

Study on slag forming mechanism of hot metal containing titanium in converter

H B Wang, Y C Lv, L Y Qin, Y Liu, C W Ma, X T Kong

¹ Shougang Research Institute of Technology, Beijing, 100043

² Beijing Key Laboratory of Green Recyclable Process for Iron & steel Production Technology, Beijing, 100043

³ Beijing Engineering Research Center of Energy Steel, Beijing, 100043

wanghaibao1982@shougang.com.cn

Abstract. The use of titanium containing molten iron can expand the sources of raw materials, reduce the cost, but the process produce serious foaming slag, low dephosphorization proportion and the consumption of lime is high. The technicians have improved the operation process through experiments and solved the problem of efficient and smooth blowing of hot metal containing titanium. Through mine phase composition analysis of slag using SEM and EDS, the distribution of titanium and the regularity of phosphorus retention are found, and measures to prevent phosphorus recovery in the later stage of converter are put forward.

1 Introduction

In order to ease the tension of the ordinary iron ore resources, reduce raw material procurement costs, a certain amount of ore which containing titanium and vanadium is added in the blast furnace in the ironmaking plant and about 0.4% trace elements appear in molten iron. Its characteristics are that the content of titanium in molten iron is high, and the content of titanium is 0.15% ~ 0.45%, results in low melting point and poor slag splashing effect in the steelmaking process. There will be a series of problems by the use of high titanium and vanadium contented hot metal, such as poor dephosphorization effect, serious foaming slag, serious splash, higher lime consumption, lower furnace age and so on [1-3].

In view of the above problems, the technical staff of the steel plant started the experiment and improved the original “double slag” steelmaking method and achieved good results.

The new BOF steelmaking process is divided into three periods, detitanium period dephosphorization period and decarburization period. With oxygen supply to the converter detitanium period begin and end after three minutes. In detitanium period the basicity should be low and the oxygen lance keep high, with a small batch of ore added.

Liquid slag in the converter mainly from Ti, Si, Mn, Fe oxidation during the early period of blowing, the slag is removed from the converter before the severe carbon oxidation period, and the titanium rich slag is poured out. The ore is added into the converter and the lime is used to make the dephosphorization slag. Then, the traditional “double slag” process is carried on until tapping [4-8].

Through the observation of slag micro morphology and analysis of the mine phases in the process of converter steelmaking, the process of steelmaking can be further optimized to lay a foundation for reducing the smelting cost and increasing the efficiency.



2 Experimental materials and methods

2.1 Experimental materials

The sample is taken from a 100t top and bottom combined blown converter. Chemical components of the slag are shown in table 1.

Table1. Chemical composition of slag for experiment (wt %)

Sample No.	TFe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	P ₂ O ₅	TiO ₂	R
detitanium	11.18	11.7	20.22	1.26	37.91	3.16	7.91	2.43	8.84	1.87
dephosphorization	8.36	5.14	14.92	2.26	53.28	4.31	3.55	3.52	4.03	3.57
tapping	14.26	10.8	12.77	2.1	48.73	4.24	3.41	2.29	3.03	3.81

As can be seen from table 1, the main components of slag used in this experiment are Ca, Fe, Si, Mn, Mg and Ti, and the slag is basic.

2.2 Experimental methods

The slag is broken and inlaid, and the sample is prepared by grinding and polishing with a polishing machine. The experimental equipment is S-3400N scanning electron microscope. The acceleration voltage is from 0.3 to 30KV, the magnification is 50~300 thousand times.

Using SEM backscatter low vacuum mode, micro morphology of the specimen was observed. The backscattered electron energy is higher and sensitive to the atomic number of the sample material. The larger the average atomic number is, the more the backscattered electron appeared which make the image brighter. Through material qualitative analysis; and using X-ray spectrometer to determine the components of micro elements, the mineral compositions of slag obtained finally.

3 Experimental results

3.1 Morphology observation and energy spectrum analysis of detitanium slag

Using SEM backscatter low vacuum mode, micro morphology of the specimen was observed. As shown in Figure 1, the morphology of the main minerals can be roughly divided into 3 phases: white phase (A1 and A2), gray phase (B1 and B2) and black and white stripe phase (C1, C2, C3).

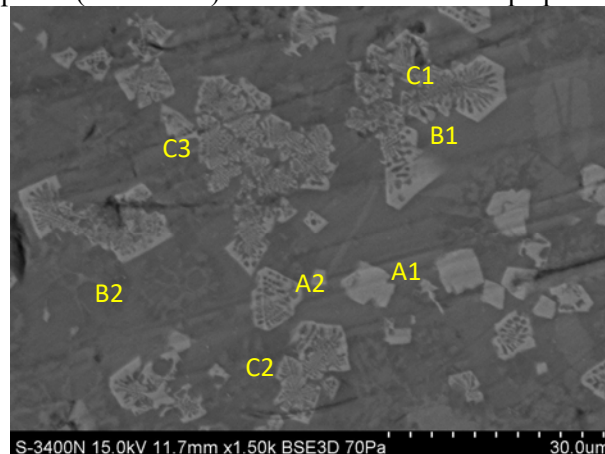


Figure1. Morphology and energy spectrum position of detitanium slag

The matrix of the converter slag is grey phase, and the irregular white phase is distributed intermittently in the matrix. Some of the white phase boundaries are clear and rectangular, and some of the white phases have black and white stripes in the middle.

The results of energy spectrum analysis are shown in table 2.

Table2. Composition analysis of energy spectrum of detitanium slag (wt %)

Position	Color	O	Mg	Al	Si	P	Ca	Ti	V	Mn	Fe
A1	white	36.98	3.19	1.06	5.04		9.17	11.32	4.52	10.92	17.8
A2		41.68	2.55	1.12	4.74	0.62	8.8	9.65	2.39	9.55	18.9
B1	gray	45.97	1.48	1.34	13.22	1.08	20.37	3.25		6.11	7.18
B2		43.49	2.25	0.5	12.96	1.08	20.05	3.1		8.21	8.38
C1	stripes	40.59	2.27	0.46	8.78	1.36	19.16	6.68	1.64	7.63	11.44
C2		43.28	1.93	0.88	8.82	1.34	17.62	5.77	1.57	8.08	10.72
C3		40.91	2.1	0.52	9.32	1.51	20.47	5.14	1.87	7.28	10.89

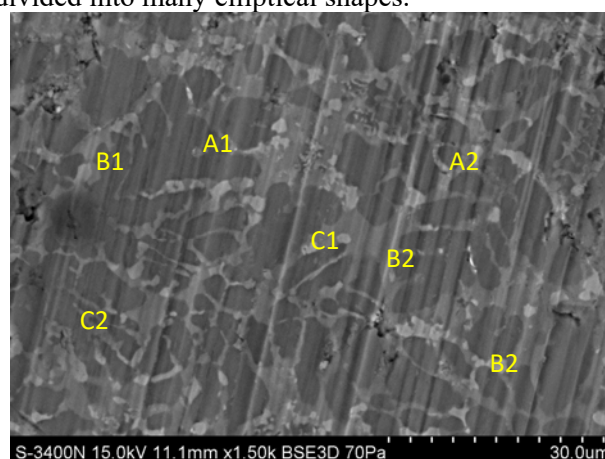
Through spectrum analysis showed that the white phase mainly contains Fe, Ti, Mn, Ca and other elements, the content of Fe is about 18%, the content of Ti is about 10%, the content of Mn is about 10%, the content of Ca in about 9%, and a small amount of Si and Mg elements, it can be deduced that the white phase consists mainly of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $\text{TiO}_2 \cdot \text{Fe}_2\text{O}_3$ and manganese oxide, as well as a small amount of silicate.

The grey matrix was mainly composed of Ca, Si, Fe and Mn elements, the content of Ca is about 20%, the content of Si is about 13%, the content of Fe is about 8%, the content of Mn is about 8%, it can be inferred that the grey phase consists mainly of $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and manganese oxide.

The black and white combined phase was mainly composed of Ca, Fe, Si, Mn and Ti elements, the content of Ca is 18% ~ 21%, the content of Fe is about 11%, the content of Si is about 9%, the content of Mn is about 8%, the content of Ti is about 6%, it can be inferred that black and white combined phase consists mainly of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $\text{CaO} \cdot \text{SiO}_2$, manganese oxide and $\text{TiO}_2 \cdot \text{Fe}_2\text{O}_3$. All of the three phases contained Ti and a small amount of phosphorus.

3.2 Morphology observation and energy spectrum analysis of dephosphorization slag

Using SEM backscatter low vacuum mode, micro morphology of the specimen was observed. As shown in Figure 2, the morphology of the main minerals can be roughly divided into 3 phases: white phase (A1 and A2), gray phase (B1 and B2) and light gray phase (C1, C2, C3). The distribution of white phase and light gray phase is uneven. The shape of the two phase distribution is consistent, and the gray matrix phase is divided into many elliptical shapes.

**Figure2.** Morphology and energy spectrum position of dephosphorization slag

The results of energy spectrum analysis are shown in table 3.

Table3. Composition analysis of energy spectrum of dephosphorization slag (wt %)

Position	Color	O	Mg	Al	Si	P	Ca	Ti	V	Mn	Fe
A1	white	36.7	1.27	0.64	2.85	0.84	15.51	0.88		9.02	32.28
A2		36.68	1.49	0.51	2.48	0.57	15.49	0.91		9.18	33.7
B1	gray	42.82	0.73	1	9.36	2.45	35.95	1.43	1.06	0.85	4.35
B2		45.86	1.08	0.61	9.66	2.48	35.33	1.55			3.43
B3		44.79	1.13	0.86	9.49	2.45	34.97	1.37		1.13	3.81
C1	light	40.78	1	5.59	2.71	0.71	30.39	2.54	1.72	1.31	13.25
C2	gray	38.97	0.88	5.18	2.85	0.99	30.11	2.64	1.74	2.2	14.44

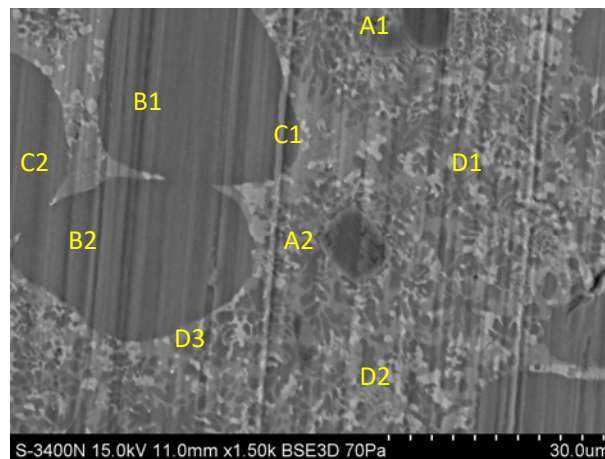
Through spectrum analysis showed that the white phase mainly contains Fe, Ca, Mn elements, the content of Fe is about 33%, the content of Ca is about 16%, the content of Mn is about 9%, a small amount of Si and Mg elements, it can be inferred that the white phase is mainly composed of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2$ and manganese oxide.

The gray matrix was mainly composed of Ca and Si elements, the content of Ca is about 35%, the content of Si is about 10%, also contains a small amount of Fe elements, it can be inferred that the grey phase consists mainly of $2\text{CaO} \cdot \text{SiO}_2$ and a small amount of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$.

The light gray phase mainly contains Ca, Fe and Al elements, the content of Ca is about 30%, the content of Fe is about 14%, the content of Al is about 5%, also contains a small amount of Ti element, it can be inferred that the light gray phase consists mainly of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, and a small amount of TiO_2 . In the gray phase, the content of phosphorus is highest, about 2.5%, in white or light gray phase the content of phosphorus is below 1%.

3.3 Morphology observation and energy spectrum analysis of tapping slag

Using SEM backscatter low vacuum mode, micro morphology of the specimen was observed. As shown in Figure 3.

**Figure3.** Morphology and energy spectrum position of tapping slag

the morphology of the main minerals can be roughly divided into 4 phases: dark gray phase (A1 and A2), gray phase (B1 and B2), and light gray phase (C1 and C2) and white phase (D1, D2, D3). Dark gray phase embedded in the matrix, the boundary is clear, shape is rectangular. Light gray and white phase morphology consistent, distributed in the grey matrix and the grey matrix is mostly all covered by white and light grey phase in some area.

The results of energy spectrum analysis are shown in table 4.

Table4. Composition analysis of energy spectrum of tapping slag (wt %)

Position	Color	O	Mg	Al	Si	P	Ca	Ti	Cr	Mn	Fe
A1	dark	42.77	24.14		2.16	0.62	11.6	0.66	0.78	4.39	12.88
A2	gray	43.06	22.36	0.6	1.98	0.57	12.25		1.11	3.88	14.18
B1		46.54	0.65	0.61	8.98	2.51	34	0.91			5.81
B2	gray	45.09	0.98	0.51	9.21	2.87	34.45	1.09			5.8
C1	light	36.86	1.13	2.55	2.88	0.89	29.33	1.63		2.32	20.84
C2	gray	40.55	1.32	2.13	2.95	0.67	30.22	2.15		1.49	19.5
D1		36.39	3.56	0.65	3.07	0.78	17.79	0.94		6.49	30.34
D2	white	35.15	3.19	0.46	2.11	0.58	18.17	0.8		6.41	32.71
D3		39.13	3.17	0.43	2.67	0.69	16.06	1.03	0.78	5.49	30.54

Through the energy spectrum analysis shows that the dark gray phase mainly contains Mg, Fe, Ca elements, Mg content is about 23%, the content of Fe is about 13%, the content of Ca in about 12%, also contains a small amount of Mn element, it can be inferred that the dark gray phase is mainly composed of MgO and $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and a small amount of $\text{CaO} \cdot \text{SiO}_2$.

the gray phase mainly contains Ca, Si and Fe elements, the content of Ca is about 34%, the content of Si is about 9%, the content of Fe is about 6%, it can be inferred that

the gray phase is mainly composed of $2\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Fe}_2\text{O}_3$.

The light gray phase mainly contains Ca, Fe elements, the content of Ca is about 30%, the content of Fe is about 20%, also contains a small amount of Si element and Al element, it can be inferred that the light gray phase is mainly composed of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and a small amount of $3\text{CaO} \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The white phase mainly contains Fe, Ca and Mn elements, the content of Fe is about 30%, the content of Ca is about 17%, the content of Mn in about 5%, also contains a small amount of Mg and Si, it can be inferred that the white phase is mainly composed of $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ manganese oxide and a small amount of $\text{CaO} \cdot \text{SiO}_2$. All of the four phases contain a certain amount of phosphorus.

4 Analysis and discussion

4.1 The distribution and regularity of Ti element

(1)Through the observation of slag micro morphology and analysis of the mine phase shows that all of the three phases contain Ti elements. The reason is that TiO_2 have relatively stable performance and poor surface activity so the binding ability with other oxides is not strong, as a result the distribution is dispersed in the slag.

(2)There is a significant correlation between Ti content and Fe content, this is because the Fe element level is a measure of oxidizability of the slag. With a Sufficient oxidation in converter, the content of TiO_2 is higher. When the Fe element is about 30% and higher temperature in the converter, Ti elements decrease in the content of mineral phase.

(3)There is a significant correlation between the Ti element and the content of Al, that because of the Al_2O_3 surface tension in molten steel is large, easily combined into aggregates particle groups and adsorption of TiO_2 increased.

(4)With the increase of slag oxidation, the phase colored with white and black will gradually change into white phase with higher Ti content, which will be beneficial to the removal of Ti elements. All of the three phase in the detitanium slag contain P elements, which is widely distributed in the slag, but the content of phosphorus in each phase is low.

4.2 Analysis of control measures in dephosphorization period

In detitanium period all the Si element is oxidized and the SiO_2 content is low in dephosphorization period after the detitanium slag poured out. Therefore, in order to increase the dephosphorization

capacity of the slag, silica was added to increase the SiO_2 content of the slag and lime was added to adjust the basicity.

Dephosphorization period is concentrated in about 3 ~ 6min, At this stage, in order to better remove phosphorus in molten iron, the blowing temperature should not be too high, so as to avoid the rephosphorization. In addition, the high temperature will lead to the decomposition of ferric phosphate, so be sure to increase the basicity before the temperature rises and turn the ferric phosphate into calcium phosphate.

4.3 Analysis of phosphorus recovery during decarburization period

Through the observation of decarbonized slag by micro morphology and analysis of the mine phase shows that the highest phosphorus contented phase is $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$ mixing phase in converter. When the FeO in slag increases, the phase of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$ translated to low melting point phase, such as calcium ferrite, ferric phosphate and ferric silicate. At the same time, the solid phase of phosphorus is decomposed into small particles, and the phosphorus elements return to the liquid steel during the decomposition of solid phosphorus, and the phenomenon of phosphorus recovery occurs. Therefore, the FeO content should be reduced in the later period of converter blowing.

5 Conclusion

Through the study following conclusions can be obtained.

(1) In detitanium period, there is a significant correlation between Ti content and Fe content, this is because the Fe element level is a measure of oxidizability of the slag. With a Sufficient oxidation in converter, the content of TiO_2 is higher. When the Fe element is about 30% and higher temperature in the converter, Ti elements decrease in the content of mineral phase. All of the three phase in detitanium slag contain P element, which is widely distributed in the slag, but the content of phosphorus in each phase is low.

(2) In the dephosphorization period be sure to increase the basicity before the temperature rises and turn the $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ into $3\text{CaO} \cdot 2\text{P}_2\text{O}_5$.

(3) In the decarburization period, when the FeO in slag increases, the phase of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$ translated to low melting point phase, such as $\text{CaO} \cdot \text{Fe}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2$. At the same time, the phenomenon of phosphorus recovery occurs.

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