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Preparation of titanium-based alloy by self-propagating aluminothermic reduction of high titanium slag

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Abstract: In this paper, the effects of different aluminum ratios on the preparation of titanium-based alloys by aluminothermic reduction of high titanium slag were studied. Titanium-based alloys were successfully 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 process of high titanium slag were calculated. The results show that high titanium slag can be used to prepare titanium-based alloys by 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 of the aluminum ratio, the mass fraction of Ti element in the titanium-based alloy gradually decreases, and the mass fraction of Al element gradually increases. At the same time, there are a small amount of alloying elements such as Fe, Mn and Si in the titanium-based alloy. Phase analysis shows that under the condition of low aluminum ratio, the main phase is Ti_3Al, under the condition of high aluminum ratio, the main phase is transformed into TiAl. The results of chemical composition analysis showed that the composition of the prepared titanium-based alloy was 51.6 wt.% Ti, 40.6 wt.% Al, 7.6 wt.% Fe, 3.4 wt.% Mn and 1.3 wt.% Si under the experimental conditions of 1.0 aluminum ratio. The microstructure analysis shows that the prepared titanium alloy is composed of base phase region, iron-rich phase region and silicon-rich phase region. This study provides a new technical path for the high value utilization of high titanium slag.

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

China is rich in titanium resources, accounting for 48% of the world's titanium reserves, most of which exist in the form of vanadium-titanium magnetite[1]. Iron-vanadium alloy and high titanium slag can be produced by carbothermic reduction of vanadium-titanium magnetite in electric furnace. At present, the main utilization methods of high titanium slag are sulfuric acid method and chlorination method to prepare titanium dioxide, but there are problems of high pollution and high energy consumption, and the high value utilization of high titanium slag has not been realized[2]. The content of TiO_2 in high titanium slag can reach about 80%, which can be used as a high-quality titanium-containing raw material to prepare titanium-based alloy by aluminothermic reduction method. During the aluminothermic reduction process, a small amount of iron oxides, manganese oxides and silicon oxides in the high titanium slag will be reduced to metals and enter the titanium-based alloy. At the same time, the equilibrium constant of the reaction between Al and TiO_2 is small, so 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 most effective α phase strengthening element, which can effectively improve the strength and oxidation resistance of the alloy[3,4]. Fe and Mn are β stable elements, which can refine grains and promote precipitation strengthening, and significantly improve the yield strength and tensile strength of titanium alloys[5]. Si element can produce dispersion strengthening effect and effectively improve the heat resistance and thermal strength of the alloy[6]. At present, the traditional methods for preparing titanium-based alloys mainly

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include sintering method, melting method and additive manufacturing method[7–10]. However, these processes all use metal titanium as raw material, resulting in high cost. Therefore, it is urgent to develop a new low-cost titanium-based alloy preparation technology. If high titanium slag is used as raw material and aluminum powder is used as reducing agent to directly prepare titanium-based alloy, the process of preparing metal titanium by Kroll method with high energy consumption and high pollution can be bypassed, and the production cost can be greatly reduced. For this reason, many researchers have carried out related research work. Lei et al.[11] prepared Ti-Al-Si master alloy by aluminothermic reduction of titanium-containing blast furnace slag, and combined with electromagnetic directional solidification to efficiently separate silicon elements to obtain titanium aluminide based alloys. Zhang et al.[12] used waste SCR catalyst, titanium-bearing blast furnace slag and waste aluminum scraps as raw materials to prepare $TiSi_3$-$TiAl_3$ alloy precursor by aluminothermic reduction method, and then separated Ti-Si-Al melt by electromagnetic directional solidification method to successfully prepare $TiSi_3$ and $TiSi_3$-$TiAl_3$ 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°C~2000°C, and the slag floated up by igniting the mixture of TiO_2-$KClO_4$-Al(Mg)-CaF_2. TiO_2 was successfully reduced to Ti-rich ingots by optimizing Al/Mg ratio, Al particle size and CaF_2 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 $TiAl_2$, which also contains $TiSi_3$, TiAl and other intermetallic compounds. Song et al.[15] prepared TiAl alloy by reducing TiO_2 with 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 systematically 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, the existing research mostly relies on external heating to achieve aluminothermic reduction reaction. In this study, titanium-based alloys were prepared by self-propagating aluminothermic reduction method, which has the advantages of high reaction efficiency and short process flow. There is still a lack of in-depth research on the reaction mechanism, product phase and microstructure of titanium-based alloys prepared by aluminothermic reduction of high-titanium slag. In this paper, a new method for the direct preparation of titanium-based alloys by aluminothermic reduction using high titanium slag as raw material is proposed. This method has the advantages of short process, simple operation and low cost. It not only realizes the high value utilization of high titanium slag, but also effectively solves the problems of high cost and long process in the preparation of traditional titanium-based alloys.

1 Experiment

1.1 Materials

High titanium slag (average particle size 2.5 μm, produced by Inner Mongolia Yu Xiao Meng Da Titanium Industry Co., Ltd.) was used as raw material, and its chemical composition was determined by inductively coupled plasma spectrometer. The results are shown in Table 1. Al powder (purity⩾99.5%, average particle size 2.5 μm, produced by CITIC Jinzhou Ferroalloy Co., Ltd.) was used as reducing agent. $KClO_3$ (purity⩾99.6%, produced by Sinopharm Chemical Reagent Co., Ltd.) 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: 100~200 mesh, produced by XILONG SCIENTIFIC Co., Ltd.) was used as ignition agent.

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

Composition	TiO_2	Fe_2O_3	Al_2O_3	SiO_2	MnO_2
High titanium slag	87.9	5.79	2.05	1.71	2.51

1.2 Experimental method

The high titanium slag, $KClO_3$ and CaO were dried at 150°C for at least 12 hours, weighed according to the ratio in Table 2, and then mixed in a mixer for 30 minutes. The mixture was loaded into a self-made graphite reactor, and an appropriate amount of magnesium powder was added to the surface of the material as an ignition agent and ignited to initiate the reaction. After the reaction, it was cooled to room temperature by natural cooling. The titanium-based alloy ingot and slag were separated and used for subsequent detection and analysis.

Table 2 Mass of high titanium slag, Al powder, $KClO_3$ 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

1.3 Analysis and characterization

The phase of titanium aluminum alloy and reducing slag was analyzed by X-ray diffractometer (Bruker D8, copper target, Germany). The microstructure of titanium aluminum alloy was analyzed by scanning electron microscope equipped with energy dispersive spectrometer (Hitachi SU3800, Japan). The chemical composition of titanium-aluminum alloy was analyzed by inductively coupled plasma spectrometer (PE Avio500, America). The differential thermal analysis of Al-TiO_2 was carried out by high temperature synchronous thermal analyzer

(Nanjing Huicheng STA-1550, China).

2 Results and Discussion

2.1 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:

$$4Al + 3TiO_2 = 3Ti + 2Al_2O_3 \tag{1}$$

$$2Al + Fe_2O_3 = 2Fe + Al_2O_3 \tag{2}$$

$$4Al + 3MnO_2 = 3Mn + 2Al_2O_3 \tag{3}$$

$$4Al + 3SiO_2 = 3Si + 2Al_2O_3 \tag{4}$$

$$3Ti + Al = Ti_3Al \tag{5}$$

$$Ti + Al = TiAl \tag{6}$$

$$Ti + 2Al = TiAl_2 \tag{7}$$

$$Ti + 3Al = TiAl_3 \tag{8}$$

$$Ti + Fe = TiFe \tag{9}$$

$$Ti + 2Fe = TiFe_2 \tag{10}$$

$$5Ti + 3Si = Ti_5Si_3 \tag{11}$$

$$Ti + Si = TiSi \tag{12}$$

$$Ti + 2Si = TiSi_2 \tag{13}$$

$$3Fe + Al = Fe_3Al \tag{14}$$

$$Fe + Al = FeAl \tag{15}$$

$$Fe + 2Al = FeAl_2 \tag{16}$$

$$2Fe + 5Al = Fe_2Al_5 \tag{17}$$

$$Fe + 3Al = FeAl_3 \tag{18}$$

$$Fe + 2Si = TiSi_2 \tag{19}$$

$$Fe + Si = TiSi \tag{20}$$

$$5Fe + 3Si = Fe_5Si_3 \tag{21}$$

$$3Mn + Si = Mn_3Si \tag{22}$$

$$5Mn + 3Si = Mn_5Si_3 \tag{23}$$

$$Mn + Si = MnSi \tag{24}$$

The melt produced by the reaction of the composition of high titanium slag and the ratio of raw materials in Table 1 and Table 2 is taken as the calculation object. When the reaction reaches equilibrium, the formation reaction equation, standard Gibbs free energy and mass action concentration of each structural unit in the melt are shown in Table 3. The $n_i(i = 1, 2, \cdots, 33)$ 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 Formula 25.

$$\sum n_i = n_1 + n_2 + \cdots + n_{33} \tag{25}$$

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 formul 26. $K_i(i = 8, 9, \cdots, 33)$ 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 Formula 27.

$$N_i = \frac{n_i}{\sum n_i} \tag{26}$$

$$\Delta G_i^{\theta} = \text{-RTln}(K_i) \tag{27}$$

According to the definition of the mass action concentration of each structural unit in the melt, the Formulas 28~34 can be obtained.

$$(N_1 + N_8 + 3N_{15} + N_{16} + N_{17} + N_{18} + N_{19} + 5N_{21} + N_{22} + N_{23})\sum n_i = n_{Ti} \tag{27}$$

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

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

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

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

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

$$(N_7 + 2N_8 + 3N_9 + 3N_{10} + 2N_{11} + 2N_{12} + N_{13})\sum n_i = n_O \tag{34}$$

Due to the sum of the mass action concentrations of each structural unit in the melt is 1, Formula 35 can be obtained:

$$N_1 + N_2 + \cdots + N_{33} = 1 \tag{35}$$

According to the relationship between the mass concentration and the equilibrium constant in Formulas 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 is the thermodynamic model analysis results of the mass action concentration of Al on the preparation of titanium aluminum alloy by aluminothermic reduction of high titanium slag at 1800°C. It can be seen from Fig.1 that the content of TiAl intermetallic compounds in titanium aluminum alloy increases with the increase of aluminum ratio. The reduction of TiO_2 by Al is a step-by-step reduction process, and the reaction path is: $TiO_2 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO \rightarrow Ti$, in which the reduction step of TiO to Ti is the most difficult. During the whole reduction process, TiO_2 cannot be completely reduced to Ti by Al. Therefore, even under the condition of low aluminum ratio, there is still residual metal Al in the titanium-based alloy that 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. Due to the reaction between Ti and Si has a low Gibbs free energy, they can form a stable TiSi phase and exist in the titanium-based alloy.

Table 3 The formation reaction equation, reaction standard Gibbs free energy and mass action concentration of each structural unit.

Structural Unites	Reactions	ΔG^{θ}(J/mol)	*Ni*
[Ti]	-	-	N_1
[Al]	-	-	N_2
[Fe]	-	-	N_3
[Mn]	-	-	N_4
[Si]	-	-	N_5
[Ca]	-	-	N_6
[O]	-	-	N_7
(TiO_2)	$[Ti]+2[O]=[TiO_2]$	$-1{,}413{,}710+293.35\cdot T$	$N_8=K_8N_1N_7^2$
(Al_2O_3)	$2[Al]+3[O]=(Al_2O_3)$	$-1{,}202{,}000+386.00\cdot T$	$N_9=K_9N_2^2N_7^3$
(Fe_2O_3)	$2[Fe]+3[O]=(Fe_2O_3)$	$-1{,}599{,}740+459.82\cdot T$	$N_{10}=K_{10}N_3^2N_7^3$
(MnO_2)	$[Mn]+2[O]=(MnO_2)$	$-532{,}782+118.93\cdot T$	$N_{11}=K_{11}N_4N_7^2$
(SiO_2)	$[Si]+2[O]=(SiO_2)$	$-1{,}447{,}262+326.41\cdot T$	$N_{12}=K_{12}N_5N_7^2$
(CaO)	$[Ca]+[O]=(CaO)$	$-1{,}287{,}755+225.48\cdot T$	$N_{13}=K_{13}N_6N_7$
$[Ti_3Al]$	$3[Ti]+[Al]=[Ti_3Al]$	$-29{,}633+6.71\cdot T$	$N_{14}=K_{14}N_1^3N_2$
[TiAl]	$[Ti]+[Al]=[TiAl]$	$-37{,}455+16.79\cdot T$	$N_{15}=K_{15}N_1N_2$
$[TiAl_2]$	$[Ti]+2[Al]=[TiAl_2]$	$-43{,}858+11.02\cdot T$	$N_{16}=K_{16}N_1N_2^2$
$[TiAl_3]$	$[Ti]+3[Al]=[TiAl_3]$	$-40{,}349+10.36\cdot T$	$N_{17}=K_{17}N_1N_2^3$
[TiFe]	$Ti+Fe=[TiFe]$	$-62{,}704+25.12\cdot T$	$N_{18}=K_{18}N_1N_3$
$[TiFe_2]$	$[Ti]+2[Fe]=[TiFe_2]$	$-162{,}397+63.73\cdot T$	$N_{19}=K_{19}N_1N_3^2$
$[Ti_5Si_3]$	$5[Ti]+3[Si]=[Ti_5Si_3]$	$-775{,}050+140.62\cdot T$	$N_{20}=K_{20}N_1^5N_5^3$
[TiSi]	$[Ti]+[Si]=[TiSi]$	$-188{,}195+35.61\cdot T$	$N_{21}=K_{21}N_1N_5$
$[TiSi_2]$	$[Ti]+2[Si]=[TiSi_2]$	$-274{,}638+68.47\cdot T$	$N_{22}=K_{22}N_1N_5^2$
$[Fe_3Al]$	$3[Fe]+[Al]=[Fe_3Al]$	$-65{,}376+6.07\cdot T$	$N_{23}=K_{23}N_3^3N_2$
[FeAl]	$[Fe]+[Al]=[FeAl]$	$-17{,}743-14.75\cdot T$	$N_{24}=K_{24}N_3N_2$
$[FeAl_2]$	$[Fe]+2[Al]=[FeAl_2]$	$-87{,}945+14.70\cdot T$	$N_{25}=K_{25}N_3N_2^2$
$[Fe_2Al_5]$	$2[Fe]+5[Al]=[Fe_2Al_5]$	$-207{,}746+29.12\cdot T$	$N_{26}=K_{26}N_3^2N_2^5$
$[FeAl_3]$	$[Fe]+3[Al]=[FeAl_3]$	$-127{,}185+22.82\cdot T$	$N_{27}=K_{27}N_3N_2^3$
$[FeSi_2]$	$[Fe]+2[Si]=[FeSi_2]$	$-196{,}358+83.99\cdot T$	$N_{28}=K_{28}N_3N_5^2$
[FeSi]	$[Fe]+[Si]=[FeSi]$	$-73{,}695+2.17\cdot T$	$N_{29}=K_{29}N_3N_5$
$[Fe_5Si_3]$	$5[Fe]+3[Si]=[Fe_5Si_3]$	$-456{,}469+113.60\cdot T$	$N_{30}=K_{30}N_3^5N_5^3$
$[Mn_3Si]$	$3[Mn]+[Si]=[Mn_3Si]$	$-196{,}720+50.36\cdot T$	$N_{31}=K_{31}N_4^3N_5$
$[Mn_5Si_3]$	$5[Mn]+3[Si]=[Mn_5Si_3]$	$-333{,}341+40.50\cdot T$	$N_{32}=K_{32}N_4^5N_5^3$
[MnSi]	$[Mn]+[Si]=[MnSi]$	$-86{,}852+9.50\cdot T$	$N_{33}=K_{24}N_4N_5$

2.2 Kinetic analysis of preparation of titanium aluminum alloy by aluminothermic reduction of high titanium slag

Fig.2 is the DSC curve of Al-TiO_2 system. From Fig.2, it can be seen that the curve has the first peak at 638°C, which is the endothermic peak of Al melting. When the temperature rises to 955°C, the second peak appears, which is the exothermic peak of the reaction between Al(liquid) and TiO_2(solid). Kinetic parameters were calculated by analysis of the DSC curves using Freeman–Carroll method. The dynamic equation obtained by the simplified transformation is Formula 36. The data of the exothermic peak of Al-TiO_2 were analyzed, and $\Delta\lg\varDelta T/\Delta\lg S''$ - $\Delta\lg(1/T)/\Delta\lg S''$ curve was drawn, as shown in Fig.3. The slope is $-E/(2.303R)$, the intercept is n, E is the apparent activation energy of the reaction, and n is the order of the reaction[18–20]. According to the fitting equation in Fig.3, the apparent activation energy of the reaction of Al and TiO_2 is calculated to be $E = 274.4$ kJ/mol, and the reaction order $n = 1.04$.

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

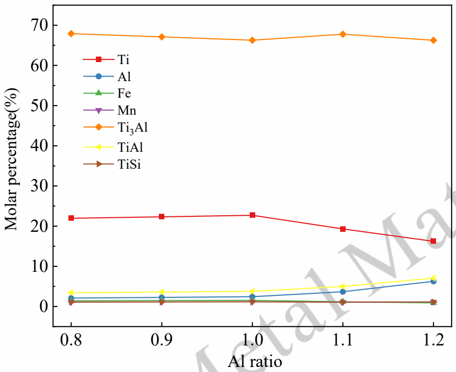

Fig.1 Calculation results of mass action concentration of aluminothermic reduction of high titanium slag

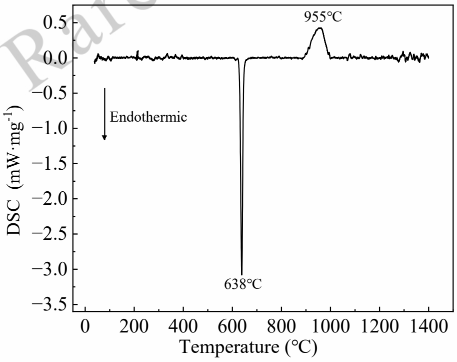

Fig.2 DSC analysis of Al-TiO_2 system

2.3 Effect of Aluminum ratio on the chemical composition of Ti-based alloy

Fig.4 shows the mass percentage of each element in the preparation of titanium-based alloy by aluminothermic reduction of high titanium slag in the range of aluminum ratio of 0.8~1.2. It can be seen from Fig.4 that the main components of the titanium-based alloy obtained by the aluminothermic reduction of high titanium slag are Ti and Al, which also contain a small amount of Fe, Mn and Si. With the increase of aluminum ratio, the mass percentage of Ti in the titanium-based alloy gradually decreases, the mass percentage of Al gradually increases, and the mass percentage of Fe, Mn and Si basically remains 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.

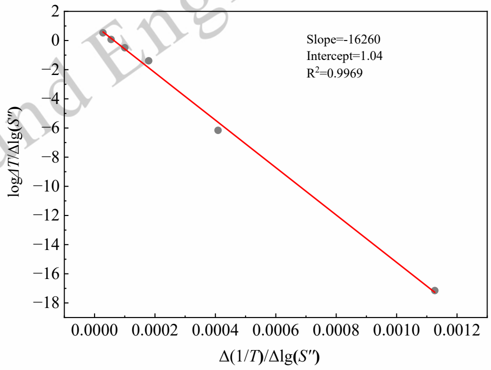

Fig.3 Freeman-Carroll analysis of Al-TiO_2 system

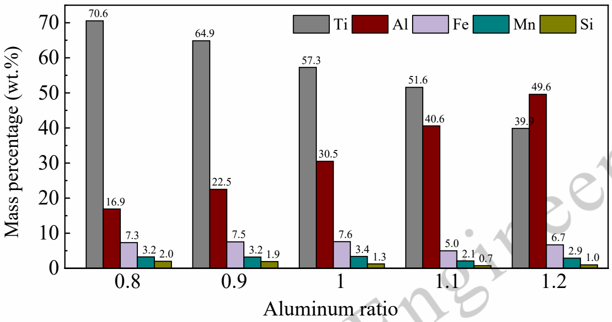

Fig.4 Mass percentage of each element in the preparation of titanium-based alloy by aluminothermic reduction of high titanium slag in the range of 0.8~1.2.

2.4 Effect of Aluminum ratio on the phase composition of titanium-based alloys

The titanium-based alloys prepared under the experimental conditions of aluminum ratio of 1.0 and 1.1 were analyzed by XRD, and 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 Ti_3Al phase, and the main phase of the titanium-based alloy prepared under the experimental conditions with an aluminum ratio of 1.1 is TiAl phase. According to the percentage of the amount of substance of the titanium-based alloy in Table 4, it can be found that as the aluminum ratio increases from 1.0 to 1.1, the alloy composition enters the stable region of the TiAl phase from the Ti_3Al phase stable region in the Ti-Al binary phase diagram. The main phase of the Ti-based alloy prepared under the condition of Al content of 1.0 is Ti_3Al phase, which is hexagonal crystal system, and the $Ti_3Al(002)$ diffraction peak is obviously enhanced compared with the standard peak. This is due to the existence of a small amount of TiAl phase in the titanium alloy prepared under the experimental condition of Al content of 1.0. The TiAl(101) diffraction peak is superimposed with the $Ti_3Al(002)$ diffraction peak, resulting in the enhancement of the $Ti_3Al(002)$ 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 $Ti_3Al(002)$ diffraction peak, indicating that the titanium-based alloy prepared at the aluminum ratio of 1.0 contains almost no Ti_3Al phase. Due to the existence of iron oxides, manganese oxides and silicon oxides in the high titanium slag, they will be reduced into the titanium-based alloy during the aluminothermic reduction process. From Fig.5, it can be found that the elements Fe and Mn in the titanium-based alloy form $Fe_{19}Mn_{10}$ phase, and the elements Ti and Si form TiSi phase.

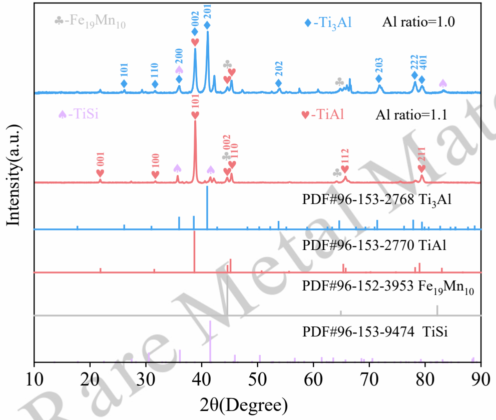

Fig.5 XRD patterns of titanium-based alloys prepared under experimental conditions with Aluminum ratio of 1.0 and 1.1.

2.5 Effect of aluminum ratio on 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 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 were also observed in the microstructure of titanium alloy, which was caused by the insufficient floating time of slag caused by rapid solidification during the self-propagating aluminothermic reaction. The inclusions can be eliminated by refining process. 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 Fe, Mn and Si elements produced by the reduction of high titanium slag in the base phase. Therefore, it is necessary to analyze the distribution characteristics of alloying elements in titanium-based alloys by EDS analysis to determine the composition distribution characteristics of each element in its microstructure.

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

Aluminum ratio	Ti	Al	Fe	Mn	Si	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

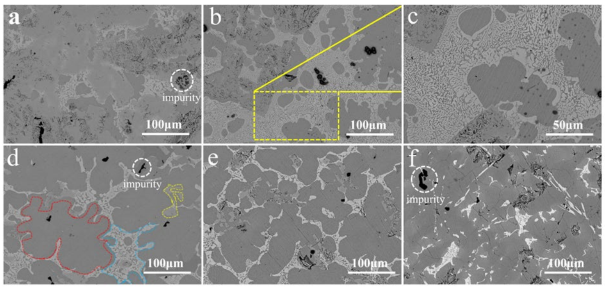

Fig.6 Microstructure of titanium alloy prepared by aluminothermic reduction of high titanium slag, a is the aluminum ratio to 0.8, b is the aluminum ratio to 0.9, c is the enlarged graph of the yellow region in b, d is the aluminum ratio to 1.0, e is the aluminum ratio to 1.1, f is the aluminum ratio to 1.2.

SEM-EDS analysis was performed on the titanium-based alloys prepared under the experimental conditions with Al content of 0.9 and 1.1. The results are shown in Fig.7a and Fig.7b, respectively. The quantitative analysis results of the key regions in the EDS test results are shown in Table 5. According to the distribution characteristics of each element in the titanium-based alloy, the microstructure of the titanium-based alloy can be divided into three regions, which are the basic phase region composed of titanium and aluminum, the iron-rich phase region rich in Fe and Mn, and the silicon-rich phase region rich in Si. The distribution of Fe element and Mn element is similar, and the content of Ti element decreases obviously in the area where Fe element and Mn element appear, which indicates that Ti element migrates back from the Fe-rich phase area during the cooling and solidification process. From the distribution characteristics of Si element in Fig.7b, it can be found that there is almost no Al element in the Si-rich region. This is because the Gibbs free energy of Ti and 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.

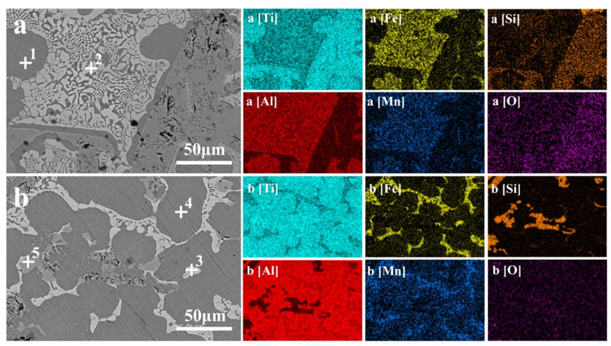

Fig.7 Distribution of elements in the microstructure of titanium-based alloy prepared by high titanium slag aluminothermic method, a and b are the SEM-EDS test results of titanium-based alloy prepared under the experimental conditions with aluminum ratio of 0.9 and 1.1, respectively.

Table 5 EDS results of titanium-based alloys synthesized with different aluminum ratios.

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

3 Conclusions

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

2) With the increase of 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; under the experimental conditions of aluminum ratio of 1.0, a titanium-based alloy with the main phase of Ti_3Al was successfully obtained.

3) The microstructure of titanium-based alloy prepared by aluminothermic reduction of high titanium slag can be divided into titanium-based phase region, Fe-rich phase region and Si-rich phase region. The basic phase region is mainly composed of titanium-based intermetallic compounds and a small amount of dissolved Fe and Mn elements. The formation of Fe-rich phase is mainly due to the substitution of Fe and Mn elements for the atomic position of Ti in Ti-based intermetallic compounds. The Si-rich phase region contains almost no Fe, Mn and Ti elements, but is rich in Si elements, which is due to the fact that Ti and Si can form stable TiSi compounds.

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高钛渣自蔓延铝热还原制备钛基合金

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摘　要：本文通过研究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，成功通过自蔓延铝热还原法制备出钛基合金。本文对高钛渣铝热还原过程的热力学和动力学进行了计算，分析结果显示，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 738.5 kJ/mol，反应级数为 5.49。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 wt% Ti、40.6 wt% Al、7.6 wt% Fe、3.4 wt% Mn 和 1.3 wt% 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

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