet SiO_2$ is Raoultian activity of $2CaO \bullet Al_2O_3 \bullet SiO_2$ based on pure solid $2CaO \bullet Al_2O_3 \bullet SiO_2$ and the activity of the product is unity, the same as in other equations. Assuming that local equilibrium between the inclusions and the molten steel is maintained. The phase stability diagrams are quantified by solving simultaneous equations based on the Gibbs principle of minimum free energy and mode of Wagner. The dissolved oxygen content was taken as 0.0001% when activity coefficients of aluminum and calcium were estimated. Figur.6a has shown the calculated stability diagram of Si-Ca-Al-O system in the Fe-13Cr stainless steel.

The liquid area in 1873K covered $2CaO \bullet Al_2O_3 \bullet SiO_2$, $Al_2O_3 \bullet CaO$ and $7Al_2O_3 \bullet 12CaO$ is shown in Figure 4a. The Figure 4a show the content of [Ca], [Al] in 90min sample. As seen in Figure.6a, three relatively high basicity experiment date point located in liquid area, excessive high basicity experiment date point and excessive high Al_2O_3 content experiment located in solid area. This result indicate that high content of [Al] in molten steel is not helpful inclusions plastic. Besides, relatively high basicity top slag and enough reaction time could make inclusions plastic. The thermodynamic calculation shows a good agreement with experimental results. The range content of [Al] in SiFe deoxidation stainless steel is shown in Figure.6a, and in this area the low melt point inclusions is $2CaO$-Al_2O_3-SiO_2.

4.2 Formation Mechanism of Mg-Al-O system inclusions

Spinel inclusions are harmful to both the quality of products and the castability of the steel because of their high melting temperature and high hardness[17]. Steelmakers have been always making great efforts to control the population of $MgAl_2O_4$ in stainless steel. A stability diagram for Mg-Al-O system can be calculated as shown in Figure 4b. It was established based on the Gibbs principle of minimum free energy and mode of Wagner. Here, the way how to calculate the diagram is explained.

The following reaction was considered to calculate the $MgO/MgAl_2O_4$ boundary.

$$4MgO(s)+2Al= MgAl_2O_4+3[Mg] \qquad \log (K)=-33.09+50880/T^{[18]} \qquad \text{Equation (12)}$$

To calculate the $MgAl_2O_4/Al_2O_3$ boundary, the following reaction was considered.

$$3\ MgAl_2O_4\ (s)+2[Al]=4Al_2O_3\ (s)+3[Mg] \qquad \log(K)=-34.37+46950/T^{[18]} \qquad \text{Equation (13)}$$

Fujii[19] give the activity of MgO was taken as unity because of negligibly small solubility of Al_2O_3 into MgO while that of $MgAl_2O_4$ as 0.80 in $MgO/MgAl_2O_4$ boundary, the activity of $MgAl_2O_4$ was taken as 0.47 in $MgAl_2O_4/Al_2O_3$ boundary, while that of Al_2O_3 as unity because of negligibly small solubility of MgO into Al_2O_3.

Both high basicity and high Al_2O_3 content in slag can lead high content of [Al] and [Mg] in stainless steel. Therefore, it's not appropriate for high basicity slag add high content of Al_2O_3. The content of Al_2O_3 in slag and slag-steel reaction time are not the more, the better, but has a limitation.

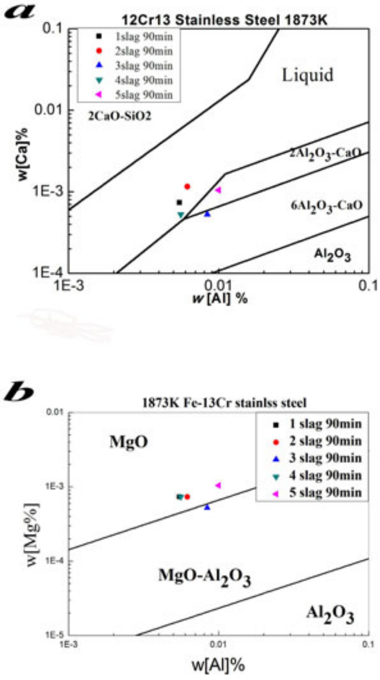

Figure 4. Effects of Al - Ca content Al - Mg content on the inclusion compositions for Fe-13Cr stainless steels at 1873K

5 Conclusions

Ladle treatment of Fe-13Cr stainless steel was simulated on a laboratory scale. The effects of slag chemistry on the steel and inclusions' compositions were discussed with thermodynamic considerations. The steel cleanliness in terms of factors for different types of slag are compared.

The main results are as follows:

1. Add right amount of Al_2O_3 in a relatively high basicity slag would reduce the usage of CaF_2. Those Al_2O_3 in slag didn't lead $MgO-Al_2O_3$ formation in stainless steel.

2. Relatively high basicity slag has good deoxidation ability and it also accelerates the transition from high Al_2O_3 inclusions to low melt point $CaO-Al_2O_3-SiO_2-MgO$ system inclusions. High basicity slag also has a good effect on absorb inclusions. But excessive high basicity has no effect on T.O, but causes high content of [Al] in liquid iron which would promote the $MgO-Al_2O_3$ formation.

3. In the same basicity level, inclusions evolved to $CaO-MgO-Al_2O_3-SiO_2$ system instead of spinel inclusions with increasing Al_2O_3 content in top slag. However, when Al_2O_3 content reached 21% or higher, complex inclusion as Mg-Al-O system wrapped by $CaO-MgO-Al_2O_3-SiO_2$inclusion was generated. Moreover, the relative higher Al_2O_3 content also increase the T.O in stainless steel and has a negative effect on absorb inclusions.

3. In SiFe(Al) alloy killed stainless steel, $Al_2O_3-SiO_2$ system inclusion formed at initial as expected, and then change to Ca-Mg-Al-Si-O complex inclusions characteristic with high Al_2O_3 composition， which composition was near to Al_2O_3 corner in $Ca(Mg)O-SiO_2-Al_2O_3$ diagram. The modification role of top slag on inclusions made the inclusion composition to relative lower melting point region. A proper reaction time is necessary to obtain low melting point inclusions, but long reaction time would lead to generate high-MgO inclusion.

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