Mechanism of Melt Separation in Preparation of Low-Oxygen High Titanium Ferroalloy Prepared by Multistage and Deep Reduction

Chu Cheng, Zhihe Dou and Tingan Zhang

Abstract: A novel method to prepare low-oxygen and high-titanium ferroalloy by multistage and deep reduction was proposed in this study. Specifically, the raw materials, high titanium slag and iron concentrate are firstly reduced by insufficient Al powder to obtain high temperature melt. Secondly, CaO and CaF2 are added into the melt to adjust the basicity of the molten slag. Then, a melt separation under the heat preservation is carried out to intensify the slag-metal separation. Finally, calcium or magnesium is added into the metal melt for a deep reduction. Thereafter, high titanium ferroalloy with an extra-low oxygen content can be obtained. Effects of slag basicity and melt separation time on the slag-metal separation removal were systematically studied. The results indicate that the high titanium ferroalloy, produced by the thermite method, contains a lot of Al2O3 inclusions. This leads to a high oxygen and aluminum content in the alloy. With a melt separation with high basicity slag treatment, the Al2O3 inclusions can be effectively removed from the alloy melt, and the slag-metal separation efficiency is greatly improved. With the addition of high basicity slag during melt separation, Ti content in the alloy is improved from 51.04% to 68.24%. Furthermore, and the Al and O contents are reduced from 10.38% and 9.36% to 4.24% and 1.56%, respectively. However, suboxides, such as Ti2O and Fe0.9536O, still exist after a melt separation. This indicates that a deep reduction is needed to obtain extra-low oxygen high titanium ferroalloy.

Keywords: multistage and deep reduction; low-oxygen high titanium ferroalloy; inclusions; melt separation; slag-metal separation

1. Introduction

High titanium ferroalloy is one of the most important alloys in the melting of special steel and structural steel. It is also an important directive alloy in aviation and space [1]. At present, the major method for the industrial production of high titanium ferroalloy is vacuum remelting process. However, this method has disadvantages with respect to the limited source of titanium scrap and a high production cost [2]. It has been a hotspot issue to directly prepare titanium or titanium alloy from titanium oxides by the electrochemical reduction. Molten salt electrolytic methods, as a short process and direct preparation of titanium alloys, is becoming an issue with an increased concern, while it has not been used in a real production due to the limits of electrode materials and current efficiency [3–8]. Thermite method (also called thermite reduction), using aluminum as a reductant and high-grade ilmenite as raw materials, is another short process of directly producing high titanium
ferroalloy. However, this method has some disadvantages of incomplete reduction of titanium oxide due to the weak reducing action of aluminum and incomplete slag-metal separation with a direct casting, which results in a high residual oxygen (up to 12%) and aluminum contents [9,10]. All industrial production lines, using the thermite method to produce high titanium ferroalloy have been shut down. In recent years, researchers in titanium industry have studied the preparation and deoxidation mechanism of high titanium ferroalloy with the thermite reduction method. They all agreed that low-oxygen high-titanium ferroalloy cannot directly be produced from titanium oxides by thermite reduction [11–13]. Chunarev et al. [14] researched technological possibility of manufacturing high-titanium ferroalloy form crude ore. The results show that high ferrotitanium (Ti, 60% to 70%) with oxygen content less than 5% (wt.%) cannot directly be produced by thermite method and the oxygen exists in the forms of Ti$_4$Fe$_2$O phase.

Dou et al. [15,16] has investigated the formation mechanism of oxygen in high titanium ferroalloy. The result indicates that the oxygen in high titanium ferroalloy exists in forms of Al$_2$O$_3$, suboxides and titanium-oxygen solid solution. He has further researched the effects of physical properties of molten slag on the slag-metal separation and eliminating inclusions in the high titanium ferroalloy prepared by thermite reduction. The results indicate that the appropriate addition of CaF$_2$ and high basicity of the slag improves the effects of slag-metal separation and inclusion removal [17,18].

Based on our previous researches, a novel methodology for directly preparing low oxygen and high titanium ferroalloy from high titanium slag and iron concentrate by multistage and deep reduction is put forward [19,20]. This method is described as follows: (1) Thermite reduction. High titanium slag and iron concentrate as raw materials are firstly reduced by insufficient Al powder to obtain high temperature melt. (2) Melt separation under heat preservation. CaO and CaF$_2$ are added into the melt by thermite reduction to adjust the basicity of the molten slag and a melt separation under the heat preservation is carried out to strengthen the slag-metal separation. (3) Deep reduction. Calcium or magnesium is added into the metal melt to carry out a deep reduction and extra-low oxygen high titanium ferroalloy is obtained. In this paper, the effects of slag basicity and melt separation time on the slag-metal separation during the melt separation under heat preservation were systematically studied.

2. Experimental Part

High-titanium slag (86.03% TiO$_2$, particle size: ≤ 3 mm, Panzhihua Iron & Steel Group Co. China) and iron concentrate (63.07% TFe, particle size: 0.1–0.5 mm, Fortescue Metals Group Ltd, Pilbara, Australia) were used as the raw materials. The chemical composition of the raw materials is shown in Table 1. Aluminum powder (Al, 98.5%, particle diameter: ≤ 3 mm, Jinzhou Metal Co., Ltd., Jinzhou China) was used as the reductant. KClO$_3$ (99.5%, particle diameter: ≤ 3 mm), CaO (99.5%, particle diameter: ≤ 250 µm), magnesium powder (99.5%, particle diameter: 0–0.2 mm) were produced by Sinopharm Chemical Reagent Co., Ltd. City, Shanghai, China.

| Raw Material      | TiO$_2$ | TFe | Al$_2$O$_3$ | SiO$_2$ | CaO | MgO | Others |
|-------------------|---------|-----|-------------|---------|-----|-----|--------|
| High-Titanium Slag| 86.03   | 2.40| 3.30        | 5.60    | 0.17| 0.98| Bal.    |
| Iron Concentrate  | -       | 63.07| 2.71        | 3.40    | 0.54| 0.45| Bal.    |

The workflow of the experiment is shown in Figure 1. High-titanium slag, iron concentrate, CaO and KClO$_3$ were put into the oven to dry at 110 °C for 24 h, then they were evenly mixed with Al powder in proportion by a barreltype mixer for 40 min. The mass ratio of high-titanium slag, Al powder, iron concentrate, KClO$_3$ and CaO is 1: 0.61: 0.23: 0.35: 0.13, the stoichiometric ratio of Al powder used as the reductant for TiO$_2$ is 0.9. The reactants were preheated at 150 °C for 2 h, and then were put into a homemade graphite reactor (dia. 350 mm, 480 mm in height). Magnesium powders (about 3 g) were covered with on the top of the reactants and then were ignited to introduce thermite reaction. After a complete thermite reaction, a high temperature melt was obtained and then was
teemed into a furnace (SPZ-160A, dia. 150 mm, 200 mm in deep) for a heat preservation. Next, two group of experiments were separately carried out for melt separation, and the experimental process is as follows. Group 1: the high temperature melt was directly carried out a melt separation at 165 °C for 30 min, 60 min, 90 min respectively. Group 2: eliminated 90% of the upper slag and added Al₂O₃, CaO and CaF₂ into the molten slag to adjust the basicity, making its composition that the mass ratio of Al₂O₃, CaO and CaF₂ was 1: 1: 0.05, and then kept the melt at 1650 °C for 30 min, 60 min, 90 min, respectively. After the melt separation, it was cast into a graphite crucible and the alloy ingot was obtained.

![Figure 1](image-url) The workflow of the experiment.

The alloy and slag were analyzed by X-ray diffractometry (XRD, Model D8, Bruker, Karlsruhe, Germany; working conditions: Cu Kα1, 40 kV, 40 mA). The composition of high basicity slag after melt separation was analyzed by X-ray fluorescence (XRF, Model S4, Bruker, Karlsruhe, Germany). The oxygen contents of alloy samples were measured by the oxygen and nitrogen hydrogen analyzer (Type G8, Bruker, Karlsruhe, Germany). The compositions of alloys were analyzed by inductively coupled plasma atomic emission spectrometry (ICP, Optima 4300DV, PerkinElmer, Waltham, USA). The microstructures of alloy samples were observed by Scanning Electron Microscope (SEM, SU-8010, Hitachi, Tokyo, Japan) and Energy Dispersive Spectrometer (EDS, Bruker, Karlsruhe, Germany).

3. Results and Discussion

3.1. Characteristics of Slags

Figure 2 shows XRD patterns of slags after melt separation without addition of Al₂O₃-CaO-CaF₂ slag. The diffraction peaks can be indexed to Al₂O₃, TiO, Ti₀.₉₁₃O₀.₇₃₀₄, Fe₃.₃Ti₉.₇O₃ and FeTi₂.₆₀₃O₀.₃₅. The existence of Al₂O₃ indicates that, in thermite method, it is difficult to completely remove Al₂O₃ inclusions from the alloy prepared by thermite reaction with direct casting. The slag-metal separation is strengthened by a melt separation after thermite reaction, but this process will decrease the yield of Ti and Fe. This is due to that TiO, Ti₀.₉₁₃O₀.₇₃₀₄, Fe₃.₃Ti₉.₇O₃ and FeTi₂.₆₀₃O₀.₃₅ will be separated from alloy. The existence of TiO, Ti₀.₉₁₃O₀.₇₃₀₄, Fe₃.₃Ti₉.₇O₃ and FeTi₂.₆₀₃O₀.₃₅ indicates that thermite
reaction in this experiment is incomplete. This is mainly attributed to the inadequate aluminum powder (90% stoichiometric ratio of Al powder used as reductant for TiO$_2$) in ingredients. Therefore, a deep reduction using calcium or magnesium as a reductant is necessary. The titanium sub-oxides and Ti-Fe-O complex oxides in slags indicate that they will be absorbed into the refining slag during a melt separation process, which will decrease the recovery rate of Ti and Fe. In addition, the diffraction peaks intensity of Al$_2$O$_3$ are improved with the increase of melt separation time. This means that Al$_2$O$_3$ is effectively removed in the metal melt. Table 2 shows that the content of Al$_2$O$_3$ increases with the melt separation time. This result agrees well with the XRF analysis.

![Figure 2](image_url)  
**Figure 2.** XRD (X-ray diffractometry) patterns of slags after melt separation without addition of Al$_2$O$_3$-CaO-CaF$_2$ slag: (1) 30 min; (2) 60 min, (3) 90 min.  

**Table 2.** XRF (X-ray fluorescence) analysis result of slags after different melt separation time (1,2,3: without addition of Al$_2$O$_3$-CaO-CaF$_2$ slag, 4,5,6: with addition of Al$_2$O$_3$-CaO-CaF$_2$ slag), wt.%.  

| Number | Separation Time | Al$_2$O$_3$ | CaO | TiO$_2$ | CaF$_2$ | SiO$_2$ | MgO | Fe$_2$O$_3$ | Others |
|--------|----------------|-------------|-----|---------|---------|--------|-----|------------|--------|
| 1      | 30 min         | 12.01       | 0.64| 67.03   | -       | 4.54   | 0.03| 13.39      | Bal.   |
| 2      | 60 min         | 12.56       | 0.14| 67.41   | -       | 3.96   | 0.01| 13.57      | Bal.   |
| 3      | 90 min         | 12.94       | 0.56| 65.97   | -       | 4.04   | 0.07| 14.38      | Bal.   |
| 4      | 30 min         | 49.76       | 33.31| 7.69   | 4.32   | 0.94  | 0.54| 0.33       | Bal.   |
| 5      | 60 min         | 52.09       | 31.06| 5.82   | 5.5    | 0.81  | 0.50| 0.2        | Bal.   |
| 6      | 90 min         | 53.17       | 28.15| 6.81   | 5.48   | 1.24  | 0.86| 0.27       | Bal.   |

**Figure 3.** XRD patterns of slags after melt separation with addition of Al$_2$O$_3$-CaO-CaF$_2$ slag. The diffraction peaks can be indexed to CaAl$_2$O$_4$ and CaAl$_4$O$_7$. It can be speculated that high basicity slag reacts with Al$_2$O$_3$ inclusions in the alloy melt obtained by thermite reduction and the reaction is as follows [21]:

$$\gamma(CaO)_{slag} + (Al_2O_3)_{inclusion} = (\gamma CaO \cdot Al_2O_3)_{liquid, slag}$$ (1)
with the increasing of the melt separation time, while that of CaAl\(_2\) increase with the increasing of the melt separation time, while that of CaAl\(_2\) increase and then gradually decrease. According to the equilibrium diagram of Al\(_2\)O\(_3\)-CaO system [22], this result is mainly attributed to that the amount of Al\(_2\)O\(_3\) inclusions from alloy melt into the slag increases with melt separation time. Comparing to the XRD patterns of slags without the addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag in Figure 2, the diffraction peaks of Ti-Fe compounds oxides and titanium suboxides cannot be observed in Figure 3. The XRF analysis results in Table 2 indicate that the Al\(_2\)O\(_3\) content in slag increases with an increased separation time. This indicates that a long melt separation time is beneficial for the slag-metal separation. In addition, the contents of TiO\(_2\) and Fe\(_2\)O\(_3\) in the slag with addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag are obviously lower than that in the slag without the addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag. It can be concluded that the slag-metal separation effect is strengthened, and the migration of alloy components is suppressed by regulating the slag basicity during the melt separation, which is beneficial to increase the recovery rate of Ti and Fe elements.

3.2. SEM Images and EDS Analysis

Figure 4 shows the SEM images of the alloys directly prepared by thermite method and after melt separation under heat preservation.

Figure 4a indicates that the microstructure of the alloy directly prepared by thermite method is loose and contains amorphous Al\(_2\)O\(_3\) inclusions with a size about 200 \(\mu\text{m}\), which indicates an incomplete slag-metal separation. Figure 4b–d shows that Al\(_2\)O\(_3\) inclusions can also be observed in the alloys after different separation time in the cases without addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag. However, the morphology and size of Al\(_2\)O\(_3\) inclusions are different with different melt separation time. Comparing to thermite method, Al\(_2\)O\(_3\) inclusions in melt separation under heat preservation go through an aggregation-floating upward-recrystallization process, which is beneficial to the Al\(_2\)O\(_3\) inclusion removal. The sizes of Al\(_2\)O\(_3\) inclusion in the alloy are uneven, ranging from 5–50 \(\mu\text{m}\) under a 30 min separation, and the size ranges from 10 to 20 \(\mu\text{m}\) after a 60 min separation. However, they are rod-like with a size about 70 \(\mu\text{m}\) at 90 min separation. This result indicates that big size Al\(_2\)O\(_3\) inclusions can float upwards and are preferentially separated out. However, small size Al\(_2\)O\(_3\) inclusions get together, recrystallize and grow up with melt separation time and then are separated out. Compared to the alloys without addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag for melt separation in Figure 4b–d, Al\(_2\)O\(_3\) inclusions can hardly be observed in the alloys for the cases with addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\)

![Figure 3. XRD patterns of slags after melt separation with addition of Al\(_2\)O\(_3\)-CaO-CaF\(_2\) slag at 1650 °C: (1) 30 min, (2) 60 min, (3) 90 min.](image-url)
slag in Figure 4c–g. In addition, the microstructure of alloys is more uniform and compact, which indicates that the effects of slag-metal separation are greatly enhanced.

According to the microscopic analysis result in Table 3, regions 1, 5 and 8 in Figure 4b–d are supposed to be Ti-O solid solution, and region 3, 4 and 7 are TiFe phase. Si is dissolved in the matrix. Regions 10, 13 and 16 in Figure 4e–g are matrix based on Ti, Fe, Al, Si. Regions 12 and 15 are supposed to be Ti-O solid solutions. Under a high-powered microscope, a “basket microstructure” structure can be observed in the regions 12 and 14 in Figure 4e,f, and they are based on Ti, Fe, Al, Si. However, coarse lath-shaped structures, in the form of titanium silicide, arise in region 17 in Figure 4g. Compared to thermite method, the microstructure of alloys becomes more uniform and denser with a longer separation time.

| Region | Ti   | Fe   | Al   | Si   | O   |
|--------|------|------|------|------|-----|
| 1      | 81.69| 2.14 | 0.78 | -    | 15.39|
| 2      | -    | -    | 59.5 | -    | 40.5 |
| 3      | 59.88| 20.74| 7.94 | 1.73 | 9.71 |
| 4      | 53.24| 32.52| 3.47 | 2.59 | 8.18 |
| 5      | 84.5 | -    | -    | -    | 15.5 |
| 6      | -    | -    | 58.3 | -    | 41.7 |
| 7      | 55.42| 28.49| 5.66 | 2.89 | 7.54 |
| 8      | 82.15| -    | -    | -    | 17.85|
| 9      | -    | -    | 61.88| -    | 38.12|
| 10     | 42.59| 40.25| 11.64| 3.18 | 2.34 |
| 11     | 54.88| 27.43| 5.71 | 5.38 | 6.6  |
| 12     | 97.28| -    | -    | -    | 2.72 |
| 13     | 43.31| 40.72| 11.2 | 3.37 | 1.4  |
| 14     | 55.61| 24.7 | 7.89 | 5.43 | 6.37 |
| 15     | 98.34| -    | -    | -    | 1.66 |
| 16     | 44.55| 43.12| 8.48 | 2.73 | 1.12 |
| 17     | 79.42| 7.67 | 4.26 | 6.65 | 2    |

### 3.3. Phase of Alloys

Figure 5 shows XRD patterns of alloys directly prepared by thermite method with a melt separation. The obvious diffraction peaks of Al₂O₃, Fe₂₃Ti₉O₃, FeTi₂₆O₀₇₅ and TiO can be observed in the alloy directly prepared by thermite method. This means that the metal and slag have an incomplete separation because of the direct casting and a rapid cooling. However, the diffraction peaks of alloys

Table 3. Microscopic analysis of the microstructures of alloys in Figure 4, wt.%.
after a melt separation with the addition of Al2O3-CaO-CaF2 slag can be indexed to Fe0.9536O, TiFe, Ti2O, Al3Ti0.75Fe0.25, Al86Fe14 and Al21Ti29, but diffraction peaks of Al2O3 cannot be observed. The existing state of elements in the alloy is determined by thermite reduction reaction at high temperature, diffusive migration and recombination of constituent element during melt separation [23]. The Ti, which is reduced by residual aluminum in the alloy, preferentially combines with Fe to form Ti-Fe metallic compound and Ti3Fe9.7O3 [24]. However, new intermetallic compounds, such as Al86Fe14, Al3Ti0.75Fe0.25, are produced after a melt separation with high basicity Al2O3-CaO-CaF2 slag. It can be supposed that the formation of Al86Fe14, Al3Ti0.75Fe0.25 is mainly due to the basicity change of slag, diffusive migration and recombination of constituent element during melt separation. As a result, melt separation has a great effect not only on regulating the microstructure of the alloys but also on the removal of Al2O3 inclusions. This result agrees well with the microstructure analysis in Figure 4e–g.

Figure 5. XRD patterns of alloys at 1650 °C: (1) directly prepared by thermite method; (2–4) 30 min, 60 min, 90 min after melt separation with addition of Al2O3-CaO-CaF2 slag.

3.4. Oxygen Content and Chemical Composition Analysis

Figure 6 shows the curves of Al and O contents in the alloy with the melt separation time. The result indicates that both the Al and O contents of the alloys dramatically decrease after a melt separation. The Al and O contents in the alloy directly prepared by thermite method are 10.38% and 9.36%, respectively. The values are reduced to 6.52% and 4.54%, respectively, after a melt separation without the addition of Al2O3-CaO-CaF2 slag. However, they are further reduced to 4.24% and 1.56%, respectively, after a melt separation with the addition of Al2O3-CaO-CaF2 slag. According to the variation of Al and O before and after melt separation (in accordance with the chemical composition of Al2O3), it is supposed that the oxygen mainly exists in the form of Al2O3. The removal efficiency of Al2O3 during melt separation with Al2O3-CaO-CaF2 slag addition is obviously higher than that without Al2O3-CaO-CaF2 slag addition. This may be due to the melting point decrease of the slag after the addition of high basicity slag. A low melting point of the slag provides a good condition for a fast metal-slag separation. In addition, the dissolution time of Al2O3 inclusion in the high basicity slag is much shorter than the separation time of Al2O3 at the slag-metal interface (< 5 s) [25]. At the same time, the dissolution rate of Al2O3 particle decreases with the increasing of the Al2O3 content in slag, due to that the driving force of Al2O3 dissolution decreases. As a result, Al2O3 inclusions float upwards and depart from the slag-metal interface. Then, they are absorbed by the melt slag. This should be the main removal procedure of Al2O3 inclusion during the melt separation. Therefore, it is important to improve liquidity of melt slag for the removal of Al2O3 inclusions. The Al2O3 inclusions are effectively removed by strengthening the separation conditions during the melt separation. However, oxygen in the form of suboxides, such as Ti2O and Fe0.9536O, still needs to be removed by a deep reduction.
Numb contents dramatically decrease from 10.38% and 9.36% to 4.24% and 1.56%, respectively. The removal of slag basicity and melt separation time on the slag-metal separation during the melt separation under heat preservation were systematically studied. The conclusions are as follows:

4. Conclusions

A novel methodology for directly preparing low-oxygen high titanium ferroalloy from high titanium slag and iron concentrate by multistage and deep reduction was proposed, and the effects of slag basicity and melt separation time on the slag-metal separation during the melt separation under heat preservation were systematically studied. The conclusions are as follows:

Table 4 shows the chemical composition of alloys. The result indicates that the Al and O contents in the alloy directly prepared by thermite method can reach to 10.38% and 9.36%, respectively. After a melt separation without the addition of Al2O3-CaO-CaF2 slag, the Al and O contents dramatically decrease, respectively, from 10.38% and 9.36% to 6.52% and 4.54%, but Ti content evidently increases from 51.04% to 62.12%. After melt separation with addition of Al2O3-CaO-CaF2 slag, the Al and O contents dramatically decrease from 10.38% and 9.36% to 6.52% and 4.54%, but Ti content evidently increases from 51.04% to 68.24%. As a result, melt separation under the heat preservation is the key to produce high titanium ferroalloys with high quality and low impurities. At the same time, the oxygen in the alloy (about 1.50%) after melt separation illustrates that a deep reduction is still needed to further decrease its content, namely a multistage and deep reduction.

Table 4. Chemical composition of high titanium ferroalloys: 1: directly prepared by thermite method; 2,3,4: without addition of Al2O3-CaO-CaF2 slag; 5,6,7: with addition of Al2O3-CaO-CaF2 slag.

| Number | Melt Separation Time | Ti (%) | Al (%) | Si (%) | O (%) | Fe (%) |
|--------|----------------------|--------|--------|--------|-------|--------|
| 1      | -                    | 51.04  | 10.38  | 5.65   | 9.36  | Bal.   |
| 2      | 30 min               | 61.20  | 7.24   | 5.26   | 5.89  | Bal.   |
| 3      | 60 min               | 62.06  | 6.68   | 5.47   | 4.65  | Bal.   |
| 4      | 90 min               | 62.12  | 6.52   | 5.36   | 4.54  | Bal.   |
| 5      | 30 min               | 66.72  | 4.56   | 5.08   | 1.75  | Bal.   |
| 6      | 60 min               | 67.76  | 4.26   | 4.64   | 1.55  | Bal.   |
| 7      | 90 min               | 68.24  | 4.24   | 4.86   | 1.56  | Bal.   |

Figure 6. The curves of Al and O contents in alloys with the melt separation time: (1) without addition of Al2O3-CaO-CaF2 slag; (2) with addition of Al2O3-CaO-CaF2 slag.

There are a lot of Al2O3 inclusions in the alloy, which is directly prepared by thermite reduction, and they can be effectively eliminated by a melt separation under a heat preservation. The metal-slag separation efficiency can be effectively improved by increasing the basicity of melt slag and by extending the separation time. After the melt separation with the addition of Al2O3-CaO-CaF2 slag, the Al and O contents dramatically decrease from 10.38% and 9.36% to 4.24% and 1.56%, respectively. The removal
mechanism of Al2O3 inclusions during the melt separation is that Al2O3 inclusions float upwards and depart from the slag-metal interface. After that, they are absorbed by the molten slag.

After a melt separation, the residual oxygen in the form of sub-oxides, such as Ti2O and Fe0.9536O, still needs a deep reduction to be further removed, namely, a deep reduction. The deep reduction process will be the object of subsequent papers.

**Author Contributions:** C.C. wrote the original manuscript and carried out the tests and data collection. Z.D. supervised experimental work and data analysis. Z.D. and T.Z. revised the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by “NATIONAL KEY RESEARCH AND DEVELOPMENT PLAN, grant number 2017YF0305401”, “THE NATIONAL NATURAL SCIENCE FOUNDATION OF CHINA, grant number 51422403, 51774078” and “THE FUNDAMENTAL RESEARCH FUNDS FOR THE CENTRAL UNIVERSITIES, grant number N162505002, N172506009, N170908001”.

**Acknowledgments:** The authors are especially thankful to the professors Yan Liu and Li-ping Niu; they gave us helpful suggestions when the tests were carried out.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Dou, Z.H.; Fan, S.G.; Cheng, C.; Zhang, T.A.; Shi, G.Y. Research Advance and Application of High Titaniumferrous with Low Oxygen. *Metall. Eng.* 2015, 2, 107–121. [CrossRef]
2. Shah, S.J.; Henein, H.; Ivey, D.G. Microstructural Characterization of Ferrotitanium and Ferroniobium. *Mater. Charact.* 2013, 78, 96–107. [CrossRef]
3. Qi, C.C.; Hua, X.Y.; Chen, K.H.; Jie, Y.F.; Zhou, Z.R.; Ru, J.J.; Xiong, L.; Gong, K. Preparation of Ferrotitanium Alloy from Ilmenite by Electrochemical Reduction in Chloride Molten Salts. *JOM* 2015, 68, 1–7. [CrossRef]
4. Yang, X.; Hu, M.L.; Bai, C.G.; Lv, X.W. Formation Behavior of CaTiO3 during Electrochemical Deoxidation of Ilmenite Concentrate to Prepare Fe-Ti Alloy. *Rare Met.* 2016, 35, 275–281.
5. Shi, R.; Bai, C.; Hu, C.; Liu, X.; Du, J. Experimental Investigation on the Formation Mechanism of the TiFe Alloy by the Molten-salt Electrolytic Ilmenite Concentrate. *Int. J. Miner. Metall. Mater.* 2011, 47, 99–104. [CrossRef]
6. Du, J.H.; Xi, Z.P.; Li, Q.Y.; Li, Z.X.; Tang, Y. Effect of TiO2 Cathode Performance on Preparation of Ti by Electro-deoxidation. *Trans. Nonferrous Met. Soc. China* 2007, 17, 514–521.
7. Cheng, C.; Zhang, T.A.; Dou, Z.H. Formation Mechanism and Distribution of Al and O in the Ferrotitanium with Different Ti Contents Prepared by Thermite Method. *JOM* 2019, 71, 3584–3589. [CrossRef]
8. Liu, X.Y.; Hu, M.L.; Bai, C.G.; Lv, X.W.; Du, J.H. The Deoxidizing Process of the Preparation FeTi Alloy by Electrolysis Ilmenite Concentrate in Molten Salt. *J. Funct. Mater.* 2011, 42, 2042–2046.
9. Pourabdoli, M.; Raygan, S.; Abdizadeh, H.; Hanaei, K. A New Process for the Production of Ferrotitanium from Titanium Slag. *Can. Metall. Q.* 2007, 46, 17–23. [CrossRef]
10. Dou, Z.H.; Zhang, T.A.; Zhang, H.B.; Zhang, Z.Q.; Niu, L.P.; He, J.C. Basic Research on Preparation of High Titanium Ferroalloy with Low Oxygen Content by Thermit Reduction. *J. Process Eng.* 2010, 10, 1119–1125.
11. Tan, S.; Örs, T.; Aydnol, M.K.; Öztürk, T.; Karakaya, İ. Synthesis of FeTi from Mixed Oxide Precursors. *J. Alloys Compd.* 2009, 475, 368–372. [CrossRef]
12. Hu, M.; Bai, C.; Liu, X.; Lv, X.I.; Du, J. Deoxidization Mechanism of Preparation FeTi Alloy using Ilmenite Concentrate. *Int. J. Miner. Metall. Mater.* 2011, 47, 193–198. [CrossRef]
13. Pazdnikov, I.P.; Dubrovskii, A.Y.; Zelyanski, A.V. Problem of Optimizing the Production of High-Quality Ferrotitanium. *Titan. Ind.* 2005, 2, 21–22.
14. Chumarev, V.M.; Dubrovskii, A.Y.; Pazdnikov, I.P.; Shurygin, Y.Y.; Sel’Menskikh, N.I. Technological Possibilities of Manufacturing High-grade Ferrotitanium from Crude Ore. *Russ. Metall.* 2008, 6, 459–463. [CrossRef]
15. Dou, Z.H.; Zhang, T.A.; Zhang, H.B.; Zhang, Z.Q.; Niu, L.P.; He, J.C. Research on Preparation of High Titanium Ferroalloy with Low Oxygen through Vacuum Secondary Reduction Refining. *Rare Met. Mater. Eng.* 2012, 41, 420–425.
16. Dou, Z.H.; Zhang, T.A.; Yao, J.M.; Jiang, X.L.; Niu, L.P.; He, J.C. Research on Properties of Al2O3-CaO Slag. *J. Process Eng.* 2009, 9, 247–249.
17. Shi, G.Y.; Zhang, T.A.; Niu, L.P.; Dou, Z.H. Research on Properties of Low Fluorine CaF$_2$-CaO-Al$_2$O$_3$-MgO-SiO$_2$ Refining Slag. *J. Process Eng.* 2011, 11, 695–697.

18. Dou, Z.H.; Zhang, T.A.; Yao, J.M.; Niu, L.P. Viscosities of Slags in CaO-Al$_2$O$_3$-CaF$_2$-SiO$_2$ System. *J. Northeast. Univ. Nat. Sci.* 2008, 29, 1000–1003.

19. Dou, Z.H.; Zhang, T.A.; Zhang, H.B.; Zhang, Z.Q.; Niu, L.P.; Yao, Y.L.; He, J.C. Preparation of High Titanium Ferrous with Low Oxygen Content by Thermite Reduction-SHS. *J. Cent. South Univ. Technol.* 2012, 41, 899–904.

20. Cheng, C.; Dou, Z.H.; Zhang, T.A.; Su, J.M.; Zhang, H.J.; Liu, Y.; Niu, L.P. Oxygen Content of High Ferrotitanium Prepared by Thermite Method with Different Melt Separation Temperatures. *Rare Met.* 2019, 38, 892–898. [CrossRef]

21. Han, Z.J.; Liu, L.; Lind, M.; Holappa, L. Mechanism and Kinetics of Transformation of Alumina Inclusions by Calcium Treatment. *Acta Metall. Sin.* 2006, 19, 1–8. [CrossRef]

22. Jerebtsov, D.A.; Mikhailov, G.G. Phase Diagram of CaO-Al$_2$O$_3$ System. *Ceram. Int.* 2001, 27, 25–28. [CrossRef]

23. Zhao, H.M.; Wang, X.H.; Xie, B. Effect of Components on Desulfurization of an Al$_2$O$_3$-CaO Base Premolten Slag Containing SrO. *J. Univ. Sci. Technol. Beijing* 2005, 12, 225–230.

24. Foadian, F.; Soltanieh, M.; Adeli, M.; Etminanbakhsh, M. A Study on the Formation of Intermetallics during the Heat Treatment of Explosively Welded Al-Ti Multilayers. *Metall. Mater. Trans. A* 2014, 45, 1823–1832. [CrossRef]

25. He, S.P.; Chen, G.J.; Guo, Y.T.; Shen, B.Y.; Wang, Q. Morphology Control for Al$_2$O$_3$ Inclusion without Ca Treatment in High-aluminum Steel. *Metall. Mater. Trans. B* 2015, 46, 585–594. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).