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Effect of Sodium Borate on the Preparation of TiN from Titanomagnetite Concentrates by Carbothermic Reduction–Magnetic Separation and Acid Leaching Process

Wen Yu¹, Xiaojin Wen¹, Jiangan Chen¹, Qiongyao Tang²,*, Wen Dong³ and Jingen Zhong³

- ¹ Faculty of Resource and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China; yuwenminer@163.com (W.Y.); xiaojinwen95@gmail.com (X.W.); jachen@jxust.edu.cn (J.C.)
- ² School of Architectural and Surveying and Mapping Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China
- ³ Hainan Wensheng New Material Technology Co., Ltd., Haikou 570203, China; dongwen@winsheen.net (W.D.); 13876611020@139.com (J.Z.)
- * Correspondence: tangyaominer@163.com

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Abstract: Carbothermic reduction–magnetic separation and acid leaching processes were used to produce TiN and direct reduced iron (DRI) from titanomagnetite concentrates. The effects of sodium borate on the reduction behavior of TMCs, the magnetic separation of the reduced products, and the purification of the impure TiN by acid leaching were investigated. Results of x-ray diffraction, scanning electron microscopy, and energy-dispersive spectroscopy analysis showed that magnesium aluminate spinel (MgAl₂O₄) was generated in the reduced products, which could hinder the purification of the TiN. Adding sodium borate not only inhibited the formation of MgAl₂O₄, but also promoted the formation of TiN by decreasing the roasting temperature and time. Adding sodium borate slightly affected the separation of metallic Fe and TiN. By adding 16% sodium borate, a DRI with 94.3% Fe, 0.6% Ti, and 0.1% V was obtained by magnetic separation. After HCl + HF leaching, the TiN product containing 74.1% Ti and 2.8% V was obtained with the Ti recovery of 94.6% and V recovery of 58.3%.

Keywords: titanomagnetite concentrates; carbothermic reduction; sodium borate; titanium nitride

1. Introduction

Titanium nitride is an important technological material due to its excellent characteristics such as high melting point (2950 °C), extreme hardness (8–9 on the Mohs scale), high chemical and thermal stability, gold color, and good thermal and electrical conductivity [1]. This material has been considerably applied in various fields such as wear-resistant coatings on machine tools and bearings, and nontoxic exteriors on medical implants. Several physical and chemical methods have been reported in the literature for synthesizing TiN such as direct nitridation of metallic Ti [2], carbothermal reduction in TiO₂ in N₂ atmosphere [3], microwave-assisted or direct carbothermic reduction–nitridation of FeTiO₃ [4], self-propagating high-temperature synthesis [5], and microwave plasma synthesis [6]. However, these processes require costly raw materials, high temperatures, long reaction time, and/or costly equipment. Therefore, affordable processes using low-cost materials for the preparation of TiN are needed.

The Panzhihua titanomagnetite deposit accounts for more than 90% of the Ti reserves in China. Titanomagnetite concentrates (TMCs) are currently used to produce molten iron through the blast



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furnace process in the Panzhihua. Nearly all amounts of Ti were concentrated into the slag after smelting in the blast furnace. As a result, more than three million tons of the slag containing 22–25% TiO₂ are produced annually [7–9]. However, no appropriate and economical method to process this slag is available to date because of the dispersed distribution of Ti in various fine-grained (<10 µm) mineral phases. Thus, this slag is treated as a solid waste and stored; this process not only wastes Ti resources, but also poses a threat to the environment [10]. Therefore, many studies have been devoted to develop a cleaner production process than before for comprehensively utilizing Fe, Ti, and V compounds of TMCs such as the direct reduction-smelting process [11], and the direct reduction-magnetic separation process [12]. Among these, iron oxides are first reduced to metallic iron, whereas titanium oxides are rarely reduced. The reduced products are then separated by smelting or magnetic separation to produce DRI and titanium slag. However, the subsequent process of extracting titanium from the titanium slag is very complicated and is not environmentally friendly due to its high impurity content and low reactivity. Moreover, several studies have been conducted on the preparation of iron-based wear-resistant material from TMCs through the carbothermal process, in which iron oxides are reduced to metallic iron while titanium oxides are transformed into TiC or Ti(C,N) [13,14]. However, all impurities contained in the TMCs and reductant remain in the prepared material, which may degrade its performance.

In our previous study, a new process was proposed to prepare TiN and direct reduced iron (DRI) from TMCs [15]. In this process, the TMCs were first reduced by anthracite to metallic Fe and TiN, and then magnetically separated to produce DRI and impure TiN. This process provides a way to realize the high value utilization of iron and titanium simultaneously from the TMCs. Our results showed that the Ti component was nearly completely transformed into TiN under the conditions of reduction temperature of 1300 °C, the anthracite dosage of 26%, and the reduction time of 90 min. Moreover, the separation results revealed that metallic iron and TiN can be separated precisely through grinding and magnetic separation. Therefore, the purification of impure TiN is the key technology of this process. Traditional beneficiation methods including flotation, magnetic separation, and gravity separation are unsuitable for purifying impure TiN because the particle size of TiN is generally less than 10 μ m. The acid leaching process can be used to remove impurities from impure TiN given that TiN has excellent acid resistance. However, large amounts of MgAl₂O₄, which are difficult to dissolve in acid solution [10], are observed in the roasted product. Magnesium aluminate spinel is also concentrated in the impure TiN after magnetic separation and will thus hinder the purification of TiN by acid leaching. Therefore, the formation of MgAl₂O₄ should be inhibited during the reduction roasting process.

Sodium roasting is a commonly used technique to convert acid-resistant substances to soluble substances in extractive metallurgy [16,17]. Sodium borate can promote the carbothermic reduction of titanomagnetite and ilmenite [18,19]. Herein, sodium borate was used as an additive to inhibit the formation of MgAl₂O₄ during reduction to create a convenient condition for purifying TiN. The effects of sodium borate on the carbothermic reduction of TMCs, the magnetic separation of the reduced products, and the acid leaching of impure TiN were also studied.

2. Materials and Methods

2.1. Materials

The titanomagnetite concentrates used in this study was obtained from Panzhihua in Sichuan Province, China. The particle size of the TMCs was 54.17%, passed through 0.074 mm. Anthracite, which was used as a reductant, was obtained from Jincheng, Shanxi Province, China. Anthracite contained 0.80% moisture, 10.91% ash, 7.18% volatiles, 81.11% fixed carbon, and 0.39% S. The anthracite used in the experiments was crushed and ground to 100%, passed through 0.1 mm.

Sodium carboxymethylcellulose (Na–CMC) was used as a binder in the pelleting process, and HCl and HF were used as lixiviants to purify TiN. Sodium borate (Na₂B₄O₇·10H₂O) was used as an

additive. All the chemicals were purchased from Sinopharm (Shanghai, China), were of analytical grade, and used as received.

2.2. Methods

As depicted in Figure 1, the experimental procedure mainly included: (1) pelleting of the mixture of TMCs and anthracite; (2) reduction roasting of pellets; (3) grinding and magnetic separation of the reduced pellets; and the (4) acid leaching of impure TiN.



Figure 1. Experimental procedure.

Pelleting of the mixture was conducted by hands following the procedure as follows. TMCs (20 g), anthracite (26%), sodium borate (0, 4%, 8%, 12%, 16%), Na–CMC (0.5%), and water (approximately 25%) were thoroughly mixed to produce material that could be shaped by hands to make pellets with a diameter of 6–8 mm. The dosages of anthracite, binder, and water were expressed as percentages that refer to their mass ratios to TMCs. The wet pellets were oven dried at 105 °C for 2 h.

Reduction roasting experiments were performed in a muffle furnace. The schematic diagram of the furnace has been previously described [20]. The reduced pellets were ground in a grinder and then separated in a magnetic separator. The reduced pellets were ground to about 80%, and passed 0.074 mm. A XCGS-50 Davis tube (Nanchang Li Yuan Mining and Metallurgy Equipment Co., Ltd., Nanchang, China) with a magnetic induction intensity of 0.04T was used to separate the slurry. The methods of roasting, grinding, and magnetic separation were based on previous studies [15,21].

Leaching experiments were carried out in a 200 L plastic conical flask. The impure TiN concentrates were first leached by HCl (36.0 mass %–38.0 mass %) for 12 h using a liquid-to-solid mass ratio of 10:1. The slurry was filtered, and the leach residue was washed with distilled water and dried. Then, the leach residue was leached using HF (\geq 40.0 mass %) with the liquid-to-solid ratio of 5:1 for 12 h. The leach residue was repeatedly washed with distilled water and dried. The types of leaching agent and the leaching method were determined based on the results of exploration experiments.

2.3. Characterization

The Fe, TiO₂, and V₂O₅ contents of the DRI were measured by an IRIS Intrepid II inductive coupled plasma emission spectrometer (ICP, Thermo Electron Corporation, Waltham, MA, USA). The composition of the TiN product was analyzed by an x-ray fluorescence analyzer (XRF) equipped with Omnian standardless analysis software (Axios max, PANalytical, Almelo, The Netherlands). The TiN product was analyzed by XRF for elements from Na to higher molar masses in the periodic table.

Crystal phases were identified in the powdered samples using a DX-2700 x-ray diffractometer (XRD, Hao Yuan Instrument, Dandong, China) with a Cu target ranging from 10° to 80° in 0.02° intervals at a scanning rate of 5°/min. The reduced pellets were mounted in epoxy resin and polished for scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS) analysis (MLA650F, FEI, Hillsboro, OR, USA).

The recoveries of Fe, Ti, and V in the DRI were calculated according to the following formula:

$$\operatorname{Recovery}(\operatorname{Fe}/\operatorname{Ti}/V) = \frac{\operatorname{Fe}/\operatorname{Ti}/V \text{ content of DRI} \times \operatorname{Weight of DRI}}{\operatorname{Fe}/\operatorname{Ti}/V \text{ content of TMCs} \times \operatorname{Weight of TMCs}} \times 100\%$$
(1)

3. Results and Discussions

3.1. Titanomagnetite Concentrate Composition

Table 1 shows that TMCs contained 56.7% Fe, 10.5% TiO_2 , 0.6% V_2O_5 , 2.6% Al_2O_3 , 3.0% MgO, 3.5% SiO_2 , 0.4% CaO, and 0.6% S. According to the XRD analyses in Figure 2, the main crystalline phases of TMCs were titanomagnetite ($Fe_{2.75}Ti_{0.25}O_4$), ilmenite ($FeTiO_3$), and magnetite (Fe_3O_4).



Table 1. Chemical compositions of TMCs (mass %).



Figure 2. XRD patterns of TMCs. 1—Fe_{2.75}Ti_{0.25}O₄(PDF#75-1374); 2—Fe₃O₄(PDF#19-0629); 3—FeTiO₃(PDF#29-0733).

3.2. Effect of Sodium Borate on the Formation of $M_gAl_2O_4$

The reduced pellets with different dosages of sodium borate were detected by XRD. The roasting conditions were as follows: the anthracite dosage of 26%, the roasting temperature of 1300 °C, and the roasting time of 90 min. Figure 3 illustrates the results.

Figure 3 shows that the dosage of sodium borate significantly affected the formation of $MgAl_2O_4$. The intensity of the peaks of $MgAl_2O_4$ decreased as the dosage of sodium borate increased. When the dosage of sodium borate increased to 16%, the peaks of $MgAl_2O_4$ disappeared. This phenomenon indicated that the formation of $MgAl_2O_4$ was completely suppressed. Therefore, the dosage of sodium borate was selected as 16% for the subsequent experiments. In TMCs, elements of Mg and Al were mainly present in the magnetite and ilmenite crystal lattices in the form of isomorphism. Specifically, Al^{3+} replaced Fe^{3+} , whereas Mg^{2+} replaced Fe^{2+} [22]. In the absence of sodium borate, the remaining MgO reacted with Al_2O_3 to form $MgAl_2O_4$ as the iron and titanium oxides were reduced. In contrast, $Na_2B_4O_7$ melted at a low temperature (751 °C) and reacted with MgO, Al_2O_3 , and other components (e.g., SiO₂ and CaO) to form a molten slag. No other crystalline substances were detected in the reduced pellets by XRD except for Fe, TiN, and Fe₃C. This may be because these sodium-containing substances form a liquid at high temperature, and then form a glass phase material after rapid cooling. Moreover, the peaks of Fe₃C increased as the dosage of sodium borate increased. This phenomenon revealed that the addition of sodium borate promoted the carburization of metallic iron. The role of sodium salt in promoting carburization has been widely recognized [23].



Figure 3. XRD patterns of the pellets with different sodium borate dosage reduced at 1300 °C for 90 min. 1—Fe(PDF#06-0696); 2—TiN(PDF#38-1420); 3—MgAl₂O₄(PDF#21-1153); 4—Fe₃C(PDF#76-1877).

3.3. Effect of Sodium Borate on the Formation of TiN

The addition of sodium borate has been reported to promote the reduction of ilmenite and titanomagnetite to Fe and titanium oxides [18,19], but the effect of sodium borate on the conversion of the TMCs to TiN has never been reported. In order to study the effect of sodium borate addition on the formation of TiN, the phase transformations of the composite pellets without sodium borate and with 16% sodium borate reduced at different conditions were detected by XRD. The results are displayed in Figures 4 and 5, respectively.

Figure 4 shows the XRD patterns of the pellets without sodium borate and with 16% sodium borate reduced at different temperatures for 90 min. Figure 4a shows that a small amount of TiN started to form at 1200 °C without the additive. As the reduction temperature increased, the diffraction peak intensity of the M_3O_5 -type solid solution decreased and the diffraction peak intensity of TiN increased gradually. The M_3O_5 -type solid solution were important intermediates during the carbothermic reduction process of titanomagnetite and ilmenite with general formulas of m((Ti,Mg,Mn,Fe)O·2TiO₂)·n((Ti,Fe,Al,Cr,V)₂O₃·TiO₂) [12,24]. When the reduction temperature increased to 1300 °C, the diffraction peak intensity of M_3O_5 disappeared, indicating that the Ti component was completely converted into TiN. In contrast, Figure 4b shows that TiN also started to form at 1200 °C when 16% sodium borate was added. However, the Ti component could be completely converted into TiN as the reduction temperature increased to 1250 °C. This result implied that the addition of sodium borate promoted the formation of TiN. Moreover, MgAl₂O₄ started to form at 1200 °C in the absence of sodium borate. In the case of 16% sodium borate, MgAl₂O₄ was not observed over the studied temperature range.



Figure 4. XRD patterns of the pellets reduced at different temperatures for 90 min: (a) without additive and (b) with 16% sodium borate. 1—Fe(PDF#06-0696); 2— M_3O_5 (Fe₂TiO₅, PDF#41-1432; Mg₂TiO₅, PDF#35-0796; Ti₃O₅, PDF#09-0309); 3—TiN(PDF#38-1420); 4—MgAl₂O₄(PDF#21-1153); 5—FeTiO₃(PDF#29-0733); 6—Fe₃C(PDF#76-1877).

Figure 5 shows the XRD patterns of the pellets without sodium borate and with 16% sodium borate reduced at 1300 °C for different times, respectively. Figure 5a shows that TiN started to form when reduced for 20 min without the additive. As the reduction time increased to 90 min, the Ti component was completely converted into TiN. Figure 5b reveals that TiN started to form at 10 min when 16% sodium borate was added, and the Ti component was completely converted into TiN when reduced for 50 min. This result also demonstrated that the addition of sodium borate promoted the formation of TiN. In addition, MgAl₂O₄ started to form after being reduced for 20 min without the additive. In contrast, MgAl₂O₄ was not observed over the studied roasting time range in the presence of sodium borate.



Figure 5. XRD patterns of the pellets reduced at 1300 °C for different time: (**a**) without additive and (**b**) with 16% sodium borate. 1—Fe(PDF#06-0696); 2— M_3O_5 (Fe₂TiO₅, PDF#41-1432; Mg₂TiO₅, PDF#35-0796; Ti₃O₅, PDF#09-0309); 3—TiN(PDF#38-1420); 4—MgAl₂O₄(PDF#21-1153); 5—Fe₃C(PDF#76-1877).

The carbothermic reduction and nitridation reactions of titanomagnetite and ilmenite could be divided into two stages. The first stage was the reduction of titanomagnetite and ilmenite to Fe and M_3O_5 , and the second stage was the reduction and nitridation of M_3O_5 to TiN/Ti(C,N) [15,25–30]. The possible reactions were described as Equations (2)–(9). Titanomagnetite was regarded as Fe₃O₄·Fe₂TiO₄ since titanomagnetite is a solid solution of magnetite-ulvospinel. FeTi₂O₅ and Ti₃O₅ were selected to represent M_3O_5 because they are the two most important substances in the M_3O_5 -type solid solution. Assuming that the carbon gasification reaction reached equilibrium in the temperature range of 500–1500 °C, the Gibbs free energy changes (ΔG , kJ/mol) of the possible reduction reactions of the titanomagnetite concentrates were calculated by using Fact-Web [31]. Plots of Gibbs free energy changes against temperature are shown in Figure 6. Standard Gibbs free energy changes instead of the ΔG of Equation (8) were provided since the reaction equilibrium constant cannot be calculated.

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
 (3)

$$FeO + CO \rightarrow Fe + CO_2$$
 (4)

$$Fe_2TiO_4 + CO \rightarrow Fe + FeTiO_3 + CO_2$$
 (5)

$$2FeTiO_3 + CO \rightarrow Fe + FeTi_2O_5 + CO_2 \tag{6}$$

$$3/5FeTi_2O_5 + CO \rightarrow 3/5Fe + 2/5Ti_3O_5 + CO_2$$
 (7)

$$1/5Ti_3O_5 + C + 3/10N_2 \rightarrow 3/5TiN + CO$$
 (8)

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \tag{9}$$



Figure 6. Plots of ΔG vs. temperature of Equations (3)–(9).

In the first stage, the reactions occurred by means of the gaseous intermediates CO and CO₂. Moreover, the overall rate of reaction was controlled by the gasification of coal. Sodium borate is a catalyst for the carbon gasification [32]. Thus, the addition of sodium borate could promote the formation of Fe and M_3O_5 .

In the second stage, M_3O_5 was reduced by solid carbon instead of CO, and the diffusion of carbon to the surface of M_3O_5 is the rate determining step for the formation of nitride. Gou reported that when the roasting temperature was above the eutectic temperature (1154 °C) of the Fe–C binary system, the liquid-phase iron and Fe₃C become an important medium for transmitting carbon to the surface of M_3O_5 [26]. As above-mentioned, sodium borate can promote the carburization of metallic iron to the formation of liquid-phase iron and Fe₃C. Thus, sodium borate could promote the formation of TiN. Therefore, the promotion mechanism of sodium borate on the formation of TiN can be summarized as follows: sodium borate first promoted the formation of Fe and M_3O_5 to TiN by accelerating the carburization of metallic iron.

3.4. SEM Observation and EDS Analysis

Figure 7 shows the SEM images and the EDS results of the pellets without an additive reduced at 1300 °C for 90 min. Figure 7a shows that the metallic iron and TiN did not form a close relationship, which was conducive to the separation process. The surface scanning results in Figure 7b indicated that the enrichment region of Mg and Al in the observed area were strongly coincident, and the Mg–Al-rich

region contained fewer contents of Ca and Si than the peripheral region. These results combined with the XRD and EDS results indicated that the Mg–Al-rich phase was MgAl₂O₄. Figure 7a also shows that TiN and MgAl₂O₄ particles were intimately intermixed. Thus, separating them by physical sorting technology was difficult. Moreover, the EDS results in Table 2 revealed that the TiN phase contained 3.1% V and 2.0% C, indicating that small amounts of V and C were dissolved in the TiN phase. TiN, TiC, VC, and VN had the same NaCl-type structures. The atomic radius of C was similar to that of N, and the atomic radius of V was similar to that of Ti. These compounds could form a continuous solid solution. Introducing the right amounts of C and V could improve the properties of TiN material [1,33,34].



Figure 7. SEM image and elemental surface scanning image of the pellets without the additive reduced at 1300 °C for 90 min: (**a**) SEM image and (**b**) elemental surface scanning image.

Table 2.	Chemical	composition	of points	indicated ir	Figure 7a	(mass %)
		1	1		0	· · · ·

Point	С	Ν	0	Mg	Al	Si	Ca	Ti	v	Fe	Phase
1	2.9	_	48.0	14.3	28.2	2.5	0.9	2.7	0.1	0.5	Spinel
2	5.0	-	-	-	-	0.5	-	-	-	94.5	Îron
3	2.0	19.3	-	-	_	-	0.3	74.8	3.1	0.7	TiN
– Not detected.											

Figure 8 shows the SEM images and the EDS results of the pellets with 16% sodium borate reduced at 1300 °C for 90 min.

The EDS element distribution map shown in Figure 8b indicated the evident overlap of the distribution areas of Mg, Al, Ca, Si, O, and Na elements, but did not detect MgAl₂O₄. This finding indicates that the addition of sodium borate inhibited the generation of MgAl₂O₄. This condition resulted in the formation of complex compounds of Na₂O–MgO–Al₂O₃–CaO–SiO₂-FeO-TiO₂. Na-containing substances are generally easily dissolved by acid; thus, the Na-containing complex compounds may be removed during acid leaching. Moreover, the EDS results in Table 3 showed that V was undetected in the metallic iron phase and the slag. These results imply that V was nearly transformed to the TiN phase.



Figure 8. SEM image and elemental surface scanning image of the pellets with sodium borate reduced at 1300 °C for 90 min: (**a**) SEM image and (**b**) elemental surface scanning image.

Point	С	Ν	0	Mg	Al	Si	Ca	Ti	Na	v	Fe	Phase
1	4.9	-	55.9	8.9	11.5	9.1	3.8	1.1	4.8	-	4.9	Slag
2	11.2	-	-	-	-	0.4	-	_	-	_	88.4	Iron
3	7.9	21.8	-	-	-	-	-	66.9	-	3.5	-	TiN
	– Not detected											

Table 3. Chemical composition of points indicated in Figure 8a (mass %).

3.5. Effect of Sodium Borate on the Separation of Metallic Iron and TiN

The pellets reduced at 1300 °C for 90 min were subjected to grinding and magnetic separation. The results are presented in Table 4.

Table 4 shows that the addition of sodium borate had no significant effect on the magnetic separation index. In the absence of sodium borate, DRI containing 95.3% Fe, 0.5% Ti, and 0.1% V was obtained. The recoveries of Fe, Ti, and V in this DRI were 90.1%, 3.9%, and 15.5%, respectively. When 16% sodium borate was added, DRI containing 94.3% Fe, 0.6% Ti, and 0.1% V was obtained. The

recoveries of Fe, Ti, and V in this DRI were 91.2%, 5.1%, and 17.3%, respectively. These results revealed that metallic Fe and TiN could be separated precisely through grinding–magnetic separation.

Additive		Yield *	Elemen	t Conten	t in DRI	Recovery		
- inditive	DRI	Impure TiN	Fe	Ti	V	Fe	Ti	V
No additive	53.6	30.9	95.3	0.5	0.1	90.1	3.9	15.5
16% sodium borate	54.9	32.0	94.3	0.6	0.1	91.2	5.1	17.3

Table 4. Production index of magnetic separation (mass %).

* Mass percentage of DRI or impure TiN to TMCs.

3.6. Effect of Sodium Borate on the Purification of TiN

Figure 9 shows the effect of sodium borate on the acid leaching of impure TiN.



Figure 9. Effect of sodium borate on the acid leaching of impure TiN: XRD of TiN products (**a**) without sodium borate and (**b**) with 16% sodium borate. 1—TiN(PDF#38-1420); 2—MgAl₂O₄(PDF21-1153); 3—Fe(PDF#06-0696); 4—CaMg₂Al₂F₁₂(FDF#25-0152); 5—C(PDF#26-1080).

Figure 9a illustrates that, without sodium borate, the main phases presented in the impure TiN concentrates were TiN, MgAl₂O₄, Fe, and C. After HCl leaching, no significant change in the diffraction peaks were observed. After HF leaching, the diffraction peaks of MgAl₂O₄ were still strong, but a new impurity of CaMg₂Al₂F₂ formed. This phenomenon revealed the difficulty in obtaining pure TiN by acid leaching in the absence of sodium borate. In contrast, Figure 9b shows that the crystal phases of the impure TiN obtained by adding 16% sodium borate were TiN, Fe, and C. This result indicates that other components were present in the form of the glass phase in the sample. After HCl leaching, the Fe was removed. After HF leaching, only TiN and a small amount of C were present in the TiN products. The XRD pattern of the TiN product was very smooth. Chemical composition of the impure TiN and TiN product are presented in Table 5. This shows that the Ti and V contents of the impure TiN product were 19.5% and 0.7%, respectively. After leaching, the Ti and V contents of the TiN product increased to 74.1% and 2.8%, respectively, and their total content was close to the theoretical Ti content of TiN (77.4% Ti). These results imply that the addition of sodium borate during the roasting stage promoted the purification of TiN by acid leaching. The total content of TiN was much less than 100% since C, N, and O were not detected. A total of 1.61 g TiN was obtained from 20 g of TMCs. Consequently, on the basis of mass balance, the Ti and V enrichments in the TiN product were calculated to be 94.6% and 58.3%, respectively. The SEM image in Figure 10 revealed that the sizes of the TiN particles were below 10 µm.

Table 5. Chemical composition of the impure TiN and TiN product (mass %), as determined by XRF analysis.

Component	Ti	V	Fe	Al	Mg	Si	Ca	Na	Total
Impure TiN	19.5	0.7	8.5	5.1	4.6	5.2	2.4	2.6	48.6
TiN Product	74.1	2.8	0.3	0.1	0.0	0.0	0.0	0.0	77.3



Figure 10. SEM image of the purified TiN product.

4. Conclusions

The main conclusions can be summarized as follows:

- (1) During the carbothermal reduction of TMCs, the addition of sodium borate not only inhibits the formation of MgAl₂O₄, but also promotes the reduction and nitridation of TMCs.
- (2) The promotion mechanism of sodium borate on the formation of TiN can be summarized as follows: sodium borate first promotes the formation of Fe and M_3O_5 by catalyzing coal gasification and then promotes the reduction and nitridation of titanium oxide to TiN by accelerating the carburization of iron.
- (3) Sodium borate reacts with MgO, Al₂O₃, and other components to form complex compounds of Na₂O–MgO–Al₂O₃–CaO–SiO₂–FeO–TiO₂ during the carbothermal reduction of TMCs.

- (4) Sodium borate slightly affects the separation of metallic Fe and TiN. Adding 16% sodium borate resulted in DRI containing 94.3% Fe, 0.6% Ti, and 0.1% V after magnetic separation. The recoveries of Fe, Ti, and V in this DRI were 91.2%, 5.1%, and 17.3%, respectively.
- (5) After HCl + HF leaching, a TiN product containing 74.1% Ti and 2.8% V was obtained with a Ti recovery of 94.6% and V recovery of 58.3%. In contrast the resulting TiN product contained a considerable amount of $MgAl_2O_4$ and $CaMg_2Al_2F_2$ without the addition of sodium borate.

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