

Research on the Deoxidation Performance of High Titanium Ferro Prepared by Thermite Reaction

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Abstract: Due to the defects of high aluminum residue and high oxygen residue, high titanium ferro alloy prepared by thermite reaction outside the furnace cannot be directly used in liquid steel refining process. In this paper, thermodynamics of the high titanium ferro with high aluminum used in liquid steel refining process were studied, and then effects of the amount and content of aluminum in high titanium ferro on the liquid steel refining process were also studied. The results indicate that using Ti and Al as composite deoxidizers, the deoxidizing product at 1873 K is Ti_2O_3 when the a_{Ti}/a_{Al} in liquid steel is above 8; in fact, however, only when the a_{Ti}/a_{Al} value in liquid steel is above 10, Ti_2O_3 precipitates as deoxidizing product. Using high titanium ferro with high aluminum content as deoxidizer, the content of aluminum and titanium in liquid steel can meet the requirements of composition for the related steel. With the increasing amount of high titanium ferro, inclusions in cast steel after refining transform from silicate into Ti-Al-Mn composite inclusions; at the same time, obvious or part of radial acicular ferrite forms around those inclusions, which refines the microstructure of steel. The a_{Ti}/a_{Al} value in the actual system is 17.78 (>8), which is consistent with the theoretical results. It is vital to control the values of a_{Ti}/a_{Al} in the liquid steel when the oxygen content in liquid steel is high.

Keywords: deoxidation in liquid steel; inclusions; thermite reaction; oxides metallurgy

High oxygen content in the liquid steel will lead to secondary oxidation of carbon during the process of condensation, which results in the bubble defects in solid steel, and the precipitation of FeO, Fe_3O_4 and other oxygen phases, thus causing the defects of hot and cold brittleness and the decrease of plasticity. Therefore, deoxidation refining has become one of the most critical links in modern steelmaking process, and its aims are as follows^[1]: one is to reduce the content of dissolved oxygen in steel, while the other is to minimize the suspended oxide inclusions in the liquid steel by making deoxidizing elements react with oxygen to generate liquid compound deoxidation product and then discharge from the liquid steel as soon as possible. In recent years, the concepts of “clean steel” and “zero inclusion” had been put up in the metallurgical sector^[2]. Takamura et al.^[3] first proposed the concept of oxides metallurgy and conducted a systematic research on the oxides of Ti, Zr and Re, and then unanimously agreed that the ideal deoxidation products were oxides of the titanium. Most scholars hold that TiO and Ti_2O_3 were the most effective nucleation agents of acicular ferrite^[4].

Many dispersion and small titanium oxide particles could be formed in the liquid steel when deoxidizer of Ti is added, which could make the grain of steel finer, thus increasing the hardness and strength of steel^[5]. The titanium deoxidation experimental results of low carbon microalloyed steel and automotive titanium deoxidizing non-hardened and tempered steel show that the structure of steel after titanium deoxidation was refined, and the size of inclusions decreased obviously^[6-10].

Researchers at home and abroad mostly think the titanium deoxidation product in liquid steel exists in the form of Ti_2O_3 , but there are no enough demonstrable experiments^[11]. Researches by Cha et al.^[12, 13] show that Ti_2O_3 will appear when the content of titanium in the Fe-Ti system is more than 0.25%. Jung^[14] calculated the thermodynamics of Al_2O_3 - Ti_2O_3 - TiO_2 system, and the results show that Al_2TiO_5 will appear when the $P_{O_2} > 1$ Pa. Researches by Kim^[15] show that Al_2O_3 , Ti_2O_3 and Ti_3O_5 are the stable phases at 1873 K in the Fe-Al-Ti-O system. When conducted the research on the composite Ti-Al deoxidation, Wang^[16] found that the

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thermodynamic stable phase was Al_2O_3 at the Ti/Al ratio of 1/4 and 1/1, but there was an obvious trend to produce transitional titanium oxide at the Ti/Al ratio of 1/1; and the thermodynamic stable phase was Al_2TiO_5 when the Ti/Al ratio increased to 15/1, and the shapes of inclusions turned from sphere into irregular shape; and the thermodynamic stable phase was Ti_3O_5 at the Ti/Al ratio of more than 75/1. Researches by Sun^[17] found that the morphology and composition of oxide inclusions changed significantly, and the inoculation time also changed obviously when different amounts of Al-Ti deoxidizer were added to the liquid steel at 1873 K. Researches by Wang^[18] found that inclusions in the liquid steel turned from $(FeO)_n \cdot (MnO)$ into Al_2O_3 when aluminum was added to the ultra-low carbon liquid steel containing titanium to deoxidize; and the inclusions of $Al_2O_3 \cdot TiO_x$ and TiN would appear at the Ti/(Al+Ti) ratio of 0.15~0.30 when titanium iron was added to deoxidize. Researches on Ti-Al deoxidation by Yang^[19] show that the inclusion of Ti_3O_5 is easy to generate when the content of oxygen is high. Researches on the deoxidation by Wang^[20] show that the key is to control the content of oxygen, aluminum and nitrogen in liquid steel in order to promote the precipitation of Ti_2O_3 at the initial stage of solidification. Researches deoxidation by Liu^[21] show that the large size solid solution of $Ti_2O_3-Al_2O_3$ will appear in liquid steel if the $w[Ti]/w[Al]$ is not controlled, which will lead to the nozzle clogging.

Therefore, different deoxidizers have great influences on the effects of deoxidation on liquid steel and the inclusions as well as its microstructure. Titanium as a deoxidizer has obvious effects of deoxidation on the liquid steel in the numerous deoxidizer; therefore titanium iron as deoxidizer draws attention widely. Over many years, high titanium ferro prepared by thermite reaction as deoxidizer cannot be applied in China for its high content of oxygen. The authors have invented a new method of the intensify aluminothermy reduction to prepare high titanium ferroalloy with low O and Al contents, which has successfully prepared high titanium ferroalloy with oxygen content less than 0.6% and aluminum content less than 0.4%. However, its deoxidation effects, especially on the condition of Ti and Al as composite deoxidizers, are still unknown. In this paper, based on thermodynamic analysis, the deoxidation performances of high titanium ferro with high aluminum prepared by thermite reaction as deoxidizer in the liquid steel were systematically researched.

1 Experiment

The liquid steel in this experiment was prepared by melting scrap, and its chemical composition is shown in Table 1. The content of oxygen of the liquid steel scrap is more than 560 $\mu\text{g/g}$.

The components of the refining slag as premelted slag used during the refining deoxidation process in the liquid steel are

shown in Table 2 and its basicity is 4.

Table 1 Composition of scrap steel (wt%)

C	Si	Mn	P	S	Al	Ti
0.186	0.287	1.710	0.024	0.021	0.038	0.012

Table 2 Composition of refining slag (wt%)

CaO	SiO ₂	MgO	Al ₂ O ₃	CaF ₂
40	30	10	15	5

The equipment was a medium frequency induction furnace named SPZ-160; the crucible used in this experiment was clay crucible, which was coated with a layer of magnesite lining about 13 mm.

First, put 5 kg scrap in the medium frequency induction furnace and heat to 1873 K to melt it; and after fully melted, take a sample with quartz pipe named 0# to test its initial composition. And then add 250 g pre-melted slag into the liquid steel, and put deoxidizer wrapped by the high titanium ferro pipe into the bottom of the liquid steel (the specific scheme of deoxidizers as shown in Table 3) to complete delivery. After the delivery of deoxidizers, take a sample every 3 min for 5 times, and the label change from the first batch to the fifth batch. And then cast the molten steel to a high purity graphite mould cooling to room temperature and take samples to test.

Dissolve the oxidable surface of the samples with dilute, and then wash them with alcohol and dry it. The oxygen content of samples (0.5 g) was examined by N/O analyzer (Bruke D8, Germany), and the chemical composition of samples was examined by ICP (Liman-Prodigy, USA).

A cylinder sample was taken from the steel after deoxidation, and then ground by turn with sandpaper from 240 to 3000, and then polished with diamond polishing paste, followed by washing. Finally, erode it with nitric acid alcohol (4 wt%) and clean with alcohol. The samples after treatment above were examined after treatment above by scanning electron microscope (SU-8010, Japan) and metallographic analysis.

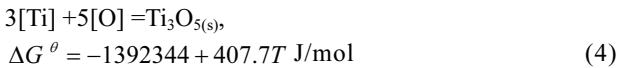
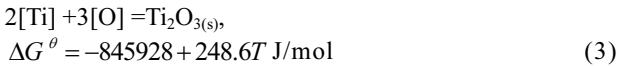
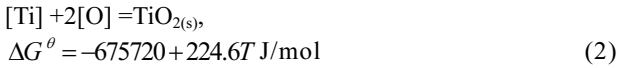
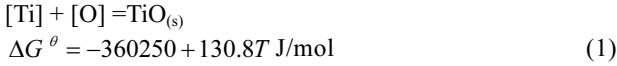
2 Results and Discussion

Table 3 Investigated factors of experiments

Batch	Compositions of deoxidizer/wt%			Amount of alloy/g
	Ti	Al	O	
1	49.61	8.07	<0.60	14
2	61.65	7.34	<0.60	14
3	61.87	4.88	<0.60	14
4	63.34	10.17	<0.60	14
5	68.90	7.24	<0.60	14
6	68.90	7.24	<0.60	21
7	68.90	7.24	<0.60	28

2.1 Thermodynamic analysis of deoxidation

The phase diagram of Ti₂O₃-TiO₂^[11] shows that titanium oxides such as TiO, TiO₂, Ti₂O₃ and Ti₃O₅ form during the process of deoxidation in liquid steel. And the related reactions are as follows^[22]:



Being calculated by equations from (1) to (4), the equilibrium of titanium and oxygen when titanium oxides precipitate at 1873 K is shown in Fig.1, which shows that the sequence of titanium oxides precipitating in the liquid steel at 1873K is first Ti₂O₃, and then TiO₂ and Ti₃O₅, and last TiO if the content of dissolved oxygen in the liquid steel is below 0.003%.

The aluminum in the high ferrotitanium alloy prepared by thermite reaction as a deoxidizer is inevitably involved in reactions during the deoxidation process. Therefore, it is a composite deoxidation using high titanium ferro with high aluminum as a deoxidizer, and titanium and aluminum will compete with each other to react with oxygen. Binary diagram of Ti₂O₃-Al₂O₃ shows that Ti₂O₃ and Al₂O₃ will be generated in liquid steel together during the deoxidation process, and Ti₂O₃ and Al₂O₃ possibly coexist in solid. And it shows that the activity of Ti₂O₃ increases and the activity of Al₂O₃ gradually decreases with the increase of aluminum content at 1873 K^[23].

During the deoxidation process in the steel liquid, the thermodynamic equilibrium of Fe(l)-Al₂O₃-Ti₂O₃ system can be calculated by the G^θ of reactions when [Ti] and [Al] coexist on the given conditions. Reaction equilibrium between titanium and oxygen, aluminum and oxygen at 1873 K is listed as follows:

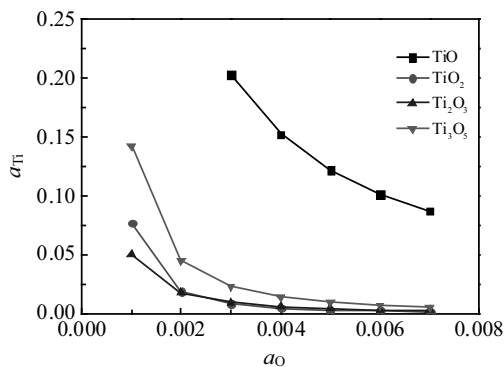
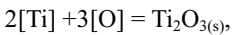
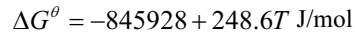
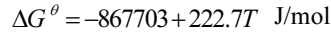
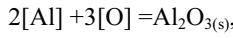


Fig.1 Equilibrium between Ti and O for generating a variety of titanium oxides at 1873 K

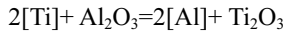


$$\lg K = \frac{56043}{T} - 18.07 \tag{5}$$



$$\lg K = \frac{63655}{T} - 20.58 \tag{6}$$

The reaction between titanium oxide and aluminum oxide calculated by the equations (5) and (6) is as follows:



$$\lg \frac{a_{Ti_2O_3} a_{Al}^2}{a_{Al_2O_3} a_{Ti}^2} = -\frac{7940}{T} + 2.49 \tag{7}$$

Formula (7) shows that the activity of inclusions precipitating in the liquid steel has much to do with the activity of aluminum and titanium (a_{Ti}/a_{Al}), just as Fig.2 shows.

Fig.2 shows that without considering the interaction coefficient between the different elements and the impact of oxygen content, oxygen content in the liquid steel is controlled by titanium and the deoxidation product is Ti₂O₃ at 1873 K, on the condition that the activity of Al₂O₃ and Ti₂O₃ are both 1 and the activity ratio of Ti and Al ($a_{Ti}/a_{Al} > 8$) is 8, when using Ti or Al alone as a deoxidizer, or the deoxidation products is not solid solution. In fact, Al₂O₃ and Ti₂O₃ can form a solid solution on the condition that the activity ratio of Ti and Al ($a_{Ti}/a_{Al} > 8$) should be controlled more than 10 to ensure small enough in liquid steel to guarantee the deoxidation product to precipitate in the form of Ti₂O₃.

Therefore, when aluminum participates in the deoxidation process, the amount of titanium must be increased to ensure the deoxidation product precipitates in the form of Ti₂O₃. But excessive titanium will lead to a large amount of titanium deoxidation products in molten steel, resulting in the deterioration of steel properties. Thus, low content of the oxygen must be ensured in the liquid steel to make sure that

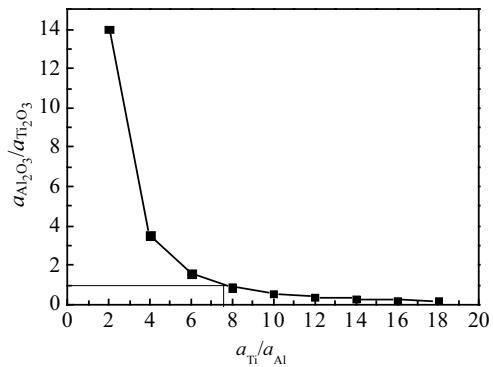


Fig.2 Relationship between activity ratio of deoxidation products and a_{Ti}/a_{Al} of liquid steel at 1873 K

the deoxidation product precipitates in the form of Ti_2O_3 .

2.2 Deoxidation results analysis

Table 4 shows the chemical composition of cast steel after deoxidation.

Fig.3 shows the variation curves of oxygen contents in liquid steel during the deoxidizing process.

Comparing the aluminum content in the steel before and after deoxidation in Table 1 and Table 4, it is known that the aluminum content in the steel after deoxidation in the first batch increases evidently, and the fifth one is basically unchanged; others decrease evidently. The titanium content in steel after deoxidation in the seventh batch increases evidently (from the initial 0.012% to 0.031%), and the third is basically unchanged, and the others decrease evidently. It is reasonable that the aluminum during the deoxidation process does not remain in steel, and may exist in the slag in the form of inclusions, using high titanium ferro with high aluminum content as a deoxidizer.

Species deoxidized with titanium include mainly bridge steel, line steel, non-quenched and tempered steel etc. And the contents of Si, Mn, Al and Ti in the bridge steel (16Mnq) are $0.2 \leq Si \leq 0.6$, $1.2 \leq Mn \leq 1.6$, $0.02 \leq Ti \leq 0.2$, $Al \leq 0.015$; the contents of Si, Mn, Al and Ti in line steel (X70) are $Si \leq 0.4$, $Mn \leq 1.7$, $Ti \leq 0.06$, $0.015 \leq Al \leq 0.06$; the contents of Si, Mn, Al and Ti in non-quenched and tempered steel (30MnVS) are $0.15 \leq Si \leq 0.8$, $1.2 \leq Mn \leq 1.6$, $0.015 \leq Ti \leq 0.025$, $0.01 \leq Al \leq 0.04$. Compared to the actual chemical composition, the other components meet their requirements except for Mn, and the oxygen content is 150 $\mu g/g$ after deoxidation. Thus, the oxygen content in the liquid steel has already met the requirements of steelmaking after deoxidation with high titanium ferro of high aluminum content as a deoxidizer and the aluminum content in the liquid steel does not increase, which indicates that it has a good effect on the deoxidation in the liquid steel, being applied in the refining.

The titanium and aluminum are both deoxidizer, the interaction coefficients between each element in molten steel with Al, Ti and O at 1873 K are shown in Table 5.

$$\lg a_i = \sum e_i^j [j] + \lg [i] \tag{8}$$

Where e_i^j stands for the interaction coefficient of the element j to i in liquid steel.

According to the chemical compositions of the steel after deoxidation in Table 4, the a_{Ti} , a_{Al} and a_O during the deoxidation every batch were calculated by formula (8), which is shown in Table 6, and $[a_{Ti}/a_{Al}]$ in this table is the ratio of the activity when the Mn content is 1.5%.

2.3 Deoxidation effect of different component deoxidizers

After deoxidization experiment, the steel ingot was sampled by wire cutting machine, the cross-section was ground and polished, and the cross-section structure was observed by metallographic microscope after etched and corroded by 4%

nitric acid alcohol solution. Trials from first to forth batch in Table 1 examined the deoxidation effect of different component titanium-ferro alloy in the liquid steel. Fig.4 shows the metallographic, SEM and EDS analysis of pre-deoxy-cast scrap. Fig.5 shows the metallurgical analysis of rear-deoxy-cast scrap.

Fig.4 shows that there are inclusions of silicate and a small amount of alumina in the pre-deoxy-cast scrap, and the majority of the inclusions are spherical, the particle size of these inclusions are large diameter, and the diameter of a portion inclusions is up to 5 μm .

Fig.5 shows that cast microstructures of the deoxy scrap are significantly refined after deoxidation using high titanium ferro with high oxygen content as a deoxidizers. And the cast microstructures of the deoxy scrap are mostly fine acicular ferrite structures and the size of inclusions is small. The nucleation of ferrite does not merit the crystal boundary of original austenite (similar to the place with arrow labelled), and there is no eutectoid ferrite along with the grain boundaries.

The ferrite in the solidification structure of the steel before deoxidation is mostly lath-shaped and grow along with the prior austenite boundaries to austenite grain inside, and the ferrite strip in the crystal is also wide.

Table 4 Chemical composition of cast steel after deoxidizing (wt%)

Batch	Composition of deoxidizer		Si	Mn	Ti	Al	O
	Ti	Al					
1	49.61	8.07	0.50	0.20	0.002	0.083	0.049
2	61.65	17.34	0.20	0.14	0.003	0.013	0.031
3	61.87	4.88	0.42	0.17	0.013	0.020	0.032
4	63.34	10.17	0.20	0.14	0.011	0.026	0.021
5	68.9	7.24	0.71	0.45	0.004	0.039	0.041
6	68.9	7.24	0.31	0.31	0.010	0.010	0.023
7	68.9	7.24	0.51	0.27	0.031	0.016	0.015

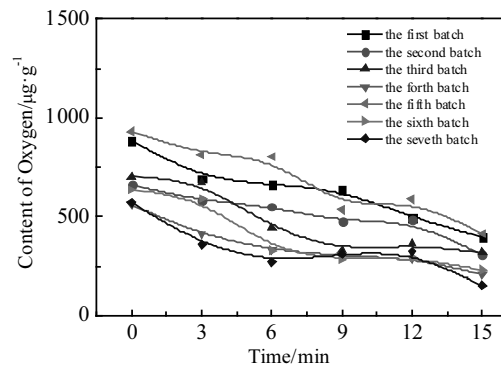


Fig.3 Variation curves of oxygen contents in liquid steel during the deoxidation process

Table 5 Interaction parameters between elements in liquid steel at 1873 K

<i>i</i>	e_i^j				
	<i>j</i> =Al	<i>j</i> =Ti	<i>j</i> =Mn	<i>j</i> =Si	<i>j</i> =O
Al	0.043	0.004	0.0065	0.0056	-1.98
Ti	0.0037	0.049	-0.43	2.1	-1.03
O	-1.17	-1.12	-0.021	-0.131	-0.17

Table 6 Values of a_{Ti} , a_{Al} and a_O

Batch	a_{Ti}	a_{Al}	a_{Ti}/a_{Al}	a_O	$[a_{Ti}/a_{Al}]$
1	0.0164	0.0670	0.2438	0.0332	0.0659
2	0.0028	0.0113	0.2476	0.0296	0.0568
3	0.0746	0.0342	2.1775	0.0225	0.7587
4	0.0784	0.0183	4.2816	0.0168	1.1259
5	0.0228	0.0217	1.0500	0.0348	0.2663
6	0.0310	0.0090	3.4148	0.0196	1.0284
7	0.2686	0.0151	17.7815	0.0112	6.1858

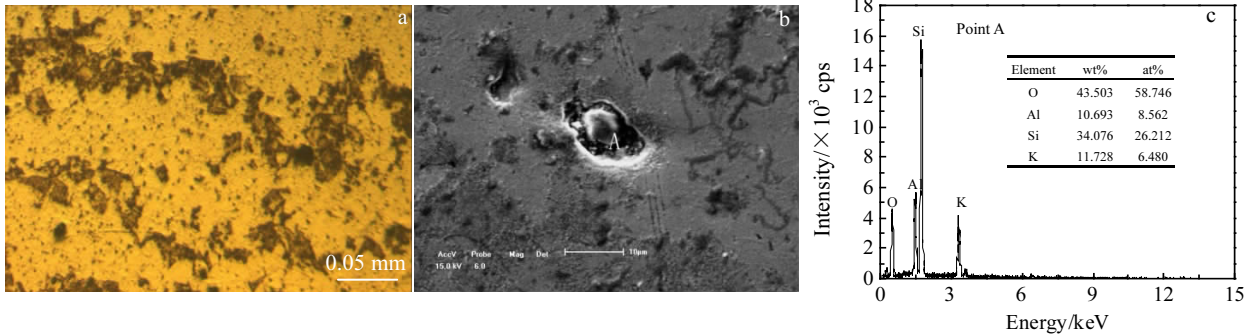


Fig.4 OM (a), SEM image (b), and EDS analysis (c) of inclusions before deoxidation

The titanium content in the steel of the first batch (Fig.5a) is similar to that of the second (Fig.5b) after deoxidation using high titanium ferro as a deoxidizer, and the contents of aluminum and oxygen are much higher than those of the second batch. The microstructure in the first batch is much coarser than that of the second batch. Comparing the third (Fig.5c) and fourth (Fig.5d) batch, the contents of aluminum and titanium are similar. However, the oxygen content of the third batch is much higher than that of the fourth batch. Compared with the microstructure of the fourth batch after deoxidation, the microstructure of the third batch is significantly refined, the microstructure of the steel after deoxidation using high titanium ferro as a deoxidizer is significantly improved and refined with the increase of the titanium content.

Fig.6 shows the SEM and EDS analysis results of cast steel after deoxidation using titanium ferro with different composition. EDS element mapping of Fig.6e~6h are in correspondence with the points (A~D) in SEM images (Fig.6a~6d). Inclusions and its surrounding tissue in the deoxy-cast steel change significantly (Fig.6a~6d). The EDS analysis indicates that inclusions in the steel are essentially silicate and Al_2O_3 , and most of inclusions contain Al, Ti and a small amount of Mn. SEM images in Fig.6 show that the microstructures of the deoxy scrap are significantly refined after deoxidation about 1~2 μm , while there is no acicular ferrite structures. Therefore, inclusions in the cast microstructures of the deoxy scrap of the first batch are significantly more and high aluminum content, and the size is too large, which indicates that the effect of deoxidation is not ideal.

The results of activity calculated in Table 6 show that, the a_{Ti}/a_{Al} of the first and second batches are both less than 1

during deoxidation refining process, and there are no titanium oxide inclusions to form judging from the thermodynamic results calculated. EDS analysis shows that there is no Mn in inclusions of the first batch steel, which indicates that there is no TiO_x formed in the liquid steel when the titanium content in the high titanium ferro deoxidizer is 49.61%, for the lack of titanium. However, the titanium oxide is the nucleation site for the inclusion of MnS. So the effect of the refining in the first batch is not obvious. The effects of the refining obviously increase with the titanium content in the high titanium ferro deoxidizer increasing to more than 60%, and the microstructures of the deoxy scrap from second to fourth batch are obviously refined and the oxygen content in the steel decreasing significantly. Comparing the third and fourth batch, it is known that the fine acicular ferrite structures induced by the titanium oxide inclusions have an increasing trend with the increase of the titanium content in the high titanium ferro deoxidizer, and the titanium content in inclusions is higher. The silicate of inclusions increases, while the titanium content decreases when the aluminum content is high in the deoxidizer. It can be speculated that the aluminum content in the deoxidizer has a relatively large impact on the formation of titanium oxide and cast microstructure. The results of activity calculated in Table 6 show that, the a_{Ti}/a_{Al} values in the third and fourth batch are 2.18 and 4.28, respectively. Combining the images of SEM, it can be speculated that some less obvious acicular ferrite structures begin to appear around the inclusions in the deoxy steel of fourth batch. The inclusions of aluminum will give priority to generate during the deoxidation refining process, and high aluminium content will inhibit the formation of titanium oxides.

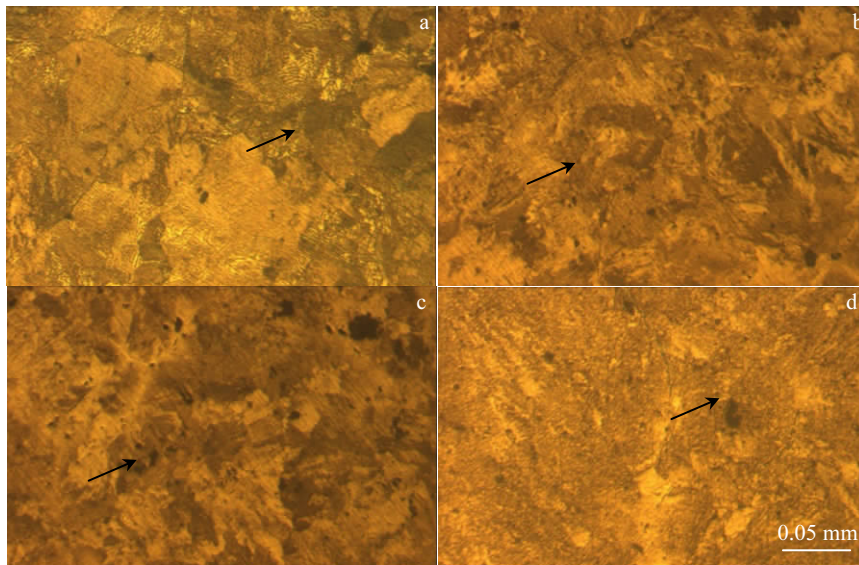


Fig.5 Microstructures of the cast steel after deoxidizing: (a) the first batch, (b) the second batch, (c) the third batch, and (d) the fourth batch

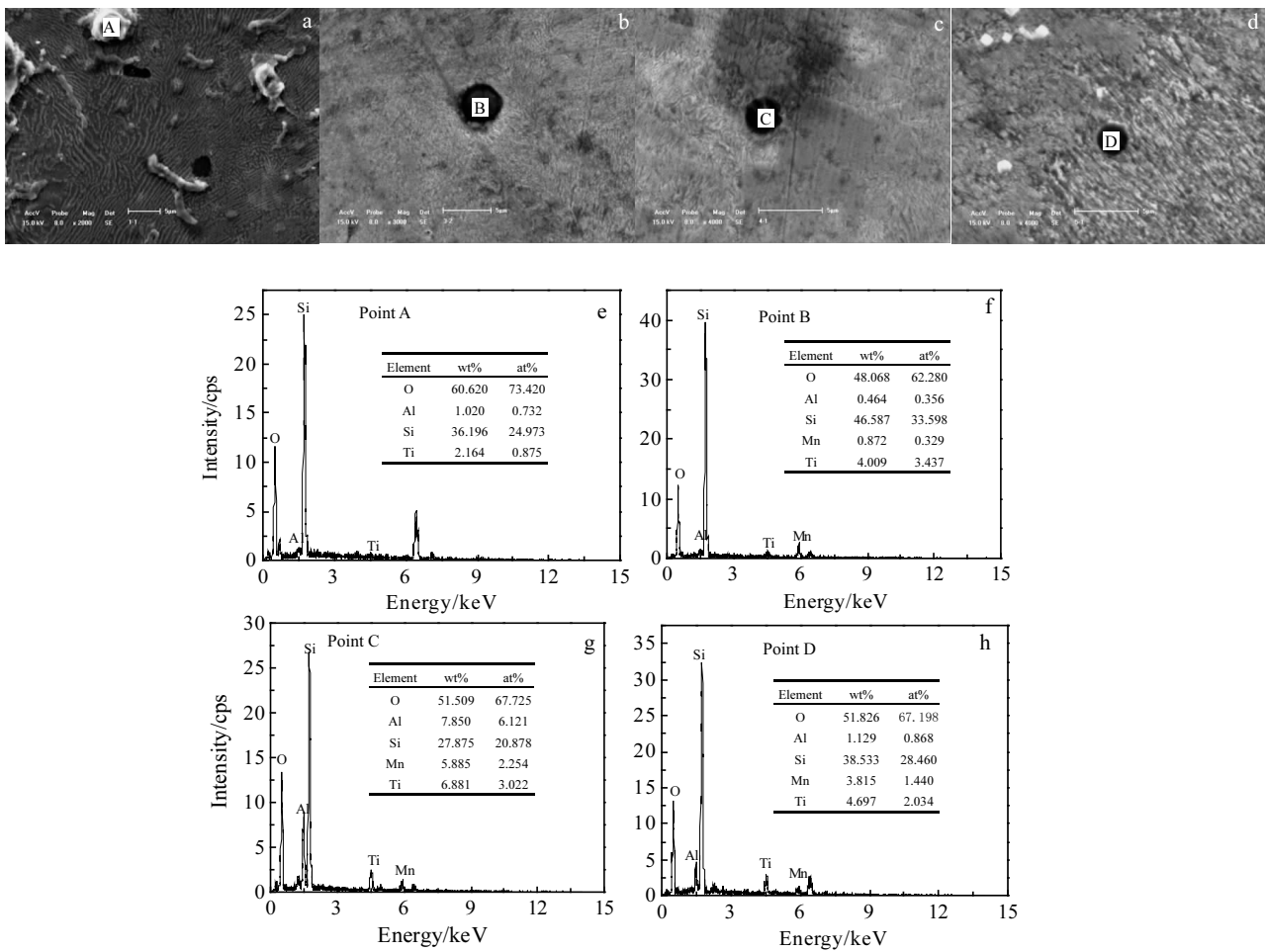


Fig.6 SEM images (a~d) and EDS analysis (e~h) of inclusions after deoxidation: (a, e) the first batch; (b, f) the second batch; (c, g) the third batch; (d, h) the fourth batch

2.4 Deoxidation effect of different amounts of deoxidizer

Trials from fifth to seventh batch in Table 3 examined the deoxidation effects of different amounts of the deoxidizer. Fig.7 shows the metallographic photographs of the cast microstructure of the steel when the different amounts of deoxidizer were used. Fig.7 indicates that the microstructures of the deoxy scrap are obviously refined with the increase amount of deoxidizer. Obviously significant acicular ferrite in the microstructure of the steel has been observed when the amount of deoxidizer is 21 g (in the sixth batch, Fig.7b), and the size of acicular ferrite is much finer and there are less inclusions when the amount of deoxidizer is 28 g (in the seventh batch, Fig.7c). Therefore, high titanium ferro deoxidizer with high aluminum content in steel refining could refine the microstructure of the steel well and change the existing state and morphology of inclusions. The analysis results of chemical composition in Table 4 show that the titanium content significantly increases and the aluminum

content decreases greatly with the increasing amount of deoxidizer, which indicates that the deoxidation effect of refining is obvious. At the same time, the microstructure is significantly refined indicating that titanium plays a significant role in refining the structures of the steel during the deoxidation process.

Fig.8 shows the SEM images (Fig.8a~8c) and EDS analysis (Fig.8d~8f) of cast steel after deoxidation with different amounts of deoxidizer. It can be seen that the microstructures of the deoxy scrap are significantly refined and the size of inclusions is decreased with the increasing amount of deoxidizer. The inclusions are about 1 μm in size with uniform distribution when the amount of deoxidizer is 28 g (Fig.8c, 8f). EDS analysis indicates that the amount of silicate inclusions significantly decreases after deoxidation refining with the increasing amount of deoxidizer, and the silicate inclusions disappear when the amount of deoxidizer is up to 28 g. The inclusions in steel after deoxidation refining are mainly composed of Ti-Al-Mn.

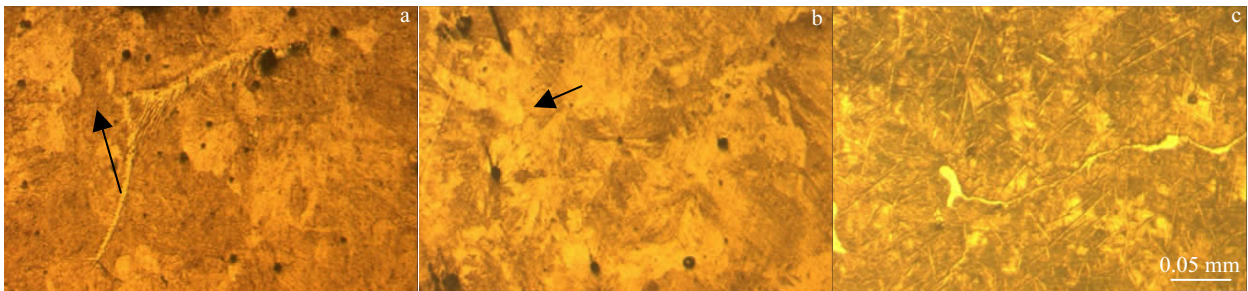


Fig.7 Micrographs of the cast steel: (a) the fifth batch, (b) the sixth batch, and (c) the seventh batch

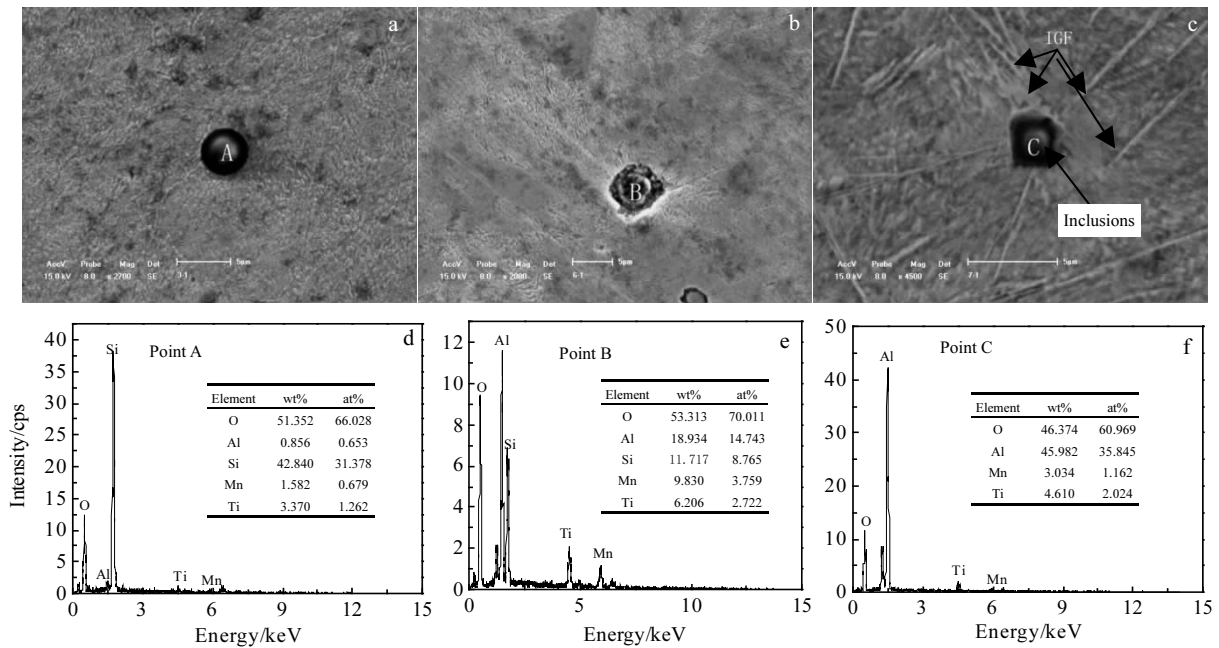


Fig.8 SEM images (a~c) and EDS analysis (d~f) of inclusions after deoxidation: (a, d) the fifth batch; (b, e) the sixth batch; (c, f) the seventh batch

The SEM photographs in Fig.8 show that the density of dislocation around the compound inclusions is high and the direction of dislocation is different. High density of dislocation causes the formation of ferrite in super fine grain of steel, and the new ferrite in super fine grain is grown up by consuming the matrix of high density of dislocation. A large amount of intragranular acicular ferrite formed around the composite inclusions greatly can refine the structure of the steel and improve the performance of the steel. The SEM photographs of the seventh batch in Fig.8 show that there is a large amount of intragranular acicular ferrite consisting of alumina and titanium oxide around the composite inclusions which plays a role of intragranular ferrite core inducing the formation of intragranular acicular ferrite (IGF) (Fig.8c), turning the harm of inclusions into good which refines the microstructure of the steel.

The result of activities calculated in Table 6 shows that, the a_{Ti}/a_{Al} in the liquid steel of seventh furnace (Fig.8c) can be up to 17.78. While the existing results of literature and research show that, the oxygen content in liquid steel using Ti-Al complex deoxidizer is controlled by titanium at 1873 K on the condition that a_{Ti}/a_{Al} is more than 8. In fact, Al_2O_3 and Ti_2O_3 can form solid solution, and the a_{Ti}/a_{Al} value should be controlled more than 10 to ensure the $a_{Al_2O_3}$ small enough to make sure that the deoxidation products precipitate in the form of Ti_2O_3 . The experimental results are in accordance with the theory calculation. The content of oxygen in steel decreases from the initial 560 $\mu\text{g/g}$ to 150 $\mu\text{g/g}$ when the amount of deoxidizer is 28 g. And it may be speculated that the a_{Ti}/a_{Al} should be controlled when the oxygen content is relatively high and it is vital to control a higher a_{Ti}/a_{Al} to ensure that the deoxidation products precipitate in the form of titanium oxide.

3 Conclusions

1) During the process of deoxidation in steel at 1873 K with titanium as deoxidizer, as long as the content of dissolved oxygen is controlled below 0.003%, particles of Ti_2O_3 firstly precipitate, and then TiO_2 and Ti_3O_5 , and TiO at last. When $a_{Ti}/a_{Al} > 8$ with titanium and aluminum as composite deoxidizer, the content of oxygen is controlled by the content of titanium and the deoxidizing product is Ti_2O_3 ; due to Al_2O_3 and Ti_2O_3 forming solid solution, only the a_{Ti}/a_{Al} in liquid steel is above 10, and Ti_2O_3 precipitates as deoxidizing product.

2) The content of aluminum and titanium in liquid steel can meet the requirements of composition in the related steel.

3) Using high titanium ferro deoxidizer with high aluminum content in liquid steel, the microstructures of steel after deoxidation refining are refined. With the increase amount of high titanium ferro, inclusions in cast steel after refining transform from silicate into Ti-Al-Mn composite inclusions; and at the same time, obvious or part of radial acicular ferrite

forms around those inclusions, which indicates that those inclusions play a role of intragranular ferrite core as a result of the formation of intragranular acicular ferrite and finer-grained microstructure. The a_{Ti}/a_{Al} value in actual system is 17.78 (>8), which is consistent with the theoretical results. It is vital to control the a_{Ti}/a_{Al} in the liquid steel with high oxygen content.

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铝热还原制备高钛铁脱氧性能的研究

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摘 要: 研究了钢液精炼过程中高铝高钛铁的热力学性能, 并研究了高钛铁中铝含量和用量对钢液精炼过程的影响。结果表明: 以 Ti 和 Al 为复合脱氧剂, 当钢液中的 a_{Ti}/a_{Al} 在 8 以上时, 1873 K 处的脱氧产物为 Ti_2O_3 ; 而事实上, 只有当钢液中的 a_{Ti}/a_{Al} 值在 10 以上时, Ti_2O_3 才沉淀为脱氧产物。采用高铝含量高钛铁作为脱氧剂时, 钢液中铝和钛的含量可满足相关钢的成分要求。随着高钛铁含量的增加, 经精炼后的铸钢中的夹杂由硅酸盐转变为 Ti-Al-Mn 复合夹杂, 同时在这些夹杂周围形成明显或部分的径向针状铁素体, 细化了钢的显微组织。实际系统中的 a_{Ti}/a_{Al} 值为 17.78 (>8), 与理论结果一致。当钢液含氧量较高时, 控制钢液中的 a_{Ti}/a_{Al} 值至关重要。

关键词: 钢液脱氧; 夹杂物; 铝热反应; 氧化物冶金

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