

Article

Titanium Impurity Control in V-Bearing Pig Iron Prepared via the Sodium Smelting of Vanadium–Titanium Magnetite

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Abstract: The sodium smelting of vanadium–titanium magnetite (VTM) can realize a multi-component comprehensive utilization of VTM. To broaden the application of the vanadium-bearing pig iron produced through this process, it is imperative to maintain the titanium content in molten iron at a very low level. In this study, the effects of temperature, the added amounts of sodium carbonate and anthracite, and the smelting time on the titanium content of molten iron were investigated using thermodynamic calculations and experiments. The results indicate that the introduction of sodium carbonate makes the reduction reaction of VTM a relatively low-temperature smelting system. In the smelting process, the Ti content in molten iron increases with the increase in temperature and decreases with the addition of sodium carbonate, while the amount of anthracite added has little effect on it. The appropriate technological parameters were determined as temperature: 1150–1250 °C, smelting time: ≥ 2 h, anthracite consumption: 25–35%, and sodium carbonate consumption: $\geq 60\%$. In addition, it was determined that the Ti impurities in the V-bearing pig iron were mainly (Ti,V)(C,N), CaTiO₃, and Na₂TiO₃. All results obtained from this work contribute to the comprehensive utilization of VTM, and also provide theoretical support for the sodium smelting of VTM.



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Keywords: vanadium–titanium magnetite; sodium smelting; V-bearing pig iron; titanium impurity; thermodynamic calculation

1. Introduction

Vanadium–titanium magnetite (VTM) is a strategic resource which is rich in vanadium, titanium, and iron [1,2]. Blast furnaces, which have the advantages of a large treatment capacity and high production efficiency, have been widely used for industrial VTM smelting. However, all titanium resources that originally occur in VTM migrate into the blast furnace slag, rendering the effective utilization of titanium challenging [3–5]. More than 3 million tons of titanium slag is produced every year, and over 80 million tons of titanium-bearing blast furnace slag has been accumulated in China [6]. Recently, some non-blast furnace direct reduction techniques, such as the pre-reduction–electric furnace melting separation process and the direct reduction–magnetic separation process, have also been proposed [7–9]. Although they could replace the blast furnace process to some extent, they still could not simultaneously recover the iron, vanadium, and titanium in VTM, and especially the titanium resource is not effectively utilized [10,11]. To efficiently recover these resources from VTM, a novel sodium smelting process, which combined pyrometallurgy and hydrometallurgy, was proposed, and a pilot test consuming 50,000 tons of VTM annually was established [12–14]. In the pyrometallurgy stage, a proportional mixture of VTM, sodium carbonate, and anthracite is smelted to obtain pig iron and vanadium-bearing titanium slag. In the hydrometallurgy stage, the vanadium-bearing titanium slag is leached with water to produce vanadium and titanium products. This technology allows for the

melting and separation of molten iron and vanadium-bearing titanium slag at relatively low temperatures. The obtained content of impurity elements in the molten iron is very low, but the titanium content fluctuates considerably. Therefore, it is imperative to study the migration law of titanium during the sodium smelting process.

Titanium is a common impurity element in molten iron, which has a strong affinity for O, N, and C [15]. It is easy to combine titanium with these three elements during the steelmaking process to form inclusions such as TiO_2 and Ti(C,N) , which pose a great threat to the performance of steel [16,17]. Therefore, some specialized steel grades, such as electrical steel, bearing steel, spring steel, etc., have strict requirements for the Ti content in the steel [18,19]. Generally, the control of titanium mainly focuses on the steelmaking stage. Taking bearing steel as an example, in order to prevent an increase in the titanium content after smelting, the amount of titanium-bearing slag in the steel tank is controlled by adopting low-titanium molten iron raw materials, less slag smelting, and slag-blocked tapping [20–22]. Meanwhile, the introduction of titanium impurities is also prevented by controlling the levels of titanium in alloy raw materials and auxiliary resistant materials. However, there is no reasonable control of the titanium content in molten iron in the long-flow ironmaking process, especially when the raw material is VTM, and the titanium content is as high as 0.3% or more [23,24]. If the titanium impurities in molten iron can be controlled at a low level before steelmaking, the burden of removing the titanium in the steelmaking stage will be greatly reduced. Li et al. [25] proposed the use of nitrogen for the pre-titanium removal of molten iron at 1300 °C, and the rate of titanium removal was 20%, indicating that nitrogen is less effective in removing titanium. Liu et al. [26] pretreated molten iron using titanium removal agents containing iron oxide, and the rate of titanium removal was 57.19–71.20%, indicating that iron oxide is a good titanium removal agent. Wei et al. [27] pretreated vanadium-bearing molten iron with sodium carbonate at about 1280 °C, and the titanium content in the molten iron was reduced from 100 ppm to 5 ppm, indicating that sodium carbonate has an excellent titanium removal effect.

Due to the presence of a large amount of Na_2O -bearing slag during the sodium smelting of VTM, it has a very good effect on the removal of impurities [28–30]. If low-titanium-content molten iron can be obtained by adjusting the process parameters, it will greatly broaden its use and enhance its value. Therefore, in order to obtain high quality V-bearing pig iron with few impurities through the sodium smelting process, the investigation of titanium removal from molten iron during the smelting process is extremely critical.

In the present work, the control of titanium impurities in V-bearing pig iron prepared via the sodium smelting of VTM was studied. The effects of temperature, the added amounts of sodium carbonate and anthracite, and the smelting time on the titanium content of molten iron after the smelting reduction were investigated through experiments and thermodynamic calculations. In addition, the optimal conditions for the production of high-quality V-bearing pig iron were included. And the existing forms of Ti inclusions in V-bearing pig iron were explored.

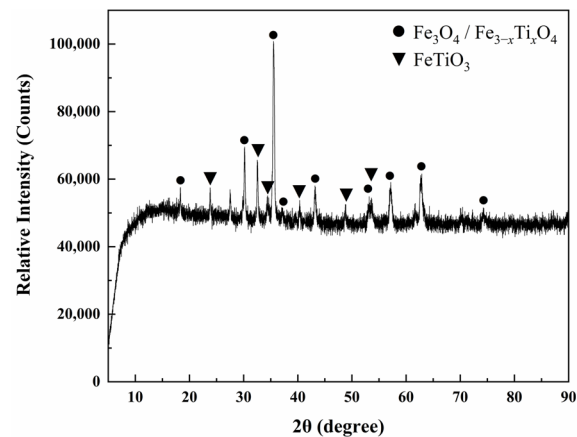
2. Calculation Settings and Experimental Procedures

2.1. Raw Materials

The VTM was from Chaoyang, Liaoning Province, China, and its chemical composition is shown in Table 1. The total iron was determined via chemical titration. Silicon, titanium, and other elements were determined using the inductively coupled plasma atomic emission spectrometric method. Figure 1 shows the X-ray diffraction (XRD, conducted using a $\text{Cu-K}\alpha$ source) patterns of the VTM. The main mineral phase of the VTM was magnetite (Fe_3O_4) and ilmenite (FeTiO_3). Reagent grade Na_2CO_3 was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The main elemental analysis of the anthracite used in the experiment is shown in Table 2, which was tested by the China National Coal Quality Supervision and Testing Center.

Table 1. Chemical compositions of the VTM (wt.%).

Components	TFe	TiO ₂	SiO ₂	CaO	Al ₂ O ₃	V ₂ O ₅	MgO	MnO	S	P
Content	47.97	19.32	6.59	2.98	2.29	1.46	0.70	0.41	0.028	0.011

**Figure 1.** XRD pattern of VTM.**Table 2.** Analysis of main elements in anthracite (wt.%).

Elements	C	H	O	N	S	P
Content	81.53	2.60	2.78	0.94	0.35	0.028

2.2. Calculation Settings

The Equilib module of FactSage 8.1 (Thermfact Ltd., Montreal, QC, Canada and GTT-Technologies, Aachen, Germany) was used for the thermodynamic calculations. The compositions were set according to the elemental analyses depicted in Tables 1 and 2. The content of the sodium carbonate was set as a variable from 0 to 100% of the VTM. The amount of anthracite was also set as a variable. The specific database, temperature, and other conditions were set as follows:

Database: FSstel; FToxid; FactPS;

Temperature: 1150–1500 °C;

Solution phase setting: FToxid-SLAGA; FT-oxid;

Compound setting: pure solids;

Equilibrium: normal;

Weight of VTM: 100 g.

2.3. Experimental Procedure

The VTM and anthracite were first crushed and ground. Subsequently, 100 g of VTM and the designated proportion of anthracite powder and sodium carbonate were mixed in an agate mortar and then moved into a silicon carbide crucible. Then, the mixed raw materials were heated at 1200–1500 °C for 2 h in a muffle furnace and cooled at room temperature. A brief flow chart of the smelting process is shown in Figure 2. The pig iron obtained from the experiments was sliced and polished, and we then performed the elemental analysis. The polished iron block samples were detected using high-sensitivity XRF (PHECDA-PRO, Beijing Ancoren Technology Co., Ltd., Beijing, China).

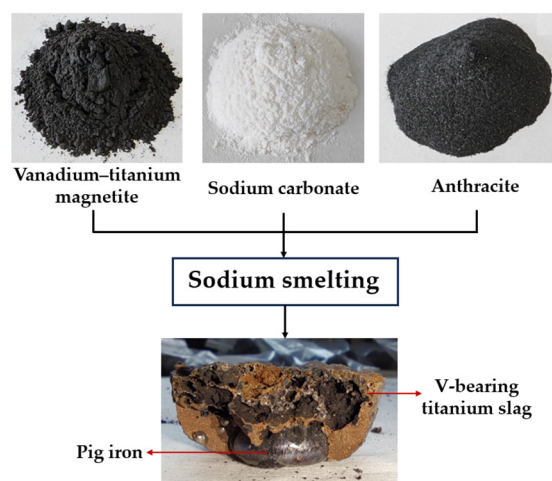


Figure 2. Flow sheet of the sodium smelting of VTM.

3. Thermodynamic Calculation

3.1. Advantageous Products in the Reduction Process

Yin et al. [14] studied the structure of slag in a VTM sodium reduction reaction at 1200 °C, and concluded that the main Ti-bearing units in the slag were $\text{CaO} \cdot \text{TiO}_2$ and $\text{Na}_2\text{O} \cdot \text{TiO}_2$. Therefore, the standard Gibbs free energy (ΔG_T^θ) of the equations for the FeTiO_3 , $\text{CaO} \cdot \text{TiO}_2$, and $\text{Na}_2\text{O} \cdot \text{TiO}_2$ sodiation reactions in the complex system were calculated using FactSage. The ΔG_T^θ of the chemical reactions at the corresponding temperature could be obtained by inputting the chemical reaction equations in the Reaction module in FactSage.

The main possible chemical reactions for FeTiO_3 during the sodium reduction reaction of VTM are listed in Table 3.

Table 3. Main reactions of reduction, carbonization, and nitridation of FeTiO_3 .

Eq.	Chemical Reactions	$\Delta G_T^\theta/\text{J} \cdot \text{mol}^{-1}$	Spontaneous Reaction Temperature/°C
(1)	$\text{FeTiO}_3 + \text{CaO} + \text{C} = \text{Fe} + \text{CaO} \cdot \text{TiO}_2 + \text{CO(g)}$	50,770–163.40T	310.71
(2)	$\text{FeTiO}_3 + \text{Na}_2\text{O} + \text{C} = \text{Fe} + \text{Na}_2\text{O} \cdot \text{TiO}_2 + \text{CO(g)}$	−104,952–137.33T	−764.23
(3)	$\text{FeTiO}_3 + \text{Na}_2\text{CO}_3 + 2\text{C} = \text{Fe} + \text{Na}_2\text{O} \cdot \text{TiO}_2 + 3\text{CO(g)}$	282,132–426.77T	661.09
(4)	$\text{FeTiO}_3 + 3/2\text{Na}_2\text{CO}_3 + 5/2\text{C} + \text{SiO}_2 + 1/2\text{Al}_2\text{O}_3 = \text{Fe} + \text{Na}_2\text{O} \cdot \text{TiO}_2 + \text{NaAlSiO}_4 + 4\text{CO(g)}$	303,442–575.43T	527.33
(5)	$\text{FeTiO}_3 + 4\text{C} = \text{Fe} + \text{TiC} + 3\text{CO(g)}$	569,851–490.88T	1160.88
(6)	$\text{FeTiO}_3 + 1/2\text{Na}_2\text{CO}_3 + \text{SiO}_2 + 1/2\text{Al}_2\text{O}_3 + 9/2\text{C} = \text{Fe} + \text{TiC} + \text{NaAlSiO}_4 + 4\text{CO(g)}$	591,707–639.98T	924.57
(7)	$\text{FeTiO}_3 + 1/2\text{Na}_2\text{CO}_3 + \text{SiO}_2 + 1/2\text{Al}_2\text{O}_3 + 7/2\text{C} + 1/2\text{N}_2\text{(g)} = \text{Fe} + \text{TiN} + \text{NaAlSiO}_4 + 4\text{CO(g)}$	465,606–568.64T	818.81

The ΔG_T^θ of the above equations at different temperatures was obtained through calculations, as shown in Figure 3. It can be seen that the spontaneous reaction temperatures of Equations (1)–(4) were very low, indicating that $\text{CaO} \cdot \text{TiO}_2$, $\text{Na}_2\text{O} \cdot \text{TiO}_2$, NaAlSiO_4 , and Fe are preferentially generated in the carbothermal reduction process. In addition, with the spontaneous reaction temperature of reaction (7) being around 818 °C, the possibility of TiC and TiN generation is very high. Chen et al. [13] tested the viscosity of slag and showed that the slag was completely melted at 1150 °C with the appropriate components, indicating that the above reactions are possible in the sodium smelting temperature range.

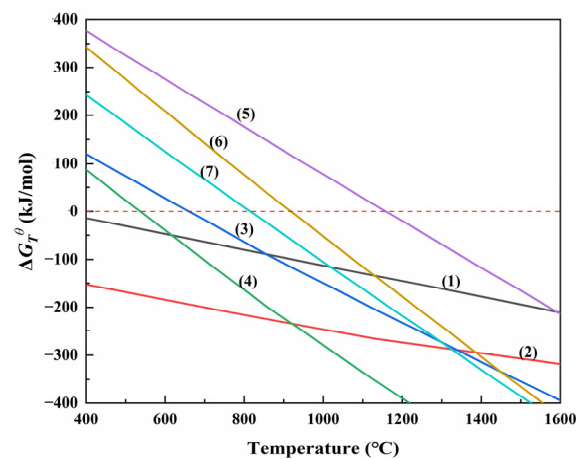


Figure 3. ΔG_T^θ -T trends of the reactions involving FeTiO_3 from (1) to (7) during the sodium reduction reaction of VTm.

During the sodium reduction reaction of VTm, $\text{CaO} \cdot \text{TiO}_2$ may undergo the following reactions listed in Table 4.

Table 4. Main reactions of reduction, carbonization, and nitridation of $\text{CaO} \cdot \text{TiO}_2$.

Eq.	Chemical Reactions	$\Delta G_T^\theta/\text{J} \cdot \text{mol}^{-1}$	Spontaneous Reaction Temperature/ $^\circ\text{C}$
(8)	$\text{CaO} \cdot \text{TiO}_2 + 3\text{C} = \text{TiC} + \text{CaO} + 2\text{CO}(\text{g})$	$519,588-328.04T$	1583.92
(9)	$\text{CaO} \cdot \text{TiO}_2 + 2\text{C} + 1/2\text{N}_2(\text{g}) = \text{TiN} + \text{CaO} + 2\text{CO}(\text{g})$	$387,936-248.02T$	1564.13
(10)	$\text{CaO} \cdot \text{TiO}_2 + 3\text{C} + \text{SiO}_2 = \text{TiC} + \text{CaO} \cdot \text{SiO}_2 + 2\text{CO}(\text{g})$	$430,020-326.67T$	1316.37
(11)	$\text{CaO} \cdot \text{TiO}_2 + 2\text{C} + 1/2\text{N}_2(\text{g}) + \text{SiO}_2 = \text{TiN} + \text{CaO} \cdot \text{SiO}_2 + 2\text{CO}(\text{g})$	$298,412-246.68T$	1209.71
(12)	$\text{CaO} \cdot \text{TiO}_2 + 1/2\text{Na}_2\text{CO}_3 + 7/2\text{C} + 2\text{SiO}_2 + 1/2\text{Al}_2\text{O}_3 = \text{CaO} \cdot \text{SiO}_2 + \text{TiC} + 3\text{CO}(\text{g}) + \text{NaAlSiO}_4$	$452,468-476.41T$	949.74
(13)	$\text{CaO} \cdot \text{TiO}_2 + 1/2\text{Na}_2\text{CO}_3 + 5/2\text{C} + 1/2\text{N}_2(\text{g}) + 2\text{SiO}_2 + 1/2\text{Al}_2\text{O}_3 = \text{CaO} \cdot \text{SiO}_2 + \text{TiN} + 3\text{CO}(\text{g}) + \text{NaAlSiO}_4$	$320,641-396.22T$	809.25

Figure 4 shows the ΔG_T^θ -T trends of the reactions involving $\text{CaO} \cdot \text{TiO}_2$ during the sodium reduction reaction of VTm. The ΔG_T^θ of reactions (1) and (2) is less than zero, but only at higher than 1550 $^\circ\text{C}$, indicating that the reduction of $\text{CaO} \cdot \text{TiO}_2$ requires a temperature of higher than 1550 $^\circ\text{C}$. And in the presence of SiO_2 , the reduction temperature of $\text{CaO} \cdot \text{TiO}_2$ can be reduced to about 1210 $^\circ\text{C}$. Further, the reduction temperature of $\text{CaO} \cdot \text{TiO}_2$ can be reduced to about 809 $^\circ\text{C}$ if Na_2CO_3 is present. In addition, $\text{CaO} \cdot \text{SiO}_2$ is the dominant product in the reactions involving $\text{CaO} \cdot \text{TiO}_2$ during the sodium reduction reaction of VTm.

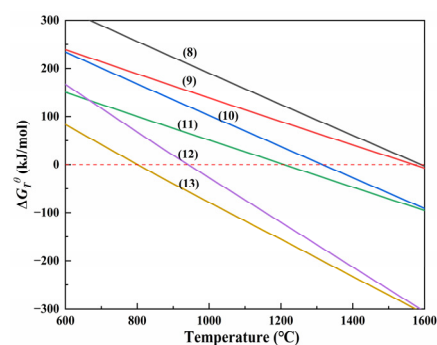


Figure 4. ΔG_T^θ -T trends of the reactions involving $\text{CaO} \cdot \text{TiO}_2$ from (8) to (13) during the sodium reduction reaction of VTm.

During the sodium reduction reaction of VTM, $\text{Na}_2\text{O} \cdot \text{TiO}_2$ may undergo the following reactions listed in Table 5.

Table 5. Main reactions of reduction, carbonization and nitridation of $\text{Na}_2\text{O} \cdot \text{TiO}_2$.

Eq.	Chemical Reactions	$\Delta G_T^\theta / \text{J} \cdot \text{mol}^{-1}$	Spontaneous Reaction Temperature/ $^\circ\text{C}$
(14)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 3\text{C} = \text{TiC} + \text{Na}_2\text{O} + 2\text{CO}(\text{g})$	673,415–352.20T	1912.02
(15)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 2\text{C} + 1/2\text{N}_2(\text{g}) = \text{TiN} + \text{Na}_2\text{O} + 2\text{CO}(\text{g})$	541,833–272.21T	1990.50
(16)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 3\text{C} + \text{SiO}_2 = \text{TiC} + \text{Na}_2\text{SiO}_3 + 2\text{CO}(\text{g})$	425,806–324.43T	1312.47
(17)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 2\text{C} + \text{N}_2(\text{g}) + \text{SiO}_2 = \text{TiN} + \text{Na}_2\text{SiO}_3 + 2\text{CO}(\text{g})$	294,205–244.47T	1203.44
(18)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 3\text{C} + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 = \text{TiC} + 2\text{NaAlSiO}_4 + 2\text{CO}(\text{g})$	331,721–362.41T	915.32
(19)	$\text{Na}_2\text{O} \cdot \text{TiO}_2 + 2\text{C} + 1/2\text{N}_2(\text{g}) + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 = \text{TiN} + 2\text{NaAlSiO}_4 + 2\text{CO}(\text{g})$	200,110–282.44T	708.50

Figure 5 shows the ΔG_T^θ -T trends of the reactions involving $\text{Na}_2\text{O} \cdot \text{TiO}_2$ during the sodium reduction reaction of VTM. It can be seen that $\text{Na}_2\text{O} \cdot \text{TiO}_2$ cannot be reduced alone below 1900°C , mainly because Na_2O is too reactive to exist independently. In the presence of SiO_2 and Al_2O_3 , the reduction temperature of $\text{Na}_2\text{O} \cdot \text{TiO}_2$ can be reduced to about 708.50°C . The dominant product of the reaction involving $\text{Na}_2\text{O} \cdot \text{TiO}_2$ is NaAlSiO_4 .

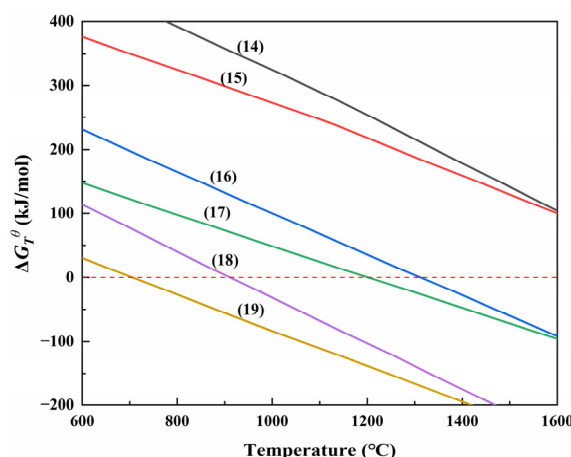


Figure 5. ΔG_T^θ -T trends of the reactions involving $\text{Na}_2\text{O} \cdot \text{TiO}_2$ from (14) to (19) during the sodium reduction reaction of VTM.

3.2. Ti Content in the Reduction Product (Melt)

Temperature has a great influence on the sodium reduction reaction of VTM, which affects the composition of molten iron. Calculations were carried out at different temperatures from 1150°C to 1500°C to investigate the effect of temperature on the composition of molten iron. The amounts of sodium carbonate in the calculation were set to 40% and 60%, and the amount of anthracite was set to 30%.

Figure 6 shows the effect of temperature on the content of Ti in molten iron. One can see from the calculated data in Figure 5 that when the amount of sodium carbonate is 40%, the Ti content in molten iron is at a lower level (<13.8 ppm) when the temperature is below 1250°C . However, when the temperature exceeds 1250°C , the Ti content in molten iron increases rapidly with the increase in temperature. When the temperature rises to 1450°C , the Ti content in molten iron reaches about 1000 ppm. And then, with the increase in temperature, the Ti content in molten iron is slightly decreased. When the amount of sodium carbonate is 60%, the titanium content in molten iron remains below 1 ppm. Therefore, it can be concluded that a relatively low temperature ($<1250^\circ\text{C}$) is conducive to the production of molten iron with less titanium impurities.

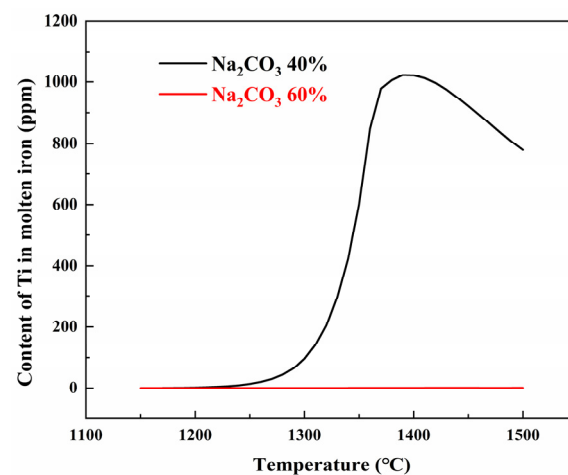


Figure 6. Ti content in molten iron at different temperatures when the ratio of VTM, sodium carbonate, and anthracite is 100:60:30.

The effect of the addition of sodium carbonate on the Ti content in molten iron was investigated at 1200 °C with a 30% anthracite addition. As can be seen in Figure 7, the Ti content in molten iron is almost constant with the increase in the added amount of sodium carbonate when the amount of sodium carbonate added is less than 10%. When the amount of sodium carbonate added is more than 10%, the Ti content in molten iron decreases rapidly. When the amount of sodium carbonate added is 40%, the Ti content in the molten iron is 1.9 ppm. When the amount of sodium carbonate is 60%, the Ti content is 0.05 ppm. The more sodium carbonate is added, the lower the Ti content in molten iron.

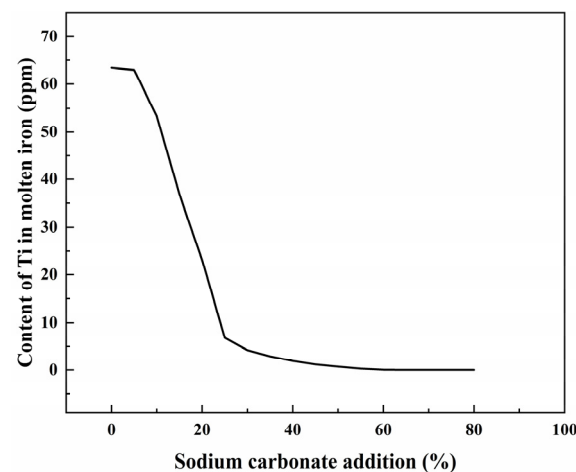


Figure 7. Ti content in molten iron at different sodium carbonate additions when the temperature is 1200 °C and the ratio of VTM to anthracite is 100:30.

The effect of the addition of anthracite on the Ti content in molten iron was investigated at 1200 °C with 40% and 60% of sodium carbonate, respectively. As can be seen in Figure 8, with the increase in the amount of anthracite added, the Ti content in the molten iron changes little and is always below 5 ppm. This indicates that the amount of anthracite does not affect the Ti content in molten iron. Therefore, a relatively small amount of anthracite can be used for smelting when slag and iron can be separated normally.

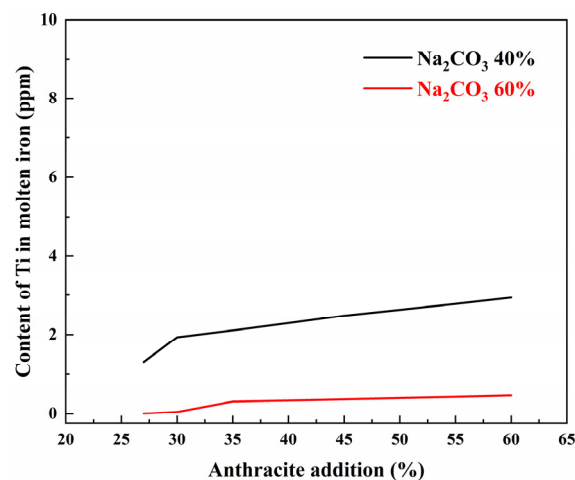


Figure 8. Ti content in molten iron at different anthracite additions when the temperature is 1200 °C and the ratio of VTM to sodium carbonate is 100:60.

The above calculation results indicate that, during the sodium smelting of VTM, if sufficient sodium carbonate is present, Ti mainly exists in the slag in the form of stable $\text{CaO} \cdot \text{TiO}_2$ and $\text{Na}_2\text{O} \cdot \text{TiO}_2$. The Ti content increases with temperature and decreases with the addition of sodium carbonate, while the amount of anthracite added has little effect on it. It can be considered that a temperature of 1200 °C, a sodium carbonate addition of 60%, and an anthracite addition of 30% are better smelting conditions.

4. Results and Discussion

4.1. Effect of Temperature

Experiments at different temperatures from 600 to 1500 °C were carried out to investigate the effect of temperature on the Ti content in molten iron. The raw materials (100 g of VTM, 60% of sodium carbonate, and 30% of anthracite) were heated at 600–1500 °C for 2 h.

As shown in Figure 9, the Ti content in V-bearing pig iron can reach over 7000 ppm at 1150 °C. At this time, the temperature is low, the slag viscosity is high, and the separation of the slag and iron is insufficient, resulting in a large amount of slag entrained in the molten iron. Therefore, the Ti content in the molten iron is abnormally high. When the temperature increases to 1200 °C, the separation between the slag and the iron is good. At this time, the quality of the molten iron is good, and the Ti content is 23 ppm. With the gradual increase in temperature, the Ti content in the molten iron also gradually increases, which is consistent with the thermodynamic calculation results. At 1300 °C, the Ti content in molten iron reaches 322 ppm. When the temperature exceeds 1400 °C, the Ti content in the iron sample abnormally increases.

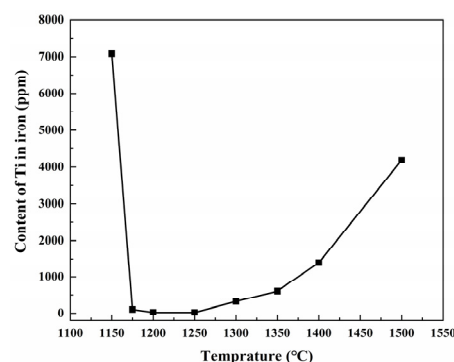


Figure 9. Ti content in pig iron at different temperatures when the ratio of VTM, sodium carbonate, and anthracite is 100:60:30.

Figure 10 shows the XRD patterns of the slag in the sodium smelting of VTM at different temperatures. It can be seen that the characteristic peaks of NaAlSiO_4 and CaTiO_3 begin to appear at 600 °C. Fe begins to be reduced at about 800 °C. When the temperature rises to 900–1100 °C, the characteristic peaks of elemental Fe rapidly strengthen, indicating that the Fe phase is formed in large quantities, while NaTiO_2 is further transformed to Na_2TiO_3 . At 1150 °C, the iron begins to separate from the slag, as this temperature is close to the range of the melting point of pig iron and, at the same time, a weak characteristic peak of TiCN appears. When the temperature rises to 1200 °C, there is almost no elemental Fe phase in the XRD, indicating that the slag and iron are fully separated. At this time, the Na_2TiO_3 in the slag begins to transform into $\text{Na}_{0.23}\text{TiO}_2$ or $\text{Na}_4\text{Ti}_5\text{O}_{12}$. At 1300 °C, it can be seen that the characteristic peak of NaAlSiO_4 begins to weaken, and the peak of sodium titanate is further altered, possibly due to the transition from $\text{Na}_4\text{Ti}_5\text{O}_{12}$ to $\text{Na}_{0.23}\text{TiO}_2$. When the temperature reaches 1400 °C, the characteristic peaks of TiCN in the slag are obviously strengthened, while the peaks of CaTiO_3 begin to weaken. At 1500 °C, only a strong TiCN phase remains in the recognizable phase, indicating that CaTiO_3 is reduced to TiCN. It is speculated that the abnormal increase in Ti content in V-bearing pig iron is closely related to the generation of the carbonitrides of Ti. Therefore, in order to control the Ti impurity content in pig iron, the smelting temperature should be controlled between 1150 and 1250 °C.

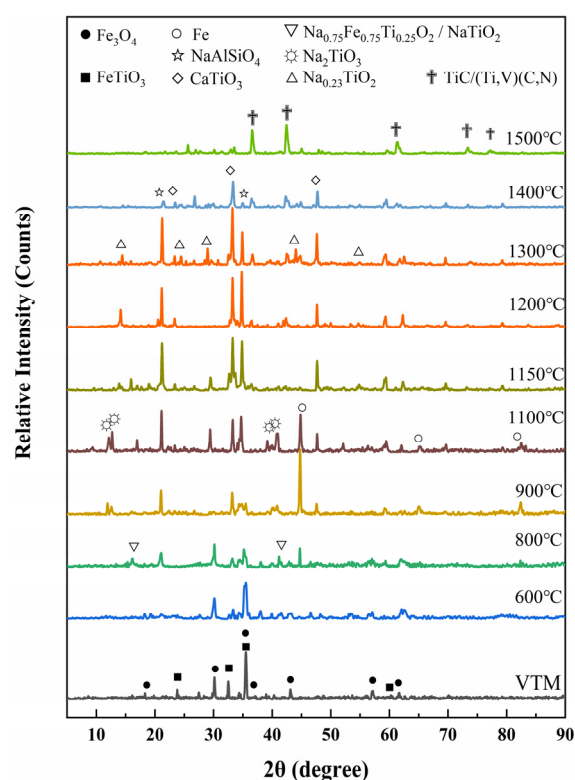


Figure 10. XRD patterns of slag in sodium smelting of VTM at different temperatures when the ratio of VTM, sodium carbonate, and anthracite is 100:60:30.

4.2. Effect of Heating Time

At 1200 °C, experiments were carried out to investigate the effect of heating time on the Ti content in molten iron by heating the mixture of 100 g of VTM, 60% of sodium carbonate, and 30% of anthracite at different heating times.

As shown in Figure 11, the reduction process of VTM is very rapid, and after about 15 min, V-bearing pig iron blocks were formed, and the Ti content in the iron sample was 229 ppm, indicating that the Ti impurities had not been completely separated. And the Ti content in the molten iron reached 23 ppm at 120 min. As the heating time was prolonged, the Ti content fluctuated within a relatively low range and could not be further reduced.

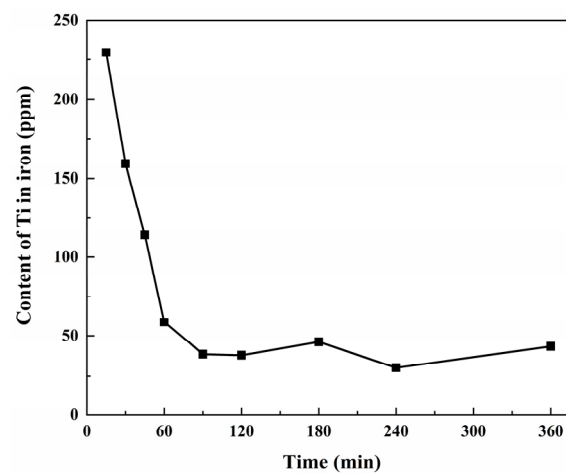


Figure 11. Ti content in pig iron at different heating times when the temperature is 1200 °C and the ratio of VTM, sodium carbonate, and anthracite is 100:60:30.

Figure 12 shows the XRD patterns of slag in the sodium smelting of VTM at different heating times. It can be seen that the sodium reduction reaction process is very fast and was completed within 10 min. At this time, there were very strong elemental Fe characteristic peaks in the slag phase, and the slag was mainly composed of Na_2TiO_3 , NaAlSiO_4 , and CaTiO_3 . However, the slag and iron were not separated, which may have been due to the low C content in the newly reduced V-bearing pig iron, which had a melting point higher than 1200 °C and could not form droplet aggregation and growth. After 15 min, the characteristic peaks of elemental Fe in the slag phase were already very weak, indicating that most of the iron droplets in the slag had been separated from the slag. After 120 min, the slag and iron were completely separated, and V-bearing pig iron with a low Ti content was obtained.

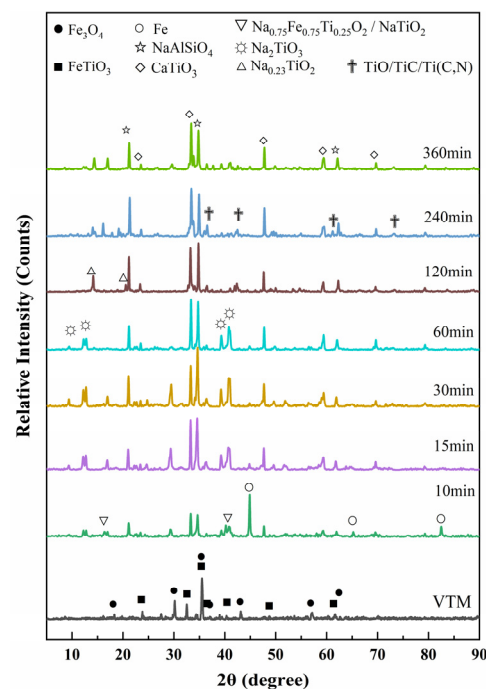


Figure 12. XRD patterns of slag in the sodium smelting of VTM at different heating times when the temperature is 1200 °C and the ratio of VTM, sodium carbonate, and anthracite is 100:60:30.

4.3. Effect of Sodium Carbonate Addition

The addition of sodium carbonate significantly lowers the melting point of slag, which drastically reduces the temperatures required for smelting VTM, and also enables the slag to have good fluidity at low temperatures as well as excellent impurity removal. A mixture of 100 g of VTM, 30% of anthracite, and varying amounts of sodium carbonate were combined and heated at 1200 °C for 2 h to investigate the effect of the addition of sodium carbonate on the Ti content in molten iron.

Figure 13 shows the variations in Ti content in molten iron with different amounts of sodium carbonate added. When the amount of sodium carbonate is less than 40%, the slag and iron can hardly be separated, and it is impossible to obtain iron blocks. When the amount of sodium carbonate is greater than 50%, the separation of slag and iron is improved, and the Ti content in molten iron gradually decreases. When the amount of sodium carbonate is 60%, the Ti content in molten iron can be controlled at 23 ppm. The Ti content in molten iron decreases with increasing amounts of sodium carbonate being added, which is consistent with the thermodynamic calculations.

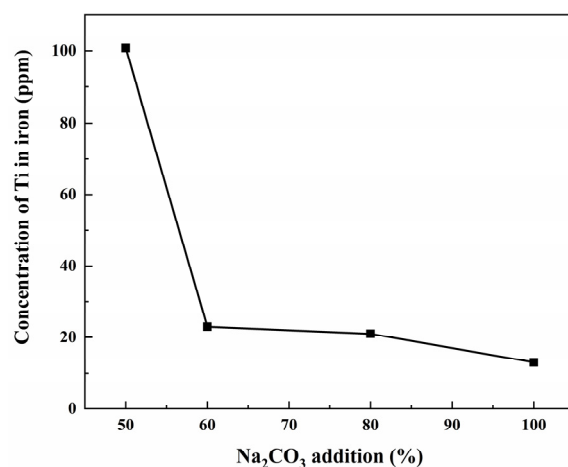


Figure 13. Ti content in pig iron at different sodium carbonate additions when the temperature is 1200 °C and the ratio of VTM to anthracite is 100:30.

Figure 14 shows the XRD patterns of slag in the sodium smelting of VTM with different amounts of sodium carbonate added. It can be seen that VTM can undergo a solid state reduction reaction when Na₂CO₃ is added at a level of less than 10%. Although there is a strong characteristic peak of Fe in the slag phase, the slag and iron cannot be separated. When the addition of Na₂CO₃ is at a level of 20–40%, Na₂TiO₃, NaAlSiO₄, and CaTiO₃ are formed in the slag phase, but the characteristic peaks of the elemental Fe are not strong. This indicates that, to obtain a complete iron block, it is necessary to ensure that there is a certain excess of Na₂CO₃ added on the premise of it fully combining with the gangue elements such as Ti, Si, and Al. When the amount of Na₂CO₃ added is at a level of 50–100%, high-quality V-bearing pig iron can be obtained. However, in the actual smelting process, excessive sodium carbonate will cause adverse effects such as increased smelting costs, severe equipment corrosion, and a poor operating environment. Therefore, it is necessary to control the amount of Na₂CO₃ used.

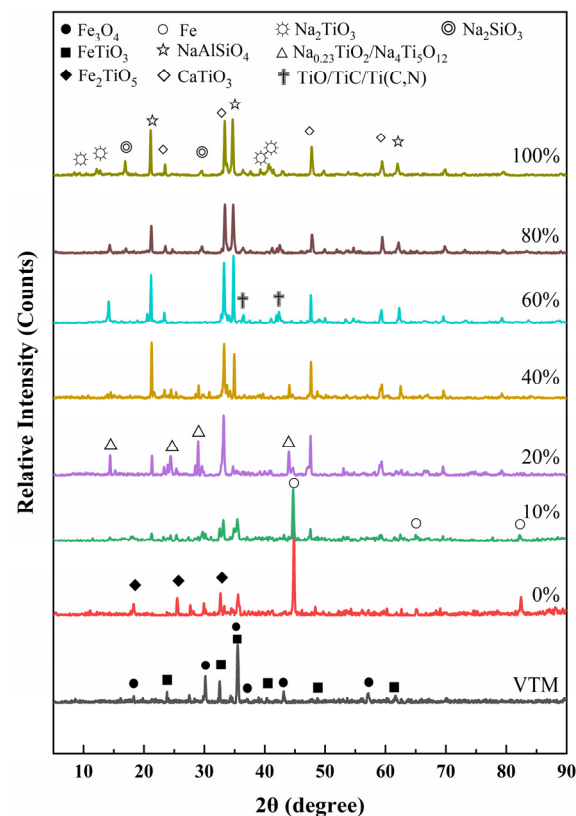


Figure 14. XRD patterns of slag in the sodium smelting of VTM at different sodium carbonate additions when the temperature is 1200 °C and the ratio of VTM to anthracite is 100:30.

4.4. Effect of Anthracite Addition

The active ingredient in anthracite is fixed carbon, which makes up part of its volatile matter, while ash has no reduction effect, but can act as a slag-forming agent. A combination 100 g of VTM, 60% of sodium carbonate, and different amounts of anthracite was taken and heated at 1200 °C for 2 h to investigate the effect of the addition of anthracite on the Ti content in molten iron.

During the experiment, it was found that the amount of anthracite had a greater effect on the iron yield. When the anthracite addition was too small, the reduction rate of the iron was low and the weight of the pig iron blocks obtained was less. When the amount of anthracite was less than 20%, the slag and iron could not be separated, and only sintered lumps were obtained.

Figure 15 shows the Ti content in molten iron with different anthracite additions. It can be seen that, when the amount of anthracite is 25%, the Ti content in the iron block obtained is about 58 ppm. When the amount of anthracite is 30%, the Ti content is about 23 ppm. But when the amount of anthracite exceeds 35%, the quality of the iron block significantly decreases, and the Ti content begins to increase. When the amount of anthracite exceeds 60%, the slag and iron cannot be separated. This is because excessive anthracite not only reduces the proportion of sodium carbonate in the entire reaction system, but also brings a large amount of ash to the coal. The influence of ash on the slag phases is relatively small (Figure 16), but it has a significant impact on the melting point of the slag, making it difficult to separate the slag and the iron.

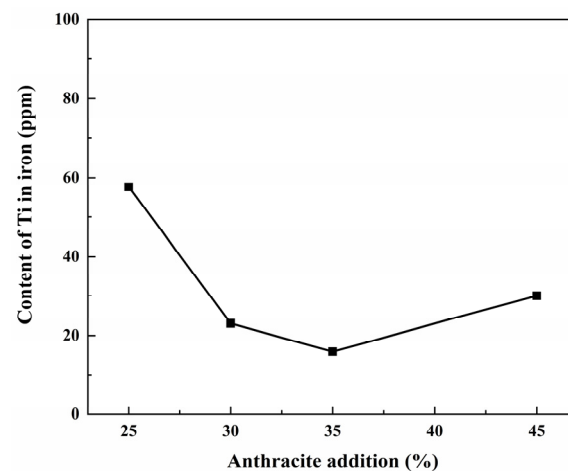


Figure 15. Ti content in pig iron at different anthracite additions when the temperature is 1200 °C and the ratio of VTM to sodium carbonate is 100:60.

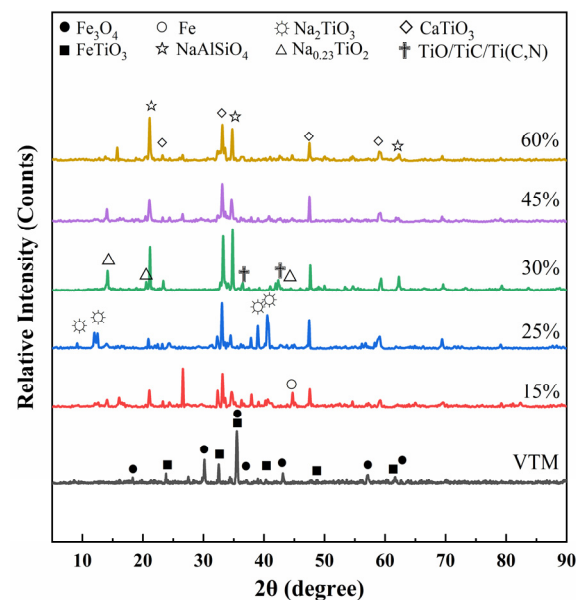


Figure 16. XRD patterns of slag in the sodium smelting of VTM at different anthracite additions when the temperature is 1200 °C and the ratio of VTM to sodium carbonate is 100:60.

In summary, if there is a high level of slag inclusion in the iron block, it may lead to an abnormally high Ti content. After process optimization, the control parameter range of titanium impurities in molten iron was determined: a smelting temperature of 1200 °C to 1300 °C, a smelting time of no less than 2 h, an anthracite consumption of 25–40%, and a Na_2CO_3 consumption of no less than 60%. Within this range, the Ti content in molten iron can be controlled at around 20 ppm. Samples of V-bearing pig iron obtained through smelting at 1200 °C with the ratio of VTM, sodium carbonate, and anthracite of 100:60:30 for 2 h were tested via glow discharge mass spectrometry (GDMS), and the content of the main impurity elements are shown in Table 6.

Table 6. Content of main impurity elements in V-bearing pig iron (wt.%).

Elements	V	Mn	Si	Ti	P	S
Content	0.25	0.20	0.00057	0.0015	0.0020	0.00072

4.5. Existing Forms of Titanium Impurities

The obtained V-bearing pig iron was sampled, cut, ground, and polished for XRD analysis and SEM-EDS morphology analysis. The XRD pattern and SEM morphology of V-bearing pig iron are shown in Figures 17 and 18, respectively.

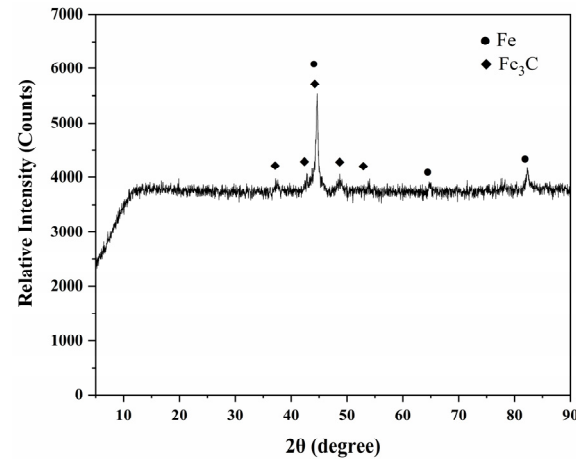


Figure 17. XRD pattern of vanadium-bearing pig iron.

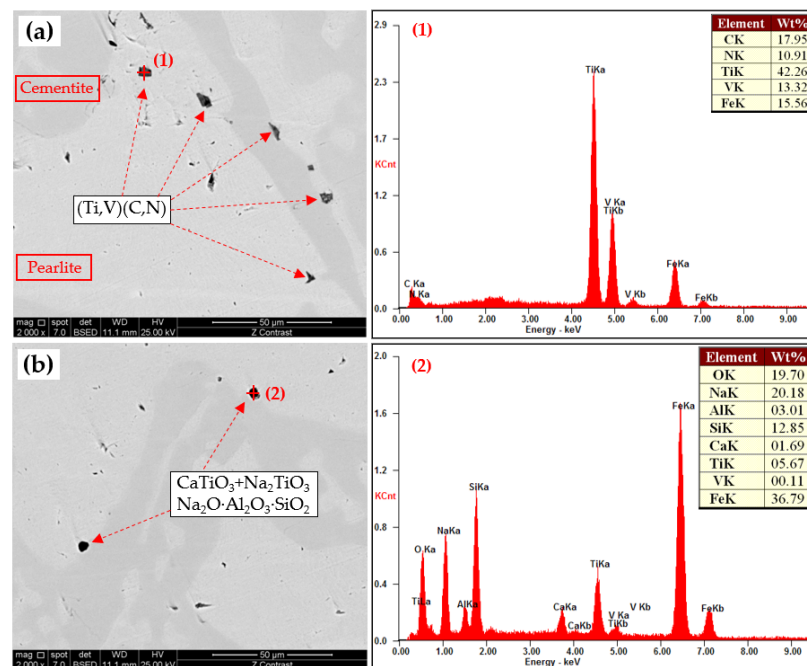


Figure 18. SEM morphology analysis of vanadium-bearing pig iron. (a) (Ti,V)(C,N) solid solution phase; (b) CaTiO₃ or Na₂TiO₃ slag phase.

As can be seen in Figure 17, XRD can only recognize the Fe and Fe₃C phases, and cannot further distinguish the complex structures in the pig iron. Due to the low Ti impurity content, the inclusions phase could not be recognized.

As can be seen in Figure 18a, the gray phase is the cementite body and the bright phase is the pearlitic body. It can be seen that the fine inclusion particles are distributed in the two phases. It was confirmed that there are two forms of Ti present in iron blocks. The first form is the CaTiO₃ or Na₂TiO₃ slag phase that fails to float into the slag phase, and this formation of titanium inclusions is the main reason for the significant fluctuation of the Ti content in pig iron. By extending the smelting time or enhancing the mass transfer, this slag inclusion can be promoted to float to the surface, ultimately reducing the Ti content in pig iron. The second form is a refractory (Ti,V)(C,N) solid solution phase formed by the

transformation of CaTiO_3 or Na_2TiO_3 . This form of titanium inclusion is mainly formed during the solidification process of molten iron, which is inevitable and a key factor in further controlling the titanium content of V-bearing pig iron at an extremely low level. In addition, Ti may also exist in the Fe-Ti alloy phase, and this form of titanium inclusion needs to be reduced through further treatment.

5. Conclusions

In this work, the effects of process conditions on the Ti content in molten iron and on the process of slag–iron separation during the sodium smelting of VTM were investigated via thermodynamic calculations and experiments. The results indicate that the introduction of Na_2CO_3 makes the reduction reaction system of VTM a relatively low-temperature smelting system. In the sodium smelting process, the Ti content in molten iron increases with the increase in temperature, and decreases with the addition of Na_2CO_3 , while the amount of anthracite that is added has little effect on it. The experimental results are consistent with the laws obtained from thermodynamic calculations. The optimized process conditions are a temperature of 1150–1250 °C, a smelting time of no less than 2 h, an anthracite consumption of 25–35%, and a Na_2CO_3 consumption of no less than 60%. Within this range, the Ti content in molten iron can be controlled at around 20 ppm. At this point, the Ti impurities in the V-bearing pig iron are mainly of the high melting point (Ti,V)(C,N) solid solution phase, as well as a small amount of the slag phase carried by CaTiO_3 or Na_2TiO_3 . This study is of great significance in broadening the application of V-bearing pig iron produced via the sodium smelting process of VTM, thus contributing to the realization of the comprehensive utilization of VTM.

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