RESEARCH ON DE-TITANIUM OF SILICOMANGANESE FERROALLOY BY BLOWING N_2

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ABSTRACT

Silicomanganese (SiMn) was melted in induction furnace under synthetic slag containing MnO, FeO, and CaO, together with N_2 blown from the bottom of furnace through the Tinject breathable-piston device. TiN particles, both formed during the refining and came from the original TiN and TiC inclusions, were captured by the N_2 blow. Then the bubbles of N_2 rose to the surface and resulted in the decrease of Ti content.The experimental results showed that the Ti content in alloys decreased to less than 0.06% and even down to 0.023% when temperature was below 1623K. The average removal ratio of Ti reached 84.75%, and the N content in alloys was as low as 50ppm after blowing.

Keywords: *silicomanganese, titanium removal, nitrogen blowing refining, titanium nitride.*

1. INTRODUCTION

A new technical requirement for silicomanganese (SiMn) products used during the production of the tire cord steels or bearing steels is that SiMn contains a very low content of titanium (Ti). There are generally two specifications of these low Ti silicomanganese, ≤0.05 mass% and≤ 0.03 mass% Ti. However, the SiMn alloy supplied in China cannot meet these requirements and some steel plants have to use metal manganese or electrolytic manganese and high purity ferrosilicon to replace SiMn. SiMn alloys were usually supplied with Ti content above 0.30 mass% because the mixed manganese ores used for producing SiMn contains more than 0.15 mass% Ti. The mixture ores mentioned here usually contain many manganese-rich slags in China. Therefore, it is important to find a method to remove Ti from SiMn.

The secondary refining technique of blowing chlorine or oxygen was widely used to produce high-purity grade ferrosilicon or silicon. The aluminum content of silicon decreases to less than 0.01 mass% with blowing chlorine to the deep part of molten silicon by using graphite tube, meanwhile, Ti content decreases by 40% to 50%[1,2].The de-aluminum ratio is up to 75% by blowing air with the pressure of 0.02~0.05MPa for 15 minutes, and the aluminum content of ferrosilicon decreases to less than 0.5 mass%[3].

L.B.Hu [4] analyzed the production process of low-Ti high-carbon ferrochrome, and presented two assumptions for decreasing Ti. They were refining the metal with oxygen blowing and reducing Ti through de-sulfur refining at heat preservation in induction furnace.

But there is no report published on the production technology of low Ti-contained silicomanganese. In this paper, the Tinject breathable-piston was installed at the bottom of the induction furnace, and experiments for decreasing Ti content of SiMn were made in the furnace by blowing N_2 from the bottom of the furnace. The experimental results show that it is a highly efficient way for the removal of Ti and nitrogen (N).

2. FUNDAMENTAL ANALYSIS

2.1. State Of Ti In Simn Alloy

When carbon is mixed with ores containing TiO_2 in the submerged arc furnace, a possible reaction is:

$$TiO_{2(s)} + 3C_{(s)} = TiC_{(s)} + 2CO_{(g)}, \quad \Delta G_1^\circ = 528937 - 337.23T \ (\mathrm{J \cdot mol^{-1}}) \qquad (1)$$

According to the standard Gibbs free energy of Reaction (1), TiC can be generated when temperature is higher than 1569K which is lower than the real melting temperature of silicomanganese. It means that TiC is formed and remains in the products from the thermodynamic aspect. However, the product TiC(s) has a certain solubility in ferrous alloys whose solution equilibrium reaction can be shown as Eq. (2). The thermodynamic data in Mn based melts is lack, so that the Gibbs free energies of Ti, C, N and other element dissolved in Fe have to be used to replace that in Mn with the standard state of 1 mass% solution.

$$TiC_{(s)}=[Ti]_{Fe,1\%}+[C]_{Fe,1\%};\quad \Delta G_2^{\circ}=184121-101.46T\ (J\cdot mol^{-1}) \qquad (2)$$

When there is nitrogen atmosphere within the furnace, the Ti dissolved can further react with nitrogen, which has been described detailed in literatures [5-8]:

$$[Ti]_{Fe,1\%}+[N]_{Fe,1\%}=TiN_{(s)};\quad \Delta G_3^{\circ}=-315774+115.34T\ (J\cdot mol^{-1}) \qquad (3)$$

$$\log K_3=16494.94/T-6.02$$

Combine Eq.(2) with Eq.(3), the reaction between TiC and N dissolved in ferroalloy can be expressed as follows:

$$TiC_{(s)}+[N]_{Fe,1\%}=TiN_{(s)}+[C]_{Fe,1\%};\quad \Delta G_4^{\circ}=-131653+13.88T\ (J\cdot mol^{-1}) \qquad (4)$$

$$\log K_4=6877.10/T-0.73;\quad K_{4,1873K}=874.39;\quad K_{4,1573K}=4384.95 \qquad (5)$$

As shown in the Eq.(5), the equilibrium constant of equation (4) is very large. Therefore, TiC, as the product of reduction reaction in submerged arc furnace, is certain to transform into TiN until Ti, N and C in liquid reach equilibrium at the same time. Ti exists mainly as the inclusions in the form of TiN in the final alloy product, except a little dissolved in the alloy melt.

2.2. Dependence Of The Ti Content Of Simn Melt On Temperature

According to Eq.(3), the relationship between the Ti content and temperature at equilibrium can be calculated with different N contents of 0.001 mass%, 0.002 mass% and 0.005 mass% respectively. In the calculation, it is assumed that Ti and N content can satisfied with Henry's Law because they both are very low. The results are shown in Fig.1. Although Fig.1 actually shows the thermodynamic data of Fe liquid, its trend is not much different from that in the actual Mn liquid (This can be proved by Fig.6). From Fig.1, the content of Ti dissolved in SiMn decreased apparently with the increase of temperature, and the effect of N on Ti content was significant especially at high temperature. The Ti content decreased with the increase of N content at the same temperature.

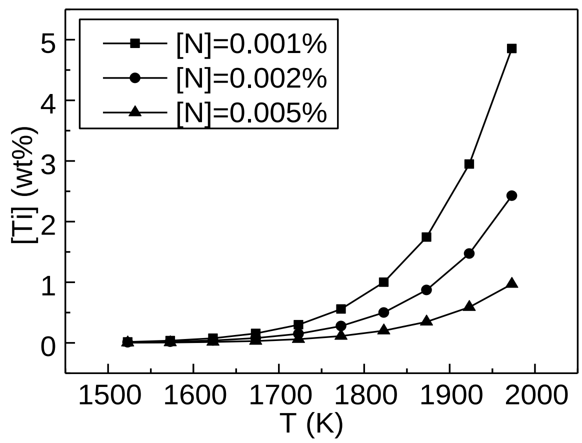

Fig.1: Relationship between Ti content and temperature at different N content (Based on the thermodynamic data of iron liquid)

2.3 Characterization of TiN in silicomanganese alloy

Fig.2 showed the SEM (Scanning Electron Microscope) image of silicomanganese. The silicomanganese sample was etched by 5% nital. TiN inclusion with approximately size of 4~7μm was found in the SEM image and it was marked by A in Fig.1. The morphology characterization of TiN was cubic, which was the same as the TiN inclusions in steels.

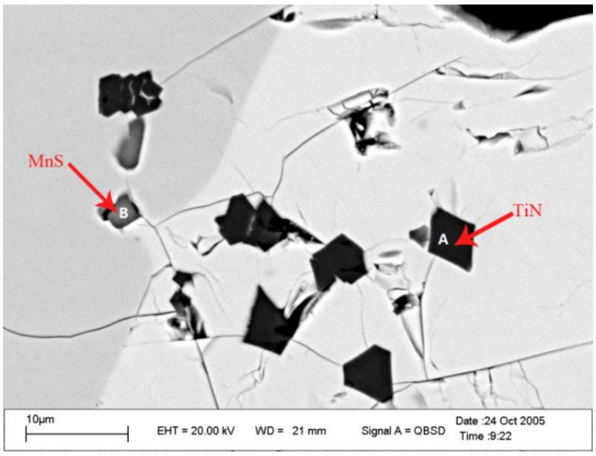

Fig.2: SEM image of silicomanganese (Etched by 5% nital)

The melting point of TiN and TiC were 3223K and 3423K respectively, which is higher than the melting temperature of silicomanganese. Thus, TiN and TiC precipitate as solid in molten alloy. Besides, the density of TiN and TiC are 5.10 g/cm^3 and 4.25 g/cm^3 respectively, lower than the density of silicomanganese. Therefore, they can be removed by the floating-separation method.

In a word, Ti exists in the liquid alloy mainly as the form of solid TiN, and dissolved Ti can be removed by the formation of TiN. The solubility of Ti decreases significantly with decreasing temperature, and the content of Ti in alloy can be below 0.05% or 0.03% when the N content in alloys is more than certain values. Therefore, in theory, the Ti silicomanganese can be removed by blowing N_2 at low melting temperature.

3. EXPERIMENTS

According to the fundamental analysis on Section 2, some experiments were conducted to remove the Ti in SiMn with blowing N_2.

Apparatus——The experimental apparatus was presented in Fig.3. This consisted mainly of a 50 kg medium-frequency induction furnace with a Tinject breathable-piston in the bottom. The structure of Tinject breathable-piston was shown in Fig.4. Besides, the furnace is connected with N_2 gas supply system. Temperature was measured using platinum rhodium-platinum thermocouple.

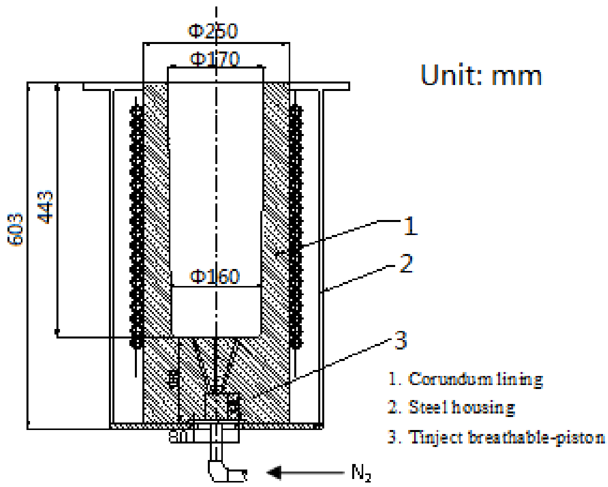

Fig.3: Induction furnace used to remove Ti from silicomanganese melts

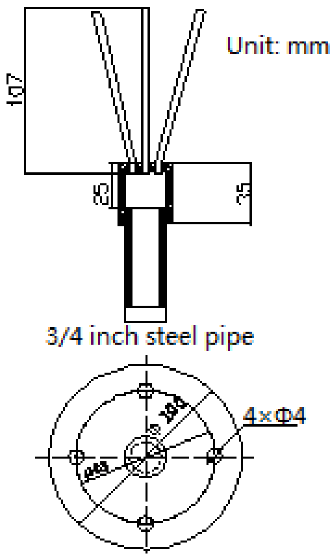

Fig.4: Structure of Tinject breathable-piston

Raw materials——Silicomanganese, N_2 and synthetic slag are used. The synthetic slag is able to absorb inclusion of TiN and TiC. The composition of synthetic slag and silicomanganese were shown in Table 1.

Table 1: The compositions and granularity of raw materials for experiment

Raw materials	Composition (%)						Granularity
Silicomanganese	Mn	Si	P	C	Al	Ti	≤80 mm
	65.5	17.5	0.2	1.8	0.05	0.3	
Slag	MnO	CaO	SiO_2	Al_2O_3	CaF_2	FeO	≤5 mm
	9.43	26.91	21.29	11.37	11.27	1.04	
N_2 gas	purity≥98						—

Procedure——A batch of raw materials included 30 kg silicomanganese and 2.0~3.3 kg slag in each run of experiment. Silicomanganese was melt with blowing N_2 gas at the rate of 7~10 liter per minute (L/min) before the end of the last minutes of refining. When the alloy was completely melted, one sample was taken as the initial sample. Then the refining process continued for about half an hour with the N_2 gas rate of 1~2 L/min. The N_2 pressure was within the range of 0.02 MPa~0.025 MPa. At the end of refining, another sample of silicomanganese was taken using vacuum sampler.

4. RESULTS AND DISCUSSION

The content of Ti in silicomanganesedecreased to less than 0.059 mass% and even down to 0.023 mass% in some run of experiment after refining with the N_2 blowing. The average removal ratio of Ti is about 84.75%. At the same time, the content of N also decreased from the original 0.022 mass% to 0.0041 mass% averagely. In contrast, the reference experiment without blowing N_2, Ti content only decreased to 0.173~0.191 mass%, and the average Ti removal ratio was 32.51%. The results are shown in Table 2.

Table 2: Experimental results of Ti removal for silicomanganese

Heat number	Ti (%)		De-Ti rate (%)	N (%)		Temp. (K)	Expt. time (min)	N_2 (L)	Slag (kg)
	Begin	Final		Begin	Final				
No.1	0.267	0.033	87.64	-	-	1568	70	585	3.0
No.2	0.252	0.059	76.59	-	--	1543	57	440	2.0
No.3	0.273	0.052	80.95	-	-	1581	50	220	2.0
No.4	0.228	0.023	89.91	0.025	0.0025	1530	67	320	3.3
No.5	0.264	0.030	88.64	0.018	0.0057	1503	68	184	2.3
Average	0.257	0.039	84.75	0.022	0.0041	1545	62	350	2.5
No.6	0.262	0.173	33.97	-	-	1746	70	0	2.0
No.7	0.277	0.191	31.05	-	-	1723	60	0	2.0
Average	0.270	0.182	32.51	-	-	1734	65	0	2.0

4.1. Effect Of Refining On Nitrogen Content

The result in the Table 2 illustrated that the total nitrogen content in alloys decreased from 0.025 mass% and 0.018 mass% to 0.0025 mass% and 0.0057 mass% after blowing N_2 respectively. It decreased by about 80.93%, which is very efficiently.

According to the chemical analysis and SEM detection shown in the Fig. 1, the total N content ($[\%N]_T$) included the N that dissolved in the alloys ($[\%N]_d$) and the N in TiN ($[\%N]_{TiN}$). The relationship between $[\%N]_T$, $[\%N]_d$ and $[\%N]_{TiN}$ is as shown

$$[\%N]_T = [\%N]_d + [\%N]_{TiN} \quad (6)$$

Therefore, the N content in alloys will decrease with the removal of TiN after melting in induction furnace.

In the same way, the total Ti content ($[\%Ti]_T$) also was composed with the dissolved Ti ($[\%Ti]_d$) and the Ti that existed as the form of TiN ($[\%Ti]_{TiN}$), expressed as:

$$[\%Ti]_T = [\%Ti]_d + [\%Ti]_{TiN} \quad (7)$$

It can be assumed that inclusion of TiN in the initial silicomanganes would be all removed by stirring from electromagnetic force and absorbed by slag in induction furnace without blowing N_2. Therefore, the total Ti content of the metal sample (No.6 and No.7, shown in Table 1), which is the sample after the refining without blowing N_2, can be seen as the dissolved Ti. It means that the average initial content of dissolved Ti ($[\%Ti]_{d,initial}$) in the silicomanganese before refining was that:

$$[\%Ti]_{d,initial} = [\%Ti]_{T,\text{average of final sample of No.6 and No.7}} = 0.182 \quad (8)$$

On the basis of Eq.(3), the relationship between dissolved Ti and dissolved N at the equilibrium condition can be gives.

$$[\%N] = \frac{1}{[\%Ti]\times 10^{16494.94/T-6.02}} \quad (9)$$

Therefore, according to Eq.(9), the content of N in silicomanganese under fully-melted condition (T=1734K, $[\%Ti]_{d,initial} = 0.182$) and refined condition with blowing N_2 (T=1545K, $[\%Ti]_{d,\,final} = 0.039$) can be calculated and the respective results were:

The initial N content in silicomanganese: $[\%N]_{d,initial} = 0.00177$

The final N content dissolved in alloy after refining: $[\%N]_{d,final} = 0.00057$

Compared to the data in Table 2, the average content of N (0.0215%) before refining was much higher than the initial content of N dissolved in alloy. It is further illustrated that a lot of TiN inclusions that existed in alloy were excreted from the melt after blowing N_2. The content of N that dissolved in the alloys decreased after refining with blowing N_2.

Both the initial TiN in the silicomanganese before refining and the regenerate TiN during the refining process will float up to the surface of liquid alloy and react with the absorbing slag [9-10].

$$TiN_{(s)} + (CaO)_{\text{in slag}} + 2(FeO)_{\text{in slag}} + 2(MnO)_{\text{in slag}} = (CaO\cdot TiO_2)_{\text{in slag}} + 2Fe_{(l)} + 2Mn_{(l)} + 1/2N_{2(g)} \quad (10)$$

In the refining process, the initial and formed TiN(s) were capatured by N_2 bubble and then rose up to the surface. The reaction of Eq. (10) happened in the interface of slag and metal and the N in TiN transformed to N_2, which would be discharge into the atmosphere. Therefore, the N content in the alloys at the end of refining will be not more than that in the alloys before refining process because of the blowing N_2.

4.2 Effect Of Refining Time On Titanium Removal

The experiment proved that [%Ti] will generally decrease to the range of 0.15 mass%~0.19 mass% after melting process and continually decrease to lower level after 10 minutes refining process. However, the effect of the blowing time on the decreasing rate of Ti content is not pronounced. Fig.5 gives the result of a run of experiment. The first point of the left in Fig. 5 showed the initial Ti content of alloy from submerged arc furnace, and the second point showed the Ti content of the sample after melting in the induction furnace without blowing refining. From the figure, the content of Ti would decrease to 0.167 mass% when the alloys were remelt in the induction furnace, and continually decreased to 0.038 mass% after the refining with 8 minutes. After this, there was no more large change in the composition of the alloys.

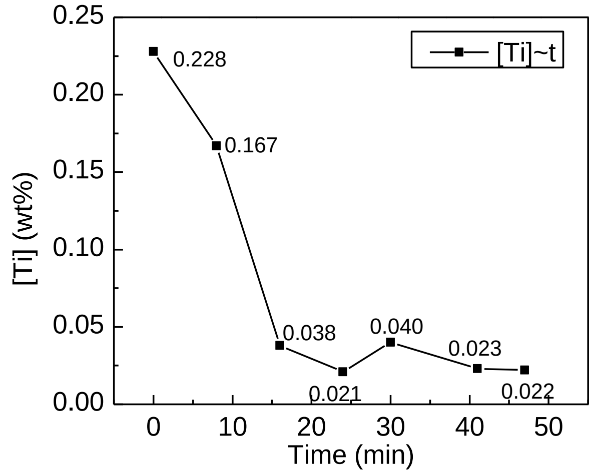

Fig.5: Relationship between Ti content and refining time (Expt. No. 4)

4.3 Effect Of Refining Temperature On Titanium Removal

Fig.6 showed the relationships between temperature and the content of Ti in experiments, some of which were shown in Table 2. The temperature played an important role on controlling the content of Ti in silicomanganese at the end of refining. When the temperature was below 1580K, the content of Ti in alloys scattered in the range of 0.023 mass%~0.059 mass%. While, the content of Ti increased obviously with the increasing of temperature when the temperature was above 1580K.

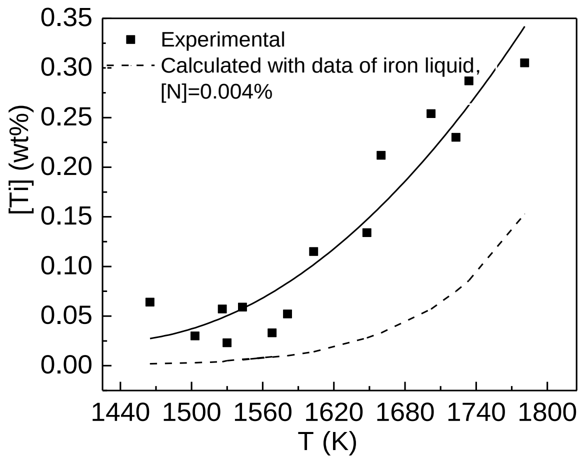

Fig.6: The relationship between $[\%Ti]_{final}$ and temperature

As shown in Fig. 6, the calculated value of solubility of Ti in liquid iron was apparently lower than experimental value at the same temperature. In the calculation, the content of N in alloy melt was assumed as 0.004 mass%, which was similar to the average of final content of N in the experiments shown in Table 2. The reason could be explained in two aspects. Firstly, some Ti-containing inclusions of TiN and TiC were not excluded. Secondly, the content of Ti in silicomanganese was lower than that of Si so as to Ti and Si were combined as $TiSi_2$, which can prevent the formation of TiN and TiC. The standard Gibbs free energy of $TiSi_2$, TiN, TiC at 1580K were –115.45 kJ/mol, -113.54 kJ/mol, -23.81 kJ/mol respectively. Besides, the melting point of $TiSi_2$ is about 1753K and it will be dissolved in silicomanganese at the high temperature. Therefore, the gap of Ti content between experimental value and calculated value was larger at high temperature than that at low temperature.

4.4 Effect Of N_2 Quantity On Titanium Removal

Table 2 showed that the highest N_2 quantity is 585 L and the lowest is 184 L, however, Ti contents at the end of refining were 0.033 mass% and 0.030 mass% respectively which were almost the same. The reason is that the theoretical value of N_2 required by titanium removal was much less than the quantity that was factually blown into the liquid and the N_2 bubble during refining mainly played a role of capturing inclusions.

When the initial content of Ti before refining is 0.182 mass%, which has been described in section 4.1, the finial content of Ti will be 0.03 mass%, and the initial content of N was neglected. According to Eq.(11), the requirement of N_2 (V_{N_2})for removing Ti from 30 kg silicomanganese was only 106 L as that was calculated by Eq. (12), which is smaller than the quantity of N_2 actually blown in the experiments.

$$[\mathrm{Ti}] + 1/2\,\mathrm{N}_{2(g)} = \mathrm{TiN}_{(s)} \tag{11}$$

$$V_{\mathrm{N}_2} = 22.4\times\frac{1}{2}\times\frac{100\times m_{alloy}\times([\mathrm{Ti}]_{\mathrm{initial}}\text{-}[\mathrm{Ti}]_{\mathrm{final}})}{M_{\mathrm{Ti}}}$$

$$= 22.4\times\frac{1}{2}\times\frac{1000\times 30\times(0.182\%\text{-}0.030\%)}{48} = 10.6\ L \tag{12}$$

where M_{Ti} was used to express molar mass of Ti.

5. CONCLUSIONS

(1) The occurrence state of titanium in silicomanganese is mainly the TiN phase and it can be expelled by blowing of N_2 during refining.

(2) By the refining with blowing N_2, the content of Ti and N in silicomanganese would decrease together by the average ratio of 84.75% and 80.93% respectively, which produced the silicomanganese product with the maximum Ti content of 0.03 mass% or 0.05 mass%。

(3) The final content of Ti in alloy increased with increasing refining temperature. The Ti content in alloys scattered in the range of 0.023 mass%~0.059 mass% when temperature was below 1580K.

(4) When N_2 was blown into the melt, the proper refining period was 10~15 minutes and the further longer refining did not cause more Ti removed.

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