

RESEARCH ON PROMOTING THE FORMATION AND CLUSTERS OF TiN PHASE IN HIGH PURITY CAST IRON

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As China is constantly striding forward from a large foundry country to a powerful one, the requirements of high purity cast iron for high-end castings have increased significantly and urgently. However, high purity cast iron produced by blast furnaces in China is always unable to meet national standard of high-end castings due to the exceeding of Ti. Based on the thermodynamic analysis, a detitanization method of increasing N in hot cast iron to promote the formation and clusters of TiN is proposed. High-temperature experiment has proved that N-addition can effectively promote the formation and clusters of TiN in hot cast iron, which provides the possibility for subsequent removal of Ti from high purity cast iron to meet the national standard.

Key words: cast iron, high purity, TiN, thermodynamic analysis, X-ray research (XRD, SEM, EDS)

INTRODUCTION

Since the 21st Century, high-end castings have become one of the key high-quality raw materials in many industries, which are derived from high purity cast iron [1]. As one of the harmful elements in cast iron, Ti is easy to form high-hardness carbonitrides [2], which frequently results in the casting embrittlement [3]. In 2014, the national standard of high purity cast iron issued by the Ministry of Industry and Information Technology of China (JB/T 11994-2014) regulated the content of Ti as Table 1. But in fact, as shown in Table 2, there are almost no blast furnace in China that can produce high purity cast iron of C1. Even though the high-priced imported low-Ti ore was reluctantly used, only C2 could be produced by few blast furnaces. The production and supply of high purity cast iron with low Ti has formed a serious bottleneck restriction on the national development strategy of a powerful foundry country. Therefore, a detitanization method for high purity cast iron should be imperatively put forward as soon as possible.

The traditional removal of Ti mainly focused on the method of oxidation for steelmaking iron, whose technical protocol oxidized Ti into TiO_2 by oxidant-addition in hot steelmaking iron and integrated TiO_2 into the slag, so that Ti was removed from steelmaking iron. Such being the case, is the method of oxidation also suitable for high purity cast iron? Based on the chemical composition of high purity cast iron produced by enterprise SXJB in Ta-

Table 1 The chemical composition national standard of high purity cast iron [4]

Level	Chemical composition / mas. %					
	C	Si	Ti	Mn	P	S
C1	≥3,3	≤0,4	≤0,01	≤0,05	≤0,02	≤0,015
C2	≥3,3	≤0,7	≤0,03	≤0,15	≤0,03	≤0,020

Table 2 The chemical composition of high purity cast iron in key domestic enterprises / mas. %

Enterprises	C	Si	Ti	Mn	P	S
HBLFS	4,1	0,38	0,016	0,046	0,018	0,014
SXJB	3,75	0,91	0,037	0,041	0,015	0,012
LNST	4,1	0,52	0,036	0,053	0,028	0,014
LNHW	3,9	0,44	0,038	0,062	0,026	0,013
SDKC	4,0	0,34	0,027	0,082	0,024	0,020
HBYL	3,8	0,36	0,025	0,010	0,025	0,025
HBCF	4,1	0,41	0,032	0,065	0,021	0,015
HBJF	4,2	0,47	0,026	0,043	0,025	0,019
SXHS	4,0	0,51	0,031	0,088	0,028	0,015
SXDC	4,1	0,33	0,047	0,121	0,032	0,028
HNLG	3,6	0,50	0,040	0,083	0,028	0,014
HNHX	3,8	0,53	0,039	0,050	0,030	0,013

ble 2, the reducibility of C, Si, Ti in the hot metal was compared by thermodynamic calculation. The calculation results are shown in Figure 1 (For $C > 1\%$, the calculation results contain the non-linear of the activity coefficient in the Wagner model) [5]. As shown, because of the higher activity of C and Si than Ti in hot iron, the process of detitanization by oxidation is often accompanied with decarburization and desiliconization, which will make a massive impact on the content of C and Si, so that the method of oxidation is not fit for high purity cast iron. Therefore, there is an urgent practical need to develop a selective deep detitanization method outside the blast furnace for high purity cast iron as this work.

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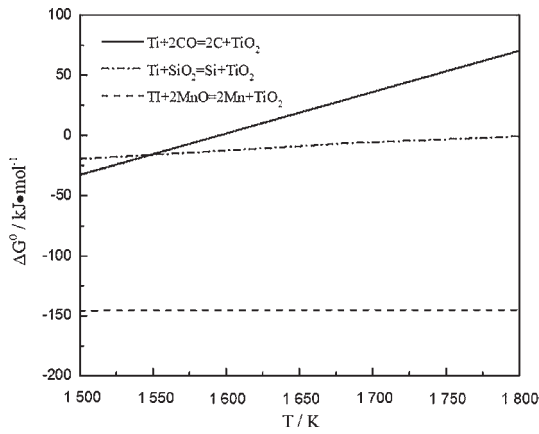
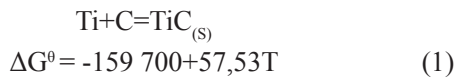


Figure 1 The reducibility of C, Si, Ti in high purity cast iron

THERMODYNAMIC ANALYSIS

On the basis of foregoing, a new method that was increasing N in hot cast iron to promote the formation, clusters and removal of TiN may realize the selective deep detitanization. In order to verify the feasibility of the method, based on the chemical composition of high purity cast iron produced by SXJB (Table 2), the thermodynamic calculation of the reactions of C, N and Ti in hot high purity cast iron were carried out as below.

TiC formation reaction is Eq. (1).



If TiC formation reaction reached the equilibrium state, $\Delta G = 0$, derived as Eq. (2):

$$\Delta G^\theta + RT \ln \frac{a_{\text{TiC}}}{a_{\text{C}} \cdot f_{\text{Ti}} \cdot \omega_{\text{Ti}}} = 0 \quad (2)$$

Where ΔG^θ is Gibbs free energy in the standard state / $\text{J}\cdot\text{mol}^{-1}$; R is molar gas constant / $8,314 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$; T is thermodynamic temperature, K; a_{TiC} is activity of TiC; a_{C} is activity of C; f_{Ti} is activity coefficient of Ti; ω_{Ti} is content of Ti in hot iron / mas. %.

f_{Ti} in hot iron could be calculated by Eq. (3) that proposed by Y. Ding [6]:

$$\lg f_{\text{Ti}} = \sum e_{\text{Ti}}^i \quad (3)$$

Where e_{Ti}^i is interaction coefficient of Ti with other components in hot iron, which was shown in Table 3.

Table 3 Interaction coefficients of Ti with other components in hot iron

i	C	Si	Mn	P
e	-0,165	0,05	0,0043	-0,0064
i	S	Ti	N	-
e	-0,11	0,013	-0,180	-

Further calculation, Eq. (4) could be derived by substituting the data.

$$\lg f_{\text{Ti}} = -0,4191 \times 10^{-3} T - 0,0566 \quad (4)$$

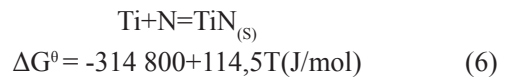
TiC whose activity is 1 is solid. The dissolution of C that is saturated in hot high purity cast iron is based on

pure substances as the standard state, so a_{C} is also 1. f_{Ti} was calculated according to Eq. (2), the relationship between ω_{Ti} and temperature in equilibrium with TiC in hot high purity cast iron was obtained as Eq. (5):

$$\lg \omega_{\text{Ti}} = 3,065 + 0,42 \times 10^{-3} T - \frac{8\,352,51}{T} \quad (5)$$

When the temperature was 1 773,15 K, ω_{Ti} was 0,12 % calculated by Eq. (5), which is much higher than the actual Ti in hot high purity cast iron. On the other hand, when ω_{Ti} was 0,034 %, T was 1 614 K calculated by Eq. (5), which is the critical temperature of TiC formation. When the temperature is lower than 1 614 K, TiC can be generated and precipitated in hot cast iron.

TiN formation reaction is Eq. (6).



If TiN formation reaction reached the equilibrium state, $\Delta G = 0$, derived as Eq. (7):

$$\Delta G = \Delta G^\theta + RT \ln \frac{a_{\text{TiN}}}{a_{\text{N}} \cdot a_{\text{Ti}}} = 0 \quad (7)$$

Where a_{TiN} is activity of TiN; a_{N} is activity of N; a_{Ti} is activity of Ti.

f_{N} is activity coefficient of N in hot high purity cast iron, which could be calculated according to Eq. (8).

$$\lg f_{\text{N}} = \sum e_{\text{N}}^i \quad (8)$$

Where e_{N}^i is interaction coefficient of N with other components in hot iron, which was shown in Table 4.

Table 4 Interaction coefficients of N with other components in hot iron

i	C	Si	Mn	P
e	0,13	0,047	-0,021	0,045
i	S	Ti	N	-
e	0,007	-0,53	0	-

The relationship between f_{N} and temperature could be deduced as Eq. (9):

$$\lg f_{\text{N}} = 0,3302 \times 10^{-3} T + 0,96 \quad (9)$$

Further calculation, Eq. (10) could be derived by substituting the data.

$$\lg \omega_{\text{Ti}} = 7,5466 + 0,0889 \times 10^{-3} T - \frac{16\,441,22}{T} \quad (10)$$

When the temperature was 1 773,15 K, ω_{Ti} was 0,026 % calculated by Eq. (10), which is lower than the actual Ti in hot high purity cast iron. When ω_{Ti} was 0,034 %, so T was 1 795 K that is the critical temperature of TiN formation in hot high purity cast iron. When the temperature is lower than 1 795 K, TiN can be formed and precipitated in hot iron.

The formations of TiC and TiN changed with different temperature and Ti were calculated based on Eq. (5) and Eq. (10) and drew as Line 1 and Line 2 respectively in Figure 2. It can be seen that if Ti in hot high purity

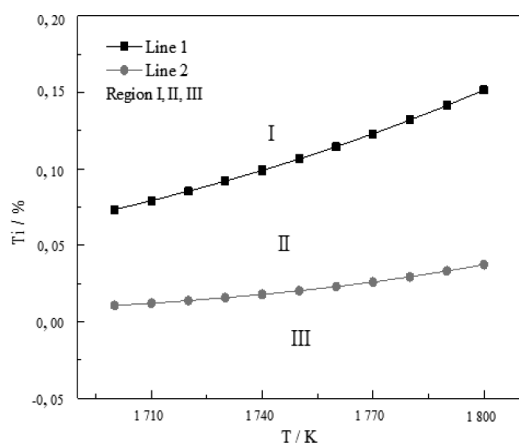


Figure 2 Relationship between ω_{Ti} , TiC and TiN in hot high purity cast iron

cast iron was under Line 2, which means Ti is lower than that required for the equilibrium with TiC and TiN, there was hardly any formation of TiC and TiN in region III. If the Ti in hot high purity cast iron is above Line 2 but under Line 1, which means Ti is lower than that required in equilibrium with TiC but higher than that required in equilibrium with TiN, there was little TiC formation but TiN formation in region II. If Ti in the hot high purity cast iron is above Line 1, which means Ti is higher than that required in equilibrium with TiC and TiN, there were continuous and stable formation of TiC and TiN in region I. The above studies show that the formation of TiC was much more difficult than that of TiN due to the original Ti (0,037 %) and the saturated C (3,75 %) in hot high purity cast iron. Therefore, it is more reasonable to promote TiN formation by increasing N in the hot cast iron, which guided that the N-containing alloy was selected as the N-addition intensifier to carry out the experiment of N-addition in hot cast iron.

N-ADDITION EXPERIMENT

The heating equipment used in this experiment was Vacuum Atmosphere Box-type Resistance Furnace. The high purity cast iron was obtained from SXJB. The N-containing alloy whose X-ray diffraction (XRD) is shown in Figure 3 was selected as the N-addition intensifier.

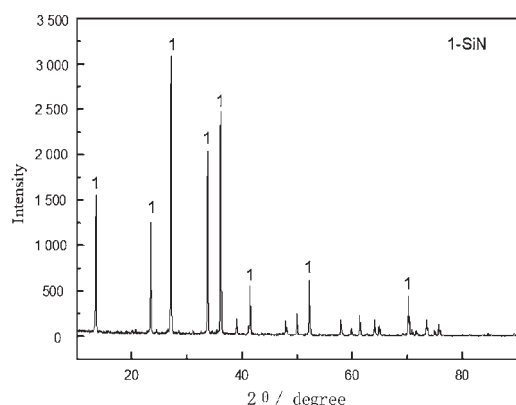


Figure 3 XRD of the N-containing alloy

Firstly, two samples of high purity cast iron was cropped and put into two corundum crucibles respectively for the high temperature experiment. Sample B was heated with N-containing alloy, Sample A was not. According to the conservation of mass and considering the loss of N increasing process, the high purity cast iron along with pure N-containing alloy were mixed at a mass ratio of 1 000: 4 so that the cast iron sample was 130 g and the N-containing alloy was 0,52 g. And then two corundum crucibles were put into the furnace.

Secondly, the furnace was vacuumed by vacuum pump to -0,75 MPa and filled with Ar to 0 MPa for three times. And then, Ar was continuously passed over the furnace to protect the high temperature experimental process. Whereafter, the furnace whose maximum heating temperature was set at 1 500 °C started heating. when the temperature reached 1 500 °C, it was kept for 180 mins and then dropped to room temperature. The two samples which had been take out off the furnace were polished for Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) test as shown in Figure 4.

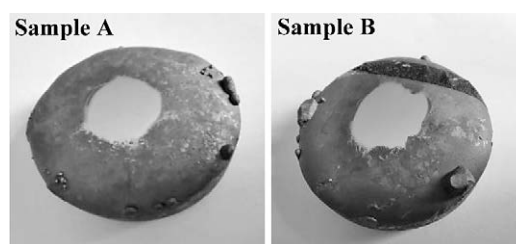


Figure 4 Polished Sample A and B

RESULT ANALYSIS

Typical TiN phase that has a regular quadrilateral structure in the iron with relatively clear edges and corners [7]. Figure 5 were the SEM of Sample A. It can be seen that there were few typical TiN precipitations (in the circle) in high purity cast iron without N-addition, but the TiN whose amount was less presented a discrete distribution.

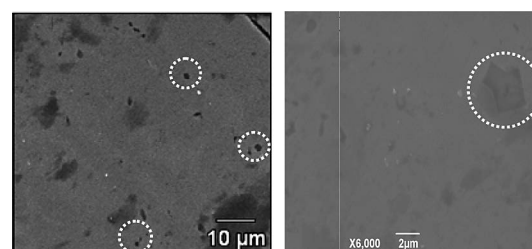


Figure 5 SEM of Sample A

Figure 6 were the SEM of sample B. It can be seen that a large amount of TiN precipitates on the surface of the cast iron after N-addition, which were obvious clusters and polymerization as shown in the circle.

The N-addition experimental results strongly show that: Firstly, the N-addition in hot high purity cast iron

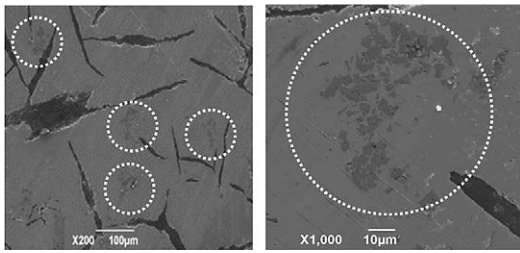


Figure 6 SEM of Sample B

can promote the formation of TiN. Secondly, the TiN in hot high purity cast iron could spontaneously float to the surface and cluster together. Thirdly, the massive precipitation and clusters of TiN in hot high purity cast iron provide the possibility for the subsequent selective deep detitination.

CONCLUSION

(1) Thermodynamic calculation analysis shows that it is more reasonable to promote TiN formation by N-addition in the hot high purity cast iron.

(2) High-temperature N-addition experiment showed that the TiN in hot high purity cast iron could spontaneously generate and float to the surface and cluster together by N-addition.

(3) The massive formation and clusters of TiN in hot high purity cast iron provide the possibility for the subsequent selective deep detitination.

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Note: Y.MA is responsible for English language, Anhui, China