

Cite this article as: Xie Wei, Dou Zhihe, Fang Shuai, et al. Preparation of Titanium-Based Alloys by Self-Propagating Aluminothermic Reduction of High-Titanium Slag[J]. Rare Metal Materials and Engineering, 2026, 55(10): 2421-2428. DOI: <https://doi.org/10.12442/j.issn.1002-185X.20250638>.

ARTICLE

Preparation of Titanium-Based Alloys by Self-Propagating Aluminothermic Reduction of High-Titanium Slag

Xie Wei^{1,2}, Dou Zhihe^{1,2}, Fang Shuai^{1,2}, Li Bingqi^{1,2}, Zhang Tingan^{1,2}

¹ School of Metallurgy, Northeastern University, Shenyang 110819, China; ² Key Laboratory of Ecological Metallurgy of Multi-metal Intergrown Ores of Ministry of Education, Shenyang 110819, China

Abstract: The effects of different aluminum ratios on the preparation of titanium-based alloys via aluminothermic reduction of high-titanium slag were investigated. Titanium-based alloys were prepared by self-propagating aluminothermic reduction using high-titanium slag, aluminum powder, KClO_3 , and CaO as raw materials. The thermodynamics and kinetics of the aluminothermic reduction of high-titanium slag were calculated. The results show that high-titanium slag can be used to prepare titanium-based alloys via aluminothermic reduction. The main reaction is the reduction of TiO_2 by Al. The activation energy of the reaction is 274.4 kJ/mol, and the reaction order is 1.04. With the increase in aluminum ratio, the mass fraction of Ti element in the titanium-based alloy gradually decreases, and that of Al element gradually increases. At the same time, there are small amounts of alloying elements such as Fe, Mn, and Si in the titanium-based alloy. Phase analysis shows that under a low aluminum ratio, the main phase is Ti_3Al ; under a high aluminum ratio, it is TiAl . The results of chemical composition analysis show that the prepared titanium-based alloy has a composition of 51.6wt% Ti, 40.6wt% Al, 7.6wt% Fe, 3.4wt% Mn, and 1.3wt% Si under the experimental conditions of aluminum ratio as 1.0. The microstructural analysis shows that the prepared titanium alloy consists of a base-phase region, an iron-rich phase region, and a silicon-rich phase region.

Key words: high-titanium slag; aluminothermic reduction; aluminum ratio; titanium-based alloy

1 Introduction

China is rich in titanium resources, accounting for 48% of the world's titanium reserves, most of which occur as vanadium-titanium magnetite^[1]. Iron-vanadium alloy and high-titanium slag can be produced by carbothermic reduction of vanadium-titanium magnetite in an electric furnace. At present, the main methods for utilizing high-titanium slag are sulfuric acid and chlorination to prepare titanium dioxide. However, they involve high levels of pollution and energy consumption, and the high-value utilization of high-titanium slag has not been realized^[2]. The TiO_2 content in high-titanium slag can reach about 80%, making it a high-quality titanium-containing raw material for preparing titanium-based alloys by the aluminothermic reduction method. During the aluminothermic reduction process, a small amount of iron, manganese, and silicon

oxides in the high-titanium slag will be reduced to metals and then enter the titanium-based alloy. At the same time, the equilibrium constant of the reaction between Al and TiO_2 is small, so that some Al will remain in the titanium-based alloy. Therefore, it is necessary to fully consider the effects of alloying elements such as Al, Fe, Mn, and Si on the properties of titanium-based alloys. Al is a common and highly effective α -phase strengthening element that can improve the alloy's strength and oxidation resistance^[3-4]. Fe and Mn are β -stabilizing elements that can refine grains, promote precipitation strengthening, and significantly improve the yield strength and tensile strength of titanium alloys^[5]. Si can produce a dispersion-strengthening effect, thereby improving the alloy's heat resistance and thermal strength^[6]. At present, the traditional methods for preparing titanium-based alloys mainly include sintering, melting, and additive manufacturing^[7-10]. However, these processes all use

Received date: December 16, 2025

Foundation item: Liaoning Revitalization Talents Program (XLYC2402029); Major Science and Technology Special Project of Liaoning Province (2024JH1/11700028-2); National Natural Science Foundation of China (52174333)

Corresponding author: Dou Zhihe, Ph. D., Professor, School of Metallurgy, Northeastern University, Shenyang 110819, P. R. China, E-mail: douzhih@smm.neu.edu.cn

Copyright © 2026, Northwest Institute for Nonferrous Metal Research. Published by Science Press. All rights reserved.

titanium metal as the raw material, resulting in high costs. Therefore, it is urgent to develop a new low-cost technology for the preparation of titanium-based alloys. If high-titanium slag is used as the raw material and aluminum powder as the reducing agent to directly prepare a titanium-based alloy, the energy-intensive, highly polluting Kroll method for preparing titanium metal can be bypassed, greatly reducing production costs. For this reason, many researchers have conducted related studies. Lei et al^[11] prepared a Ti-Al-Si master alloy by aluminothermic reduction of titanium-containing blast furnace slag and combined it with electromagnetic directional solidification to efficiently separate silicon element to obtain titanium aluminide-based alloys. Zhang et al^[12] used a waste SCR catalyst, titanium-bearing blast furnace slag, and waste aluminum scraps as raw materials to prepare a TiSi₃-TiAl₃ alloy precursor by the aluminothermic reduction method, and then separated the Ti-Si-Al melt by the electromagnetic directional solidification method to successfully prepare TiSi₃ and TiSi₃-TiAl₃ alloys. Lee et al^[13] found that the alloy melt settled to the bottom of the crucible due to gravity in the range of 1750–2000 °C, and the slag floated up by igniting the mixture of TiO₂-KClO₄-Al(Mg)-CaF₂. TiO₂ was successfully reduced to Ti-rich ingots by optimizing the Al/Mg ratio, Al particle size, and CaF₂ addition. Piao et al^[14] prepared Ti-Al-based alloys by aluminothermic reduction of acid-soluble titanium slag, and combined with electromagnetic levitation refining. The results show that the main phase after refining is TiAl₃, along with TiSi₃, TiAl, and other intermetallic compounds. Song et al^[15] prepared a TiAl alloy by reducing TiO₂ with an Al-Ca composite reducing agent. The effects of unit-mass thermal effect, reducing-agent composition and ratio, slag addition, and other factors on the self-propagating reaction rate and stability were studied. However, many studies have used titanium-containing blast furnace slag as a titanium-containing raw material to prepare titanium-based alloys. In this study, industrial-grade high-titanium slag was selected as a raw material, which can effectively reduce the introduction of impurities during the preparation of titanium alloys. In terms of preparation methods, existing research mostly relies on external heating to achieve aluminothermic reduction. In this study, titanium-based alloys were prepared by the self-propagating aluminothermic reduction method, which offers high reaction efficiency and a short process flow. There is still a lack of in-depth research on the reaction mechanism, product phases, and microstructures of titanium-based alloys produced by aluminothermic reduction of high-titanium slag. In this study, a new method for the direct preparation of titanium-based alloys by aluminothermic reduction, using high-titanium slag as the raw material, was proposed. This method has the advantages of a short process, simple operation, and low cost. It not only achieves high-value utilization of high-titanium slag but also effectively addresses the high cost and lengthy process in the preparation of traditional titanium-based alloys.

2 Experiment

2.1 Materials

High-titanium slag (average particle size of 2.5 μm, produced by Inner Mongolia Yu Xiao Meng Da Titanium Industry Co., Ltd) was used as the raw material, and its chemical composition was determined by an inductively coupled plasma spectrometer. The results are shown in Table 1. Al powder (purity≥99.5%, average particle size of 2.5 μm, produced by CITIC Jinzhou Ferroalloy Co., Ltd) was used as a reducing agent. KClO₃ (purity≥99.6%, produced by Sinopharm Chemical Reagent Co., Ltd) was used as a heating agent. CaO (purity≥98.0%, produced by Sinopharm Chemical Reagent Co., Ltd) was used as a slagging agent. Magnesium powder (purity≥99.0%, average particle size: 75–150 μm, produced by XILONG SCIENTIFIC Co., Ltd) was used as an ignition agent.

2.2 Experimental method

The high-titanium slag, KClO₃, and CaO were dried at 150 °C for at least 12 h, weighed at the ratios shown in Table 2, and then mixed in a mixer for 30 min. The mixture was loaded into a homemade graphite reactor, an appropriate amount of magnesium powder was added to the surface of the material as an ignition agent, and the mixture was ignited to initiate the reaction. After the reaction, it was allowed to cool to room temperature. The titanium-based alloy ingot and slag were separated and used for subsequent detection and analysis.

2.3 Analysis and characterization

The phases of the titanium-aluminum alloy and the reducing slag were analyzed using an X-ray diffractometer (XRD; Bruker D8, copper target, Germany). The microstructure of the titanium aluminum alloy was analyzed using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS; Hitachi SU3800, Japan). The chemical composition of the titanium-aluminum alloy was analyzed by an inductively coupled plasma spectrometer (PE Avio500, America). The differential thermal analysis of Al-TiO₂ was carried out using a high-temperature synchronous thermal analyzer (Nanjing Huicheng STA-1550, China).

Table 1 Chemical composition of high-titanium slag (wt%)

Composition	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MnO ₂
Content	87.9	5.79	2.05	1.71	2.51

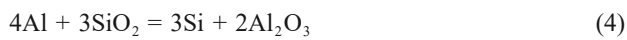
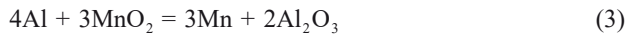
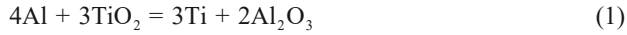
Table 2 Mass of high-titanium slag, Al powder, KClO₃, and CaO under different aluminum ratio conditions (g)

Aluminum ratio	High-titanium slag	Al power	KClO ₃	CaO
0.8	1000	536	415	355
0.9	1000	582	420	385
1.0	1000	632	434	418
1.1	1000	684	453	424
1.2	1000	736	471	429

3 Results and Discussion

3.1 Thermodynamic model of mass-action concentration of titanium-aluminum alloy prepared by high-titanium slag aluminothermic reduction

The main elements involved in the process of aluminothermic reduction of high-titanium slag are Ti, Al, Fe, Mn, Si, and O. With the help of thermodynamic software Factsage 7.3, the possible reactions are as follows:



The melt produced by reacting the high-titanium slag with the raw material at ratios listed in Table 1 and Table 2 is taken as the object of calculation. When the reaction reaches equilibrium, the formation reaction equation, the standard Gibbs free energy, and the mass-action concentration of each structural unit in the melt are shown in Table 3. The n_i ($i = 1, 2, \dots, 33$) represents the amount of substance in each unit structure during the reaction equilibrium in the melt. $\sum n_i$ represents the sum of the amount of substance of all structural units in the melt at reaction equilibrium, which can be expressed by Eq.(25).

$$n_i = n_1 + n_2 + \dots + n_{33} \quad (25)$$

According to the coexistence theory of atoms and molecules, the ratio of the amount of equilibrium material of structural unit i to the total amount of material of all structural units in the equilibrium system $\sum n_i$ is the mass-action concentration N_i of structural unit i in the melt, which can be expressed by Eq. (26). K_i ($i = 8, 9, \dots, 33$) represents the

equilibrium constant of the reaction in the melt. The equilibrium constant and the Gibbs free energy of the reaction can be expressed by Eq.(27).

$$N_i = \frac{n_i}{\sum n_i} \quad (26)$$

$$\Delta G_i^\ominus = -RT \ln(K_i) \quad (27)$$

According to the definition of the mass-action concentration of each structural unit in the melt, Eq.(28–34) can be obtained.

$$(N_1 + N_8 + 3N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + 5N_{21} + N_{22} + N_{23}) \sum n_i = n_{\text{Ti}} \quad (28)$$

$$(N_2 + 2N_9 + N_{15} + N_{16} + 2N_{17} + 3N_{18} + N_{24} + N_{25} + 2N_{26} + 5N_{27} + 3N_{28}) \sum n_i = n_{\text{Al}} \quad (29)$$

$$(N_3 + 2N_{10} + N_{19} + 2N_{20} + 3N_{24} + N_{25} + N_{26} + 2N_{27} + N_{28} + N_{29} + N_{30} + 5N_{31}) \sum n_i = n_{\text{Fe}} \quad (30)$$

$$(N_4 + N_{11} + 3N_{31} + 5N_{32} + N_{33}) \sum n_i = n_{\text{Mn}} \quad (31)$$

$$(N_5 + N_{12} + N_{21} + 2N_{22} + 2N_{28} + N_{29} + 3N_{30} + N_{31} + 3N_{32} + N_{33}) \sum n_i = n_{\text{Si}} \quad (32)$$

$$(N_6 + N_{13}) \sum n_i = n_{\text{Ca}} \quad (33)$$

$$(N_7 + 2N_8 + 3N_9 + 3N_{10} + 2N_{11} + 2N_{12} + N_{13}) \sum n_i = n_{\text{O}} \quad (34)$$

Since the sum of the mass-action concentrations of each structural unit in the melt is 1, Eq.(35) can be obtained:

$$N_1 + N_2 + \dots + N_{33} = 1 \quad (35)$$

According to the relationship between the mass-action concentration and the equilibrium constant in Eq.(28–35) and Table 3, the mass-action concentration N_i of each structural unit in the melt can be calculated^[16–17].

Fig. 1 presents the thermodynamic analysis results of Al mass-action concentration during the preparation of titanium-aluminum alloy via aluminothermic reduction of high-titanium slag at 1800 °C. It can be seen that the content of TiAl intermetallic compounds in titanium-aluminum alloy increases with increasing aluminum ratio. The reduction of TiO_2 by Al is a step-by-step reduction process, and the reaction path is: $\text{TiO}_2 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}$, in which the reduction step of $\text{TiO} \rightarrow \text{Ti}$ is the most difficult. During the whole reduction process, TiO_2 cannot be completely reduced to Ti by Al. Therefore, even at low aluminum ratios, residual Al metal remains in the titanium-based alloy and does not participate in the reaction. Since the Gibbs free energy of the reaction between Ti and Al to form Ti_3Al and TiAl is negative, indicating that the reaction is thermodynamically easy to carry out, the reduced metal Ti will combine with Al to form Ti_3Al and TiAl intermetallic compounds. Because the reaction between Ti and Si has a low Gibbs free energy, they can form a stable TiSi phase that exists in titanium-based alloys.

3.2 Kinetic analysis of the preparation of titanium-aluminum alloy by aluminothermic reduction of high-titanium slag

Fig.2 is the DSC curve of the Al-TiO₂ system. From Fig.2, the curve shows its first peak at 638 °C, corresponding to the endothermic peak of Al melting. When the temperature rises

Table 3 Formation reaction equation, reaction standard Gibbs free energy, and mass-action concentration of each structural unit

Structural unit	Reaction	$\Delta G^\ominus/\text{J}\cdot\text{mol}^{-1}$	N_i
[Ti]	-	-	N_1
[Al]	-	-	N_2
[Fe]	-	-	N_3
[Mn]	-	-	N_4
[Si]	-	-	N_5
[Ca]	-	-	N_6
[O]	-	-	N_7
(TiO ₂)	[Ti] + 2 [O] = [TiO ₂]	-1 413 710+293.35 <i>T</i>	$N_8 = K_8 N_1 N_7^2$
(Al ₂ O ₃)	2 [Al] + 3 [O] = (Al ₂ O ₃)	-1 202 000+386.00 <i>T</i>	$N_9 = K_9 N_2^2 N_7^3$
(Fe ₂ O ₃)	2 [Fe] + 3 [O] = (Fe ₂ O ₃)	-1 599 740+459.82 <i>T</i>	$N_{10} = K_{10} N_3^2 N_7^3$
(MnO ₂)	[Mn] + 2 [O] = (MnO ₂)	-532 782+118.93 <i>T</i>	$N_{11} = K_{11} N_4 N_7^2$
(SiO ₂)	[Si] + 2 [O] = (SiO ₂)	-1 447 262+326.41 <i>T</i>	$N_{12} = K_{12} N_5 N_7^2$
(CaO)	[Ca] + [O] = (CaO)	-1 287 755+225.48 <i>T</i>	$N_{13} = K_{13} N_6 N_7$
[Ti ₃ Al]	3 [Ti] + [Al] = [Ti ₃ Al]	-29 633+6.71 <i>T</i>	$N_{14} = K_{14} N_1^3 N_2$
[TiAl]	[Ti] + [Al] = [TiAl]	-37 455+16.79 <i>T</i>	$N_{15} = K_{15} N_1 N_2$
[TiAl ₂]	[Ti] + 2 [Al] = [TiAl ₂]	-43 858+11.02 <i>T</i>	$N_{16} = K_{16} N_1 N_2^2$
[TiAl ₃]	[Ti] + 3 [Al] = [TiAl ₃]	-40 349+10.36 <i>T</i>	$N_{17} = K_{17} N_1 N_2^3$
[TiFe]	Ti + Fe = [TiFe]	-62 704+25.12 <i>T</i>	$N_{18} = K_{18} N_1 N_3$
[TiFe ₂]	[Ti] + 2 [Fe] = [TiFe ₂]	-162 397+63.73 <i>T</i>	$N_{19} = K_{19} N_1 N_3^2$
[Ti ₅ Si ₃]	5 [Ti] + 3 [Si] = [Ti ₅ Si ₃]	-775 050+140.62 <i>T</i>	$N_{20} = K_{20} N_1^5 N_5^3$
[TiSi]	[Ti] + [Si] = [TiSi]	-188 195+35.61 <i>T</i>	$N_{21} = K_{21} N_1 N_5$
[TiSi ₂]	[Ti] + 2 [Si] = [TiSi ₂]	-274 638+68.47 <i>T</i>	$N_{22} = K_{22} N_1 N_5^2$
[Fe ₃ Al]	3 [Fe] + [Al] = [Fe ₃ Al]	-65 736+6.07 <i>T</i>	$N_{23} = K_{23} N_3^3 N_2$
[FeAl]	[Fe] + [Al] = [FeAl]	-17 743-14.75 <i>T</i>	$N_{24} = K_{24} N_3 N_2$
[FeAl ₂]	[Fe] + 2 [Al] = [FeAl ₂]	-87 945+14.70 <i>T</i>	$N_{25} = K_{25} N_3 N_2^2$
[Fe ₂ Al ₅]	2 [Fe] + 5 [Al] = [Fe ₂ Al ₅]	-207 746+29.12 <i>T</i>	$N_{26} = K_{26} N_3^2 N_2^5$
[FeAl ₃]	[Fe] + 3 [Al] = [FeAl ₃]	-127 185+22.82 <i>T</i>	$N_{27} = K_{27} N_3 N_2^3$
[FeSi ₂]	[Fe] + 2 [Si] = [FeSi ₂]	-196 358+83.99 <i>T</i>	$N_{28} = K_{28} N_3 N_5^2$
[FeSi]	[Fe] + [Si] = [FeSi]	-73 695+2.17 <i>T</i>	$N_{29} = K_{29} N_3 N_5$
[Fe ₅ Si ₃]	5 [Fe] + 3 [Si] = [Fe ₅ Si ₃]	-456 469+113.60 <i>T</i>	$N_{30} = K_{30} N_3^5 N_5^3$
[Mn ₃ Si]	3 [Mn] + [Si] = [Mn ₃ Si]	-196 720+50.36 <i>T</i>	$N_{31} = K_{31} N_4^3 N_5$
[Mn ₅ Si ₃]	5 [Mn] + 3 [Si] = [Mn ₅ Si ₃]	-333 341+40.50 <i>T</i>	$N_{32} = K_{32} N_4^5 N_5^3$
[MnSi]	[Mn] + [Si] = [MnSi]	-86 852+9.50 <i>T</i>	$N_{33} = K_{24} N_4 N_5$

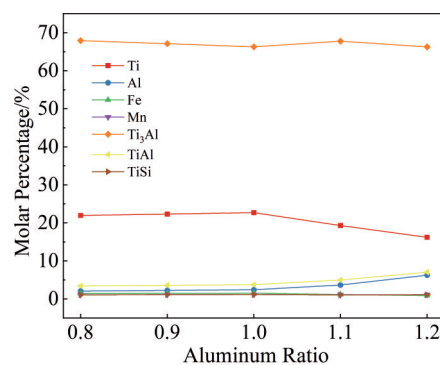
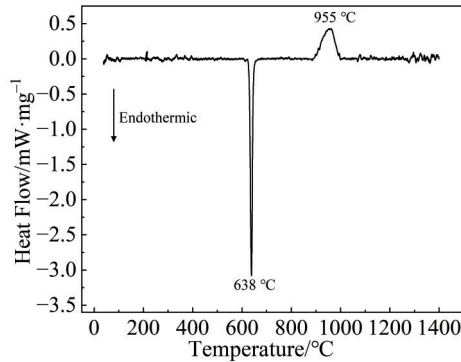
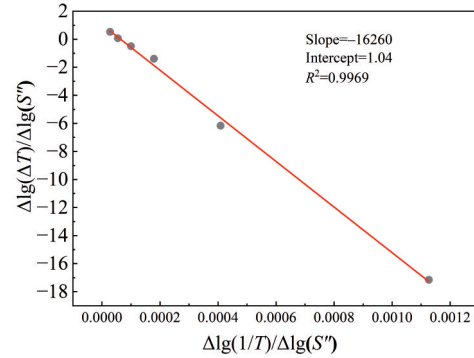


Fig.1 Calculation results of mass-action concentration of aluminothermic reduction of high-titanium slag

to 955 °C, the second peak appears, which is the exothermic peak of the reaction between Al (liquid) and TiO₂ (solid). Kinetic parameters are calculated by analysis of the DSC curves using the Freeman-Carroll method. The dynamic equation obtained from the simplified transformation is given by Eq. (36). The data for the exothermic peak of Al-TiO₂ are analyzed, and a $\Delta \lg(\Delta T)/\Delta \lg(S'') - \Delta \lg(1/T)/\Delta \lg(S'')$ curve is drawn, as shown in Fig. 3. The slope is $-E/(2.303R)$, where E is the apparent activation energy of the reaction, and the intercept is n , the order of the reaction^[18-20]. According to the fitting equation in Fig. 3, the apparent activation energy of the reaction between Al and TiO₂ is calculated to be $E = 274.4 \text{ kJ/mol}$, and the reaction order $n = 1.04$.

Fig.2 DSC analysis of Al-TiO₂ systemFig.3 Freeman-Carroll analysis of the Al-TiO₂ system

$$\frac{\Delta \lg(\Delta T)}{\Delta \lg(S'')} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \lg(S'')} + n \quad (36)$$

3.3 Effect of the aluminum ratio on the chemical composition of Ti-based alloy

Fig. 4 shows the mass percentage of each element in the titanium-based alloy prepared by aluminothermic reduction of high-titanium slag over the aluminum ratio range of 0.8–1.2. Fig. 4 shows that the main components of the titanium-based alloy obtained by aluminothermic reduction of high-titanium slag are Ti and Al, with small amounts of Fe, Mn, and Si. With increasing aluminum ratio, the mass percentage of Ti in the titanium-based alloy gradually decreases, the mass percentage of Al gradually increases, and the mass percentages of Fe, Mn, and Si remain essentially unchanged. In order to analyze the possible phases formed by the main elements Ti and Al in the titanium-based alloy, the mass percentage of each element in the titanium-based alloy is converted into a molar ratio, and the results are shown in Table 4. According to the ratio of the amount of titanium atoms to the amount of aluminum atoms in the titanium-aluminum alloy in Table 4, the main phase in the titanium-based alloy prepared under the experimental conditions with low aluminum ratio may be the titanium-aluminum intermetallic compound phase with low Al content, and the main phase in the titanium-based alloy prepared under the experimental conditions with high Al content may be the titanium-aluminum intermetallic compound phase with high Al content.

3.4 Effect of the aluminum ratio on the phase composition of titanium-based alloys

The titanium-based alloys prepared under experimental conditions with aluminum ratios of 1.0 and 1.1 were analyzed by XRD. The results are shown in Fig. 5. The main phase of the titanium-based alloy prepared under the experimental conditions with an aluminum ratio of 1.0 is the Ti₃Al phase, and the main phase of the titanium-based alloy prepared under the experimental conditions with an aluminum ratio of 1.1 is the TiAl phase. According to the composition of the titanium-based alloy in Table 4, as the aluminum ratio increases from 1.0 to 1.1, the alloy composition shifts from the Ti₃Al phase region to the stable TiAl phase region in the Ti-Al binary

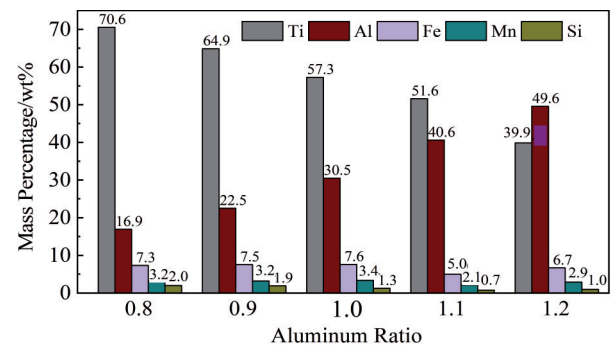


Fig.4 Mass percentage of each element in the titanium-based alloy prepared by aluminothermic reduction of high-titanium slag in the aluminum ratio range of 0.8–1.2

phase diagram. The main phase of the Ti-based alloy prepared under the condition of Al content of 1.0 is the Ti₃Al phase, which is a hexagonal crystal system, and the Ti₃Al (002) diffraction peak is obviously enhanced compared with the standard peak. This is due to the presence of a small amount of the TiAl phase in the titanium alloy prepared under experimental conditions with an Al ratio of 1.0. The TiAl (101) diffraction peak is superimposed on the Ti₃Al (002) diffraction peak, resulting in the enhancement of the Ti₃Al (002) diffraction peak. The XRD diffraction results of the titanium-based alloy prepared at the aluminum ratio of 1.1 show that there is almost no Ti₃Al (002) diffraction peak, indicating that the titanium-based alloy prepared at the aluminum ratio of 1.0 contains almost no Ti₃Al phase. Due to the presence of iron oxides, manganese oxides, and silicon oxides in the high-titanium slag, these oxides will be reduced to titanium-based alloys during the aluminothermic reduction process. From Fig. 5, it can be seen that the elements Fe and Mn in the titanium-based alloy form the Fe₁₉Mn₁₀ phase, and the elements Ti and Si form the TiSi phase.

3.5 Effect of aluminum ratio on the microstructure of titanium-based alloy

The microstructure of titanium-based alloy prepared by aluminothermic reduction of high-titanium slag is shown in Fig. 6. According to the difference of gray level in each region in Fig. 6, the microstructure of titanium-based alloy can be

Table 4 Molar percentage of each component and molar ratio of Ti to Al in titanium-based alloys

Aluminum ratio	Ti/ mol%	Al/ mol%	Fe/ mol%	Mn/ mol%	Si/ mol%	n_{Ti}/n_{Al}
0.8	62.4	26.5	5.6	2.5	3.0	2.35:1
0.9	55.3	34.0	5.5	2.4	2.8	1.63:1
1.0	46.5	44.0	5.3	2.4	1.7	1.06:1
1.1	39.4	55.0	3.3	1.4	1.0	1:1.39

divided into three regions: one is the base phase region marked by red and the largest area; the second is the reticular area marked by blue; the third is the yellow marked block area. At the same time, black oxide inclusions marked by white dotted lines are also observed in the microstructure of the titanium alloy, which is caused by the insufficient floating time of slag due to rapid solidification during the self-propagating aluminothermic reaction. The refining process can eliminate the inclusions. It is worth noting that there is an obvious network structure in the titanium-based alloy prepared under the experimental conditions with an aluminum ratio of 0.9, as shown in Fig. 6c. This network structure is caused by the transfer and enrichment of elements Fe, Mn, and Si produced by the reduction of high-titanium slag in the base phase. Therefore, it is necessary to analyze the distribution of alloying elements in titanium-based alloys using EDS to determine the elemental composition of the microstructure.

SEM-EDS analysis was performed on the titanium-based alloys prepared under the experimental conditions with Al

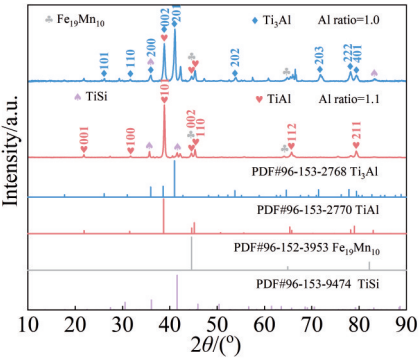


Fig.5 XRD patterns of titanium-based alloys prepared with aluminum ratios of 1.0 and 1.1

content of 0.9 and 1.1. The results are shown in Fig. 7. The quantitative analysis of the key regions in the EDS test is presented in Table 5. Based on the distribution characteristics of each element in the titanium-based alloy, the microstructure can be divided into three regions: the basic phase region composed of titanium and aluminum, the Fe-rich phase region (rich in Fe and Mn), and the Si-rich phase region. The distribution of element Fe and element Mn is similar, and the content of element Ti decreases obviously in the area where element Fe and element Mn appear, which indicates that element Ti migrates back from the Fe-rich phase area during the cooling and solidification process. From the distribution characteristics of the element Si in Fig.7b, it can be found that there is almost no element Al in the Si-rich region. This is because the Gibbs free energy of the Ti-Si reaction is very small. Combined with the phase analysis results of titanium-based alloys in Fig.5, it can be inferred that Ti and Si form stable TiSi intermetallic compounds in titanium-based alloys.

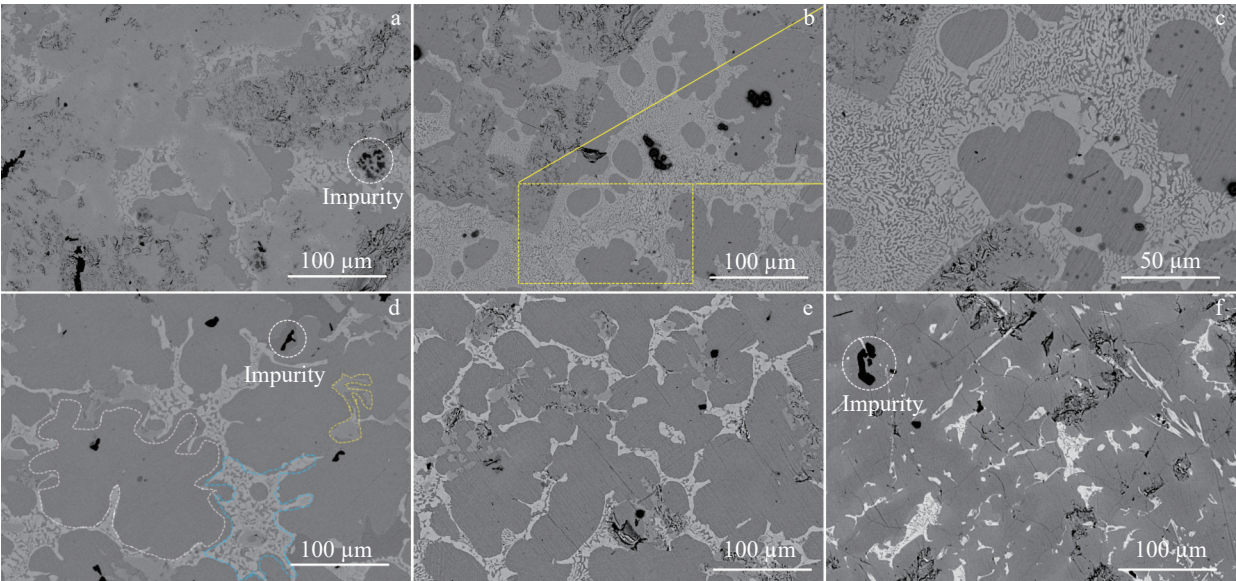


Fig.6 Microstructures of titanium-based alloy prepared by aluminothermic reduction of high-titanium slag with different aluminum ratios: (a) 0.8, (b-c) 0.9, (d) 1.0, (e) 1.1, and (f) 1.2

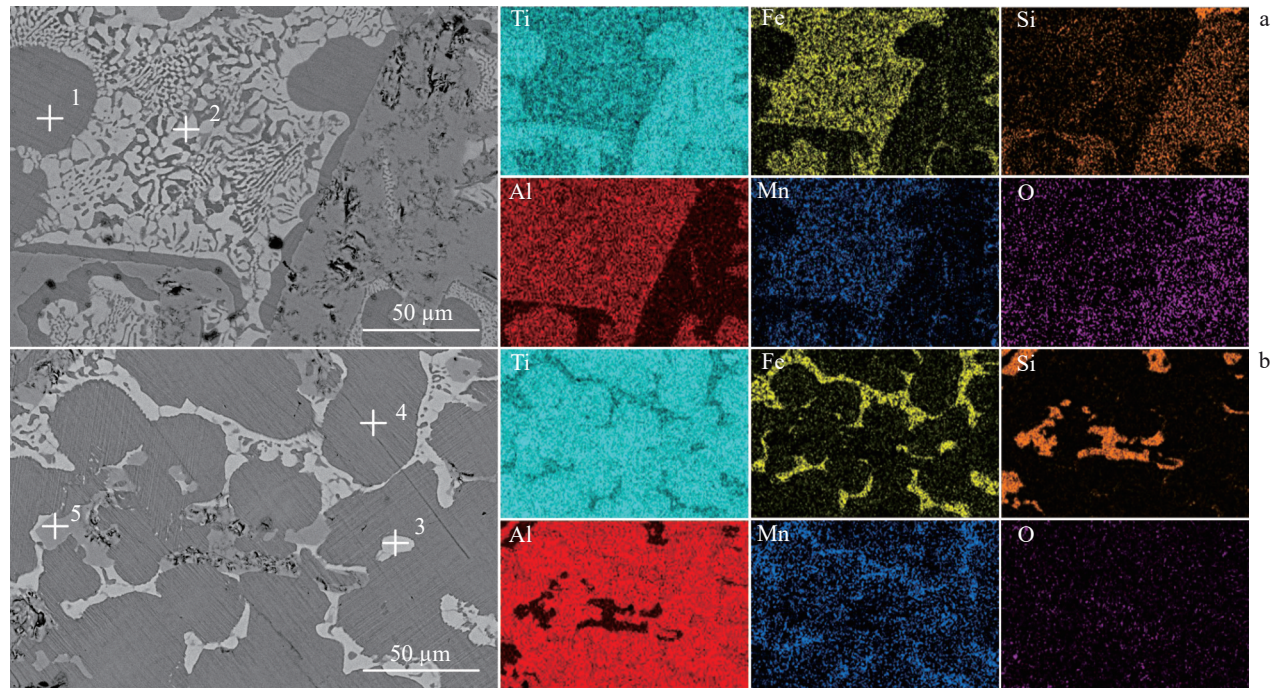


Fig.7 SEM-EDS test results of the titanium-based alloy prepared with aluminum ratios of 0.9 (a) and 1.1 (b)

Table 5 EDS results of regions 1–5 marked in Fig.7 (wt%)

Region	Ti	Al	Fe	Mn	Si	O
1	54.44	30.47	4.84	2.84	0.19	7.22
2	39.40	24.23	21.76	7.85	0.54	6.22
3	39.98	27.66	21.97	6.63	0.48	3.27
4	62.00	28.04	1.69	1.58	0.48	6.21
5	68.94	5.22	0.67	0.63	20.36	4.19

4 Conclusions

1) The thermodynamic calculation results of aluminothermic reduction of high-titanium slag show that the elements Ti and Al formed during the aluminothermic reduction of high-titanium slag form the TiAl intermetallic compound, and the elements Ti and Si form TiSi. The results of the kinetic analysis indicate that the activation energy of the TiO_2 -Al reaction is 274.4 kJ/mol, and the reaction order is 1.04.

2) With the increase in aluminum ratio, the main phase of the titanium-based alloy prepared by the aluminothermic reduction of high-titanium slag gradually changes from Ti_3Al to TiAl; at an aluminum ratio of 1.0, a titanium-based alloy with the main phase of Ti_3Al is successfully obtained.

3) The microstructure of the titanium-based alloy prepared by aluminothermic reduction of high-titanium slag can be divided into the titanium-based phase region, the Fe-rich phase region, and the Si-rich phase region. The basic phase region is mainly composed of titanium-based intermetallic compounds, with small amounts of dissolved Fe and Mn. The formation of the Fe-rich phase is mainly due to the substitution of elements Fe and Mn for the atomic positions of

Ti in Ti-based intermetallic compounds. The Si-rich phase region contains almost no elements Fe, Mn, and Ti, but it is rich in element Si, because Ti and Si can form stable TiSi compounds.

References

- 1 Zhen Y L, Zhang G H, Chou K C. *High Temperature Materials and Processes*[J], 2016, 35: 309
- 2 Zhu Xiaofang, Zheng Shili, Zhang Ying et al. *ACS Sustainable Chemistry & Engineering*[J], 2019, 7: 4821
- 3 Devaraj A, Joshi V V, Srivastava A et al. *Nature Communications*[J], 2016, 7: 11176
- 4 Wang H, Chao Q, Cui X Y, Chen Z B et al. *Materials Today*[J], 2022, 61: 11
- 5 Shu Shili, Qiu Feng, Tong Cunzhu et al. *Journal of Alloys and Compounds*[J], 2014, 617: 302
- 6 Dai Jingjie, Zhu Jiyun, Chen, Chuangzhong et al. *Journal of Alloys and Compounds*[J], 2016, 685: 784
- 7 Ding Wangwang, Tao Qiying, Liu Chang et al. *Nature Materials*[J], 2025, 24: 506
- 8 Song Tingting, Chen Zibin, Cui Xiangyuan et al. *Nature*[J], 2023, 618: 63
- 9 Fang Z Z, Paramore J D, Sun P et al. *International Materials Reviews*[J], 2018, 63: 407
- 10 Luo A A, Sachdev A K, Apelian D. *Journal of Materials Processing Technology*[J], 2022, 306: 117606
- 11 Lei Yun, Sun Luen, Ma Wenhui et al. *Journal of Alloys and Compounds*[J], 2018, 769: 983
- 12 Zhang Yakun, Lei Yun, Ma Wenhui et al. *Chemical Engineering*

- Journal*[J], 2022, 430: 132916
- 13 Lee J H, Nersisyan H, Huynh T et al. *Metallurgical and Materials Transactions B*[J], 2022, 53: 3147
- 14 Piao Rongxun, Yang Shaoli, Ma Lan et al. *Metals and Materials International*[J], 2020, 26: 130
- 15 Song Yulai, Dou Zhihe, Liu Yan et al. *Journal of Materials Engineering and Performance*[J], 2024, 33: 660
- 16 Han Yongchao, Dou Zhihe, Yang Zhanning et al. *Metallurgical and Materials Transactions B*[J], 2024, 55: 2347
- 17 Song Yulai, Dou Zhihe, Cheng Chu et al. *Journal of Wuhan University of Technology (Materials Science Edition)* [J], 2023, 38: 652(in Chinese)
- 18 Yang Jinzhong, Wang Yaowu, Peng Jianping et al. *Materials Today Communications*[J], 2022, 30: 102995
- 19 Zhang Yifan, Hu Xianwei, Liu Fengguo et al. *Journal of Alloys and Compounds*[J], 2023, 945: 169252
- 20 Chen Liyu, Yang Jiaxin, Yang Youjian et al. *Materials Today Communications*[J], 2022, 31: 103714

高钛渣自蔓延铝热还原制备钛基合金

谢 伟^{1,2}, 豆志河^{1,2}, 房 帅^{1,2}, 李丙奇^{1,2}, 张延安^{1,2}

(1. 东北大学 冶金学院, 辽宁 沈阳 110819)

(2. 多金属共生矿生态冶金教育部重点实验室, 辽宁 沈阳 110819)

摘 要: 研究了不同配铝比对高钛渣铝热还原制备钛基合金的影响。采用高钛渣、铝粉、 KClO_3 和 CaO 为原料, 通过自蔓延铝热还原法制备出钛基合金。对高钛渣铝热还原过程的热力学和动力学进行了计算。结果显示, 高钛渣可通过铝热还原制备钛基合金, 其中主要反应为 Al 还原 TiO_2 , 该反应活化能为 274.4 kJ/mol , 反应级数为 1.04 。随着配铝比的增加, 钛基合金中 Ti 元素的质量分数逐渐降低, Al 元素的质量分数逐渐上升, 同时钛基合金中存在少量 Fe 、 Mn 和 Si 等合金元素。物相分析显示, 在低铝配比条件下, 主要物相为 Ti_3Al ; 而在高铝配比条件下, 主要物相转变为 TiAl 。化学成分分析结果显示, 在配铝量为 1.0 的实验条件下, 制备出的钛基合金成分为 $51.6\text{wt}\% \text{ Ti}$ 、 $40.6\text{wt}\% \text{ Al}$ 、 $7.6\text{wt}\% \text{ Fe}$ 、 $3.4\text{wt}\% \text{ Mn}$ 和 $1.3\text{wt}\% \text{ Si}$ 。微观形貌分析表明, 所制备的钛合金由基体相区、富铁相区和富硅相区构成。本研究为高钛渣铝热还原制备钛基合金的高值化利用提供了新的技术路径。

关键词: 高钛渣; 铝热还原; 配铝比; 钛基合金

作者简介: 谢 伟, 男, 1998年生, 博士生, 东北大学冶金学院, 辽宁 沈阳 110819, E-mail: 1135256214@qq.com