

Preparation of Multi-components TiAl Based Alloy by Aluminothermic Reduction of Acid Soluble Titanium Bearing Slag

Ma Lan¹, Piao Rongxun¹, Yang Shaoli¹, Li Binbin²

¹Panzhuhua University, Panzhuhua 617000, China; ²Xihua University, Chengdu 610039, China.

Abstract: The aluminothermic reduction of high Ti acid soluble Ti bearing slag (ASTS) was carried out to prepare the multi-components TiAl based alloy. In order to control and understand the preparation of TiAl alloy, the effects of the addition of Al and CaO, and temperature were discussed. By considering materials proportioning calculations it could successfully make TiAl alloy with sound slag-alloy separation. The recovery rates of most reduced elements are high, about 95% in the all experimental conditions. The Al addition can mainly affect the composition of TiAl alloy, while CaO addition influences the slag-metal separation by varying composition of slag system. Besides, the temperature of system can increase the recovery rate and distribution ratio for most reduced elements.

Key words: multi-components TiAl; aluminothermic reduction; acid soluble titanium bearing slag

The Panzhuhua and Xichang region in the southwest of china has abundant reserves of vanadium and titanium magnetite. The average contents of Fe and TiO₂ are about 30% and 9%, respectively. In the raw ore and the titanium mineralization is accounted for about 48% of the world's resources^[1]. The magnetite and ilmenite concentrates are the two main products after the beneficiation process, which can be further used to prepare the post productions of vanadium product, and steel billet from magnetite concentrate, the intermediate product of titanium slag, and final productions of titanium sponge and titanium white from ilmenite concentrate. Compared to the rich resource, the recovery rate of elements in the slag especially Ti is very poor and the consumption of Ti bearing slag is huge^[1]. In order to reduce the consumption of Ti resource, integrated utilization of Ti resource such as Ti bearing slag has become very significant.

Titanium-Aluminum based intermetallic alloys are widely used in high temperature structural applications in the aerospace or automotive industry. Due to their good corrosion resistance, low density (3.7~4.1 g/cm³),

promising mechanical properties at high temperatures, excellent high temperature oxidation and burn resistance^[2-6], they are applied particularly in aircrafts and aircraft engines. Depending on the compositions of Ti and Al alloys, the TiAl intermetallic alloys are mainly divided into Ti₃Al phase, γ -TiAl alloy and TiAl₃ phase, Among them TiAl phase (about 50 at% Al) is one of most attracting materials due to its high performance of the overall property^[4].

At present, the preparation techniques of TiAl alloys mainly include the powder metallurgy, ingot metallurgy, remelting process etc.^[6] However, all these techniques use pure titanium as raw material, so the preparation cost is very high. In order to reduce the costs alternative production processes are highly demanded. The aluminothermic process offers great potential to replace the traditional Kroll-Process in production of titanium and provides a least expensive production method for the direct synthesis of titanium alloys^[7]. Moreover, utilization of high Ti bearing slag as raw material in the production of TiAl intermetallic alloy may be one of the promising processes to produce the TiAl alloys with low cost^[1]. However, the

Received date: May 25, 2017

Foundation item: Sichuan Science and Technology Support Project (2013GZ0146); Panzhuhua (City) Science and Technology Plan Project (2004CY-G-5)

Corresponding author: Ma Lan, Associate Professor, Material Engineering Department, Panzhuhua University, Panzhuhua 617000, P. R. China, Tel: 0086-812-3372090, E-mail: hudie5656@163.com

Copyright © 2018, Northwest Institute for Nonferrous Metal Research. Published by Elsevier BV. All rights reserved.

preparation of TiAl alloy by the aluminothermic reduction process has the difficulties of slag-metal separation and impurity (oxide inclusion or O and C, etc.) removal, so this process needs the preparation of master alloy first and further refining process.

Previously, several processes of the preparation of TiAl alloy by the aluminothermic reduction technique with various Ti materials have been reported. Masafumi Maeda et al.^[8] studied the aluminothermic reduction of titanium oxide with CaO-CaF₂-Al₂O₃ slag at 1973 K and reported that overall reaction time is within 10 min., and for the TiAl intermetallic alloy which has 36wt% of aluminum, the equilibrium oxygen content was 1.5wt%. J. Haidar et al.^[9] studied the direct production of alloys based on titanium aluminides via two-step aluminothermic reduction of titanium tetrachloride(TiCl₄) and it was shown that the various TiAl intermetallic alloys could be produced including a large number of alloying additives. Also it was estimated that for large scale production, the production cost would be significantly lower than most existing technologies. Vitaly Babyuk et al.^[10] investigated the liquid phase aluminothermic reduction of ilmenite. They could produce in pilot experiments the ferrotitanium alloy with composition (wt%) of Fe-(18.8~48.5)Ti-(0.8~17.3)Al, and the average of yield ratio of Ti is 65wt%. Recently, Huang et al.^[11] studied the preparation of Ti-(30~40) Si-(4~15) Al alloy by aluminothermic reduction of TiO₂ bearing blast furnace slag (20wt%~25wt%TiO₂) and the effect of Al content on the distribution ratio and recovery rate were investigated. It was reported that the main phases of alloy identified by XRD were Ti₅Si₃, AlTi₃ and TiSi₂, and recovery rate of Ti reached up to 80% while that of Si reached 70%.

In our previous work^[11], the preparation of TiAl intermetallic alloy was studied by aluminothermic reduction of TiO₂ under air condition followed by refining in electric arc furnace. In this process, the master alloy of TiAl intermetallic phases was prepared by aluminothermic reduction of TiO₂ with SHS (self propagating high temperature synthesis) concept. The main phases of master alloy after aluminothermic reduction were TiAl₃ and TiAl. In addition to TiAl intermetallic phases, a trace amount of Ti₇Al₃Si₁₂ and oxide compounds were also observed and they could be removed in following smelting in electric arc furnace. Finally, it could come up with 79.5% of metallization rate^[11].

In summary, the preparation of Ti alloy by aluminothermic reduction technique was previously studied for the Ti materials of titanium white(TiO₂), ilmenite, titanium tetrachloride (TiCl₄) and Ti bearing BF-slag. However, no research was reported in the production of TiAl alloy using high Ti bearing acid soluble slag (ASTS) which is one of the main Ti resources in the vanadium

titanomagnetite process. Typically ASTS contains about 70wt% of TiO₂, 10wt% of FeO and 6wt% of SiO₂, so it is expected to contain alloying element of Fe and Si in the TiAl alloys after aluminothermic reduction. Recently, Yang et al.^[12] studied the effect of Fe on the microstructure and hardness of Ti-45Al-xFe (at%) alloy and it was shown from the results that increase of Fe even up to 9at% can increase the physical property of alloy by changing morphology of B2 intermetallic phase. The effect of alloying element of Fe in Ti-Al-Si system were also reported by Pavel et al.^[13], and it showed high hardness and low wear rate. It indicated that the similar system of Fe and Si containing TiAl alloys can be produced from ASTS which contains Fe and Si. Thus in the present study, the preparation of TiAl intermetallic alloy was studied by aluminothermic reduction using acid soluble Ti bearing slag. In order to better understand and control the preparation of TiAl from aluminothermic reduction of ASTS, the effect of Al, CaO and temperature are investigated.

1 Theoretical Background

1.1 Reactions of aluminothermic reduction of high TiO₂ bearing slag

Since acid soluble titanium bearing slag (ASTS) has relatively high content of FeO and relatively low content of SiO₂ and MnO, aluminothermic reaction of slag should take into account all these oxide reduction. Based on the thermodynamic considerations, all reactions can occur in the order of Fe, Si, Mn, and Ti. Moreover, the standard free energy of all reactions are in the order of 10⁶ joule^[1], implying four types of reduction reactions are all easy to occur even in a low temperature range. Therefore, the compositions of alloy after reduction are expected to be Si, Fe, and Mn except for main species of Ti for the TiAl alloy.

1.2 Slag-alloy Separations

To produce TiAl alloy from the reduction reaction of Ti bearing slag, the slag-alloy separation should be taken into consideration. In general, slag-alloy separation can be considered as a process of droplet formation-growing-sedimentation-accumulation-separation, and this phenomena can be described by Stokes' law^[14]:

$$v_T = \frac{2gr^2}{9\eta}(\rho_m - \rho_s) \quad (1)$$

where, v_T , ρ_m , ρ_s , r , g , and η are velocity of liquid droplet of alloy (m/s), density of alloy (kg/m³), density of slag (kg/m³), radius of alloy (m), acceleration of gravity (m²/s), and dynamic viscosity of slag (Pa·s) respectively.

From the Eq.(1) it is known that in order to increase slag-alloy separation during reaction, the velocity of liquid alloy droplet should increase. This can be made by either increase of density difference between alloy and slag or decrease of slag viscosity at fixed g and r . However, from the previous investigations^[11] we found that the difference

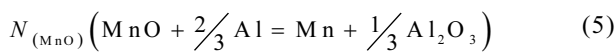
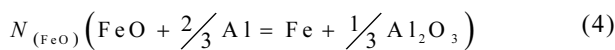
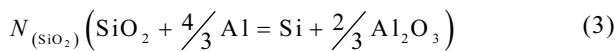
of density between TiAl alloy and Ti bearing slag is usually very small, so the slag-alloy separation could not be easily made. Thus another method by decreasing the slag viscosity may be the key to the slag-alloy separation. To obtain the best results of TiAl alloy production from aluminothermic reduction reaction, material proportioning should be carefully designed in which slag has low viscosity while compositions of alloy satisfy the target compositions of TiAl alloy.

2 Material Proportioning Calculation

2.1 Amount of Al reductant

In order to design optimum material proportioning, mass balance of aluminothermic reduction reactions was considered.

It is assumed that 1 mol of TiO₂ bearing slag contains $N_{(SiO_2)}$ mol of SiO₂, $N_{(FeO)}$ mol of FeO, and $N_{(MnO)}$ mol of MnO to be reduced. Then reduction reactions for relevant components can be written as follows:



By summing above four equations, it results in the following equation:

$$\begin{aligned} & \left[TiO_2 + N_{(FeO)}FeO + N_{(SiO_2)}SiO_2 + N_{(MnO)}MnO \right] + \\ & \left[\frac{2}{3} \left(2 + 2N_{(SiO_2)} + N_{(FeO)} + N_{(MnO)} \right) Al \right] \\ & = \left[Ti + N_{(SiO_2)}Si + N_{(FeO)}Fe + N_{(MnO)}Mn \right] + \\ & \frac{2}{3} \left[2 + 2N_{(SiO_2)} + N_{(FeO)} + N_{(MnO)} \right] Al_2O_3 \end{aligned} \quad (6)$$

With the assumption that CaO, MgO, and Al₂O₃ in the raw slag may not be reduced by Al, the overall equation of aluminothermic reactions can be written as follows:

$$\begin{aligned} & \left[TiO_2 + N_{(FeO)}FeO + N_{(SiO_2)}SiO_2 + N_{(MnO)}MnO \right] + \\ & \left[\frac{2}{3} \left(2 + 2N_{(SiO_2)} + N_{(FeO)} + N_{(MnO)} \right) Al \right] + \\ & \left[N_{(CaO)}CaO + N_{(MgO)}MgO + N_{(Al_2O_3)}Al_2O_3 \right] \\ & = \left[Ti + N_{(SiO_2)}Si + N_{(FeO)}Fe + N_{(MnO)}Mn \right] + \\ & \left[\frac{2}{3} \left(2 + 2N_{(SiO_2)} + N_{(FeO)} + N_{(MnO)} \right) Al_2O_3 \right] + \\ & \left[N_{(CaO)}CaO + N_{(MgO)}MgO + N_{(Al_2O_3)}Al_2O_3 \right] \end{aligned} \quad (7)$$

On the reactant side of Eq.(7), the first bracket term shows the amount of components reduced in the aluminothermic reaction, and the second bracket term stands for the amount of Al needed for reduction of slag; while on the product side of Eq.(7), the first bracket term stands for the components of alloy after reduction, the second bracket term is for the components of slag after reduction, and the third terms on both reactant and product sides represent the unreduced components in the slag.

Eventually, the total amount of Al needed for reducing slag can be expressed as:

$$W_{R-Al} = \frac{2}{3} \left(2 + 2N_{(SiO_2)} + N_{(FeO)} + N_{(MnO)} \right) M_{Al} \quad (8)$$

2.2 Alloy composition

In the present study, the target composition range of Al in TiAl alloys can be varied from 40 at% to 50 at%^[15,16]. To satisfy the target composition of Al, an excess amount of Al should be added in addition to Al amount used in reduction of slag. For the absolute amount of remaining components of the alloy after reduction can be obtained in product side of Eq.(7), then total amount of the alloy after reduction can be expressed as Eq.(9).

$$\begin{aligned} W_{Alloy} &= W_{Ti} + W_{Fe} + W_{Mn} + W_{Si} + W_{Al} \\ &= M_{Ti} + N_{(FeO)}M_{Fe} + N_{(MnO)}M_{Mn} + N_{(SiO_2)}M_{Si} + \\ & \quad \left(W_{Total-Al} - W_{R-Al} \right) \end{aligned} \quad (9)$$

Where W_{Alloy} , W_{Ti} , W_{Fe} , W_{Si} , W_{Al} , and $W_{Total-Al}$ are total mass (gram) of alloy, mass of Ti, Fe, Mn, Si, Al of alloy for 1mol of TiO₂ reduction and total mass of Al as raw material, respectively, and M_i is molecular weight of element i .

Eventually alloy composition can be obtained by considering relative portion of components in the alloy. It is noticed that if reduction rate for the elements of slag is below 100% the factor of reduction rate should be taken into account in the reaction.

2.3 Slag composition

At this stage, additional CaO should be considered as charge mixture of raw material in order to satisfy low viscosity of slag after reduction. With assumption of high reduction rate of each element of the slag, it is known that the main components of slag after reduction are CaO and Al₂O₃, implying the Ti-bearing slag system after reduction goes to CaO-Al₂O₃-MgO system. If the system has low MgO, the system will change to CaO-Al₂O₃ binary system, and then based on the phase diagram the composition range of slag with low melting point (or low viscosity) will be in the range of chemical composition of Al₂O₃ from 29.2 at% to 40 at%. Then the composition of the slag after reduction can be obtained from the second and the third bracket terms in product side of Eq.(7), and the total mass of the slag can be expressed as Eq.(10).

$$W_{\text{slag}} = W_{(\text{CaO})\text{int}} + W_{(\text{CaO})\text{flux}} + W_{(\text{MgO})\text{int}} + W_{(\text{Al}_2\text{O}_3)\text{int}} + W_{(\text{Al}_2\text{O}_3)\text{R}}$$

$$= \left[N_{(\text{CaO})} M_{(\text{CaO})} + W_{(\text{CaO})\text{flux}} + W_{(\text{CaO})} N_{(\text{MgO})} M_{(\text{MgO})} \right] + \left[\frac{2}{3} (2 + 2N_{(\text{SiO}_2)} + N_{(\text{FeO})} + N_{(\text{MnO})}) M_{\text{Al}_2\text{O}_3} + N_{\text{Al}_2\text{O}_3} \right] \quad (10)$$

Where W_{slag} , $W_{(\text{oxide})\text{int}}$, $W_{(\text{oxide})\text{R}}$, N_{oxide} and M_{oxide} are total mass(gram) of slag, mass of raw materials of oxide, mass of reduced oxide, number of mol of oxide, and molecular weight of oxide, respectively.

It is noticed that the above equation is for such a reaction that can be fully reduced. If the reduction rate is considered, the influence of reduction rate on the reaction should be taken into account.

3 Experiment

The chemical composition and XRD pattern of acid soluble titanium bearing slag (ASTS), supplied by Panzihua GuoTai Co., China, are shown in Table 1 and Fig.1, respectively. 50 g of ground ASTS was mixed with Al powder (99 wt%) and reagent grade of CaO (99.9 wt%). The mixture was put in an alumina crucible ($\Phi 50 \text{ mm} \times H 100 \text{ mm}$) which was again placed in a graphite crucible and heated in a preheated resistance furnace (200 mm \times 200 mm \times 200 mm). After smelting, the crucible assembly was taken out from the furnace and the sample was cooled in the ambient atmosphere. The crucible assembly was broken after weighing it and the alloy plus slag were carefully separated. Then, the alloy sample was weighed to further analyze the slag-alloy separation efficiency or metallization rate. The chemical composition of the slag was quantitatively analyzed by X-ray fluorescence, while the composition of the alloy were analyzed by chemical analysis and Inductively Coupled Plasma (ICP) spectrometer depending on the alloy elements. Phases of the slag and the alloy were identified by X-ray diffractometer(XRD) on a PANalytical X’Pert Powder.

In order to study the effect of materials constituents (mainly ©Al and CaO) and reaction condition (temperature) on the production of TiAl alloy, three sets of experiments were designed based on the material proportioning calculations shown in section 2 and the details of experimental conditions are shown in Table 2.

4 Results and Discussion

The specimens in the crucible were clearly separated into two phases in the all experiments conditions as shown in Fig.2. In Fig.2, the sample No.0 is selected to be a base sample to compare other samples at each experimental condition. The mass of the slag and the alloy after separation were weighted and the results are shown in Fig.3

Table 1 Chemical composition of acid soluble titanium bearing slag (wt%)

TiO ₂	FeO	CaO	MgO	SiO ₂	Al ₂ O ₃	MnO
72.65	9.18	1.97	5.64	6.73	2.62	1.22

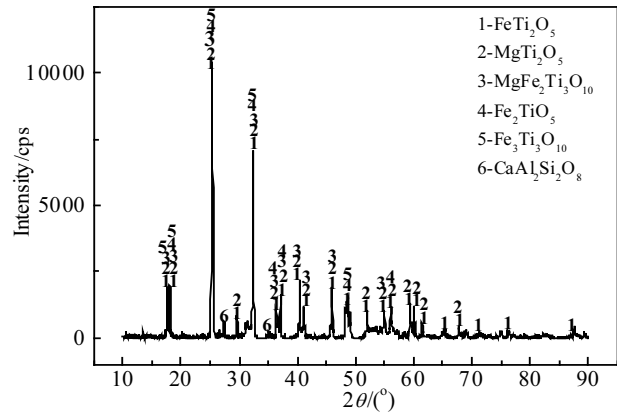


Fig.1 XRD pattern of acid soluble titanium bearing slag (ASTS)

Table 2 Experimental conditions in this study

No.	Al addition coefficient*	CaO addition coefficient**	Temperature/ °C	Heating time /min
0	0.69	0.85	1550	30
1-1	0.74	0.85	1550	30
1-2	0.656	0.85	1550	30
2-1	0.69	0.936	1550	30
2-2	0.69	0.766	1550	30
2-3	0.69	0.68	1550	30
3-1	0.69	0.85	1450	30
3-2	0.69	0.85	1500	30

*,** Material addition coefficient is the mass ratio of Al or CaO to mass of ASTS which is 50 g in all experimental conditions

under different experimental conditions. In order to see the effects of materials proportioning and experimental conditions on the product of reduction reactions, the effects of Al, CaO and temperature on the phase identification, composition change of the alloy and the slag, distribution of elements, recovery rate of elements, and reducibility (or reduction rate) were extensively investigated. Also calculations of material proportioning were conducted by assuming that reduction rate of TiO₂, SiO₂, FeO and MnO were 100% within all reactions.

4.1 Effect of Al

Addition of Al into the reduction system can affect not only the reducing reaction, but also the slag-alloy separation by varying viscosities of the slag during reduction.

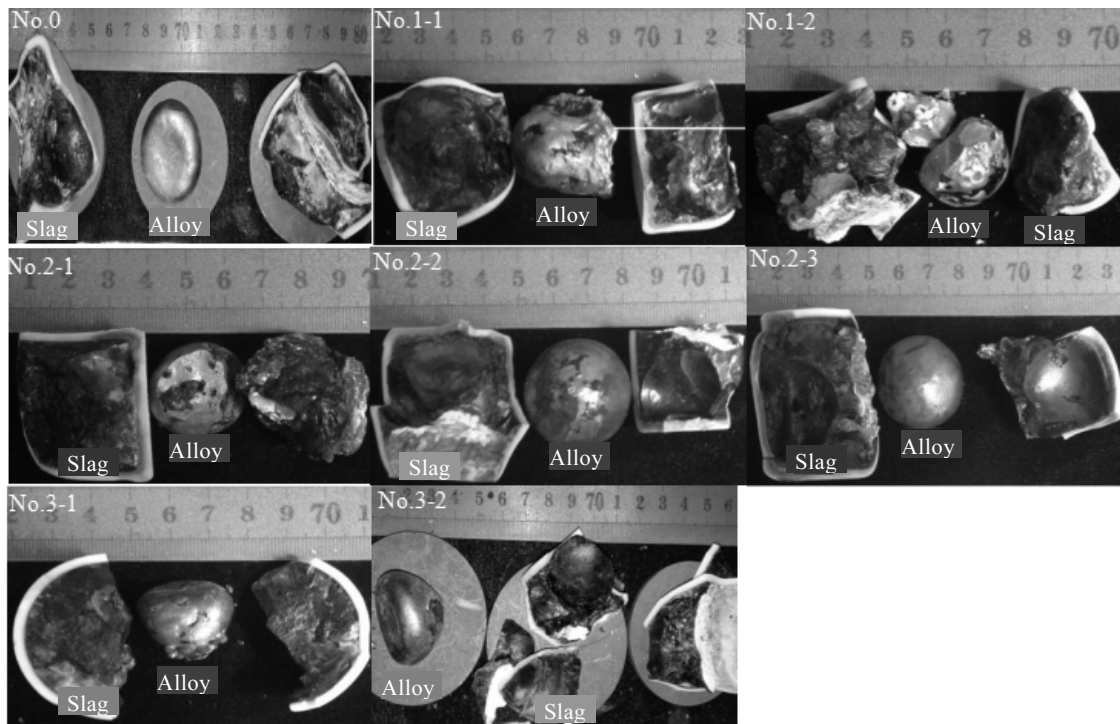


Fig.2 Macro-appearance of the alloy and the slag after reduction

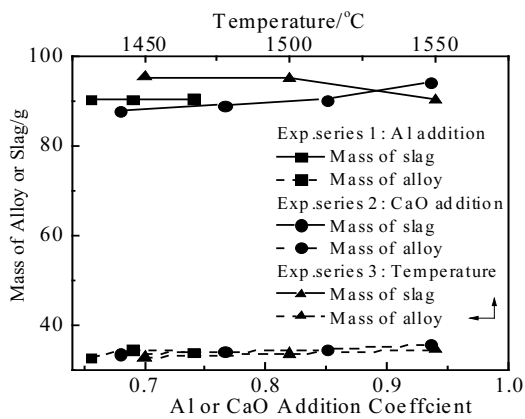


Fig.3 Mass evolution of the slag and the alloy after reducing reaction with different material additions

As can be seen in the No.1 specimen series together with the base sample No.0 in Fig.2, the alloy looks grey, while the slag mostly looks black and some part is yellow. Typical XRD pattern of slag is shown in Fig.4. The main phases of the slag are mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ or $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$), calcium aluminum oxide (CaAl_2O_4), and minor Mg-Ti-O and Ca-Fe-Si-O phases. The mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ or $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$) may be formed in a kind of wet atmosphere^[17]

of air cooling in the present study. It is noticed that the composition of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ is between CaAl_2O_4 and $\text{Ca}_3\text{Al}_2\text{O}_6$, and the formation of CaAl_2O_4 and $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phases is well consistent with the results from original design of material proportioning calculation.

Since most of these complex phases are stable at high temperatures, which causes the increase of slag viscosity, the separation is more difficult. Meanwhile, the existence of Ti other than Ca and Al indicates that slag is not fully reduced.

The main phases of the alloy after reduction are mostly titanium aluminide ($\text{Al}_3\text{Ti}_{0.75}\text{Fe}_{0.25}$ and TiAl), titanium silicide (Ti_5Si_3), and TiAl_3 , AlTi_2 , and Ti_5Si_3 phases present in all samples as shown in Fig.5. With increase of Al contents, the intermetallic alloy of TiAl phase disappears while $\text{Al}_3\text{Ti}_{0.75}\text{Fe}_{0.25}$ phase newly forms. It may be because increase of Al in the alloy can transform the phase to the high Al content intermetallic phase. Besides, since the radii of Ti and Fe are similar, Ti and Fe can possibly make solid solution^[12]. SiO_2 , Al_2O_3 , and Ti_2O_3 phases, considered as the inclusions in the alloy, are also identified, implying slag-alloy separation is not fully completed.

The composition of the alloy and the slag were measured after separation as shown in Fig.6 and Fig.7. Fig.6 shows that with the increase of Al content in the reducing reaction the mass fraction of Ti in the alloy is decreased while the content of Fe, Si and Mn are unchanged. This means

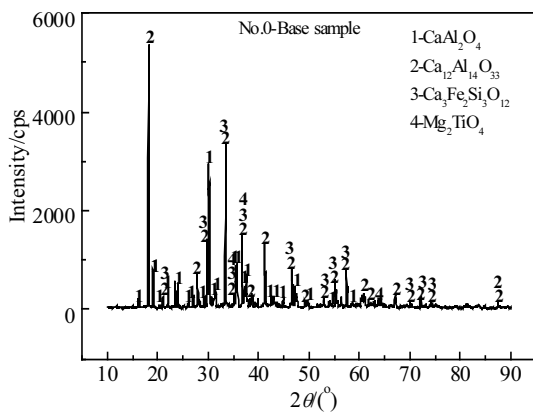


Fig.4 XRD pattern of slag of sample No.0 after reduction

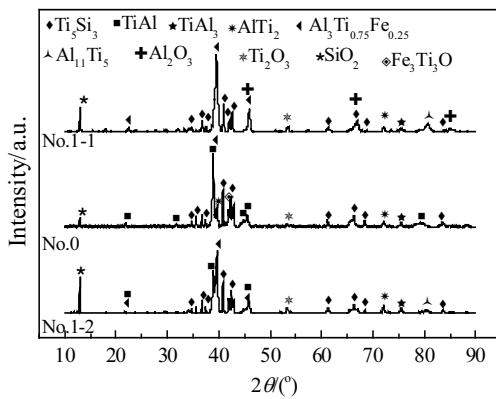


Fig.5 XRD patterns of the alloys reduced by different aluminum additions

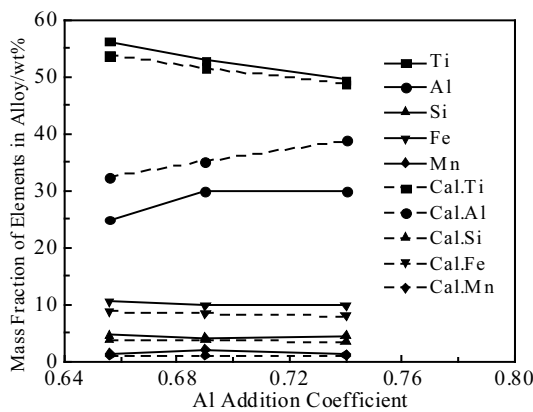


Fig.6 Chemical composition of the alloy after reducing reaction

in the present experimental condition that interaction between Ti and Al is preferentially stronger to form more titanium aluminide phases than other forms of the alloy such as titanium silicide. The composition obtained from material proportioning calculation shows a lower value of Ti and Fe as compared to experimental results. It is due to the lower efficiency of Al utilization as in Fig.6 shows that

the Al content is much lower than that after calculation.

From Fig.7, it is known that main components of the slag system after reducing reaction with different Al additions are CaO and Al₂O₃. With the increase of Al in the reaction, Al₂O₃ content is increased and it is also confirmed in XRD patterns of the alloy in Fig.6, while the CaO content is decreased due to mass balance. Although the main components of the slag vary in composition, it is known from the thermodynamic calculation by FACTSAGE that all slag systems in the present experimental temperature range are fully liquid phases, providing good condition for slag-alloy separation. The composition for FeO, SiO₂ and MnO after reduction is mostly unchanged and usually less than 1 wt%, implying reduction rate of these components is generally high.

The recovery rate of the elements can be calculated by Eq.(11)^[1]

$$r_i = \frac{W_{[i]} m_a}{W_{(i)} m_s} \times 100\% \quad (11)$$

where *i* represents the element, *W*_[*i*] and *W*_(*i*) are the mass fraction of element in alloy and slag, respectively; *m*_{*a*} and *m*_{*s*} are the mass of the alloy and slag after reducing reaction, respectively. The recovery rate of Ti, Si and Fe with Al addition is plotted in Fig.8. It shows the decrease tendency for Ti, Si, and Fe, while the calculated results are unchanged with Al. It is maybe because the Al addition causes a decrease of Ti and a slight change for other elements in the alloy as shown in Fig.6, while the changes of compositions for the Fe, Si and Ti elements in the slag are usually negligibly small with Al content as shown in Fig.7. The behavior of recovery of elements in the present study is opposite to the reported results by Huang et al.^[1], because the amount of Al in their work is only accounted for the amount needed for reduction of the slag which is shown as *W*_{R-Al} in Eq.(8), while the amount of Al in the present study is over added for alloying of Al fitted to the target composition of TiAl alloy.

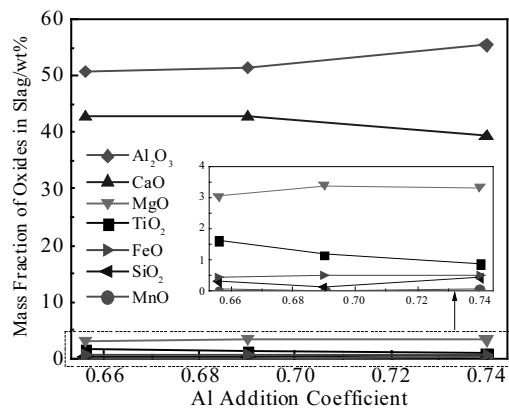


Fig.7 Chemical composition of the slag after reducing reaction

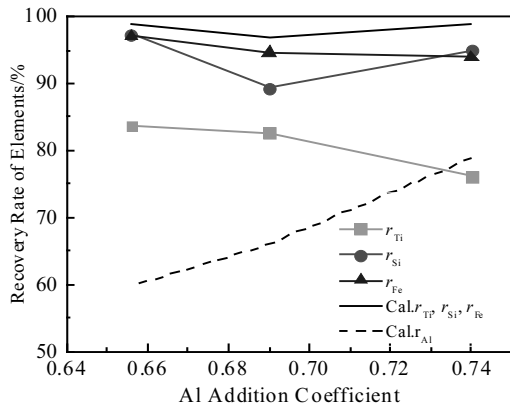


Fig.8 Recovery rate of elements after reduction

Distribution ratio of the metallic elements was defined as:

$$L_i = \frac{W_{[i]}}{W_{(io_x)}} \times 100\% \quad (12)$$

Where $W_{[i]}$ and $W_{(io_x)}$ are the mass fraction of the element i in the alloy and oxide in the slag, respectively. The distribution rate of Ti, Al, Si and Fe were investigated from experimental results together with the results based on materials proportioning calculations as shown in Fig.9. At this stage, the distribution rate of Mn element could not be estimated because the observed MnO content in the slag is negligibly small. The distribution rate of Ti is slightly increased with increasing Al while that of Si, Fe and Al are not changed, which can be understood by the change of Ti content in alloy and slag phases with Al addition as shown in Fig.6 and Fig.7. Although the Ti content in alloy is decreased during Al reduction as shown in Fig.6, the amount of TiO_2 in reduced slag becomes lower than 2% with the increase of Al content shown in Fig.7, and this would make slight increase of Ti distribution between the alloy and the slag. In comparison to calculations, the distribution rate of Ti, Si and Fe in the experimental observations shows two orders lower than the calculated one in which the 100% of reduction rate of each oxide component was assumed. Nevertheless, the distribution rates of all elements in the present study present quite large values, implying high reduction rate of reaction. Similar work has been reported previously by Huang et al^[1] in the work of preparation of Ti-Si-Al alloy by aluminothermic reduction of blast furnace slag. It was known from their results that the distribution rate of Ti and Fe were under 10 and 100, respectively. It was compared to the results from the present study, and it may be due to the large difference in composition of raw materials.

4.2 Effect of CaO

With change of CaO contents as shown in Fig.10, not much phase change was observed except for Ti_3O_5 formed

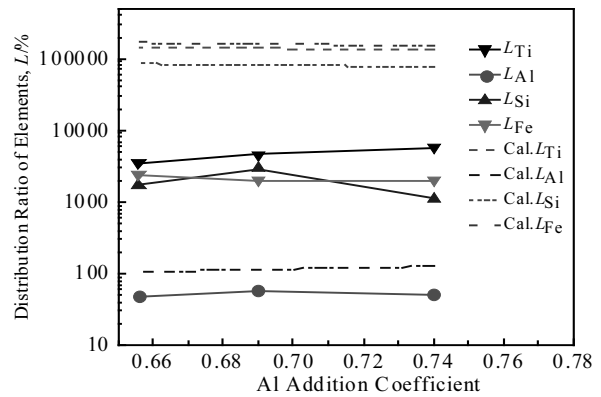


Fig.9 Distribution ratio of elements after reduction

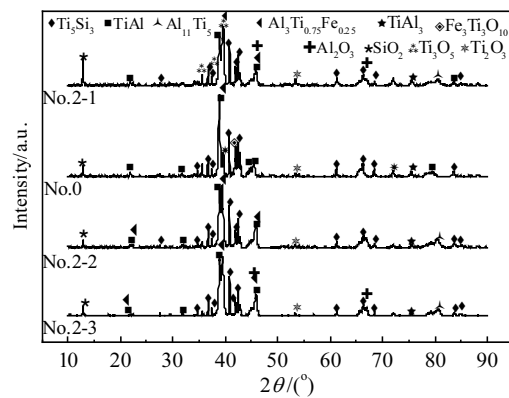


Fig.10 XRD patterns of the alloys reduced by different CaO additions

in the No.2-1 sample. The main phases of them are identified as TiAl, $Ti_{0.75}Fe_{0.25}Al_3$ and Ti_3Si_3 .

The chemical compositions of the slag with CaO addition were analyzed and the result is shown in Fig.11. It shows that with the CaO addition the mass fraction of CaO is increased and that of Al_2O_3 is decreased, while compositions of other oxide components remain very low and a constant level in the slag. Similar to the results shown in Fig.7, the reduction rate of MnO, FeO and SiO_2 generally shows high values and it can be able to reach the maximum reduction rate under the present experimental condition. Also MgO in the slag remains original composition, because it is not reduced by Al in the present study. Thus only the composition of Al_2O_3 is changed as CaO content in the slag is increased. Al_2O_3 content from the experimental observation is generally lower than results from the material proportioning calculations, probably due to the dissolution of Al_2O_3 from Al_2O_3 crucible during aluminothermic reduction reaction of the present study. Although the compositions of CaO and Al_2O_3 differ from

the calculated, the overall composition ratio between CaO and Al₂O₃ are still in the target composition range of liquid phase in the CaO-Al₂O₃ system.

Since the Al from the raw materials can be inevitably oxidized and dissolved into slag phase, the amount of Al in alloy as shown in Fig.12 presents a lower value compared to the calculated composition. It is noticed from Fig.12 that change of CaO in the slag does not affect the final composition of the alloy obviously. Compared with results discussed in Section 4.1, it implies that the CaO content can mainly contribute to the control of slag composition, while the composition of the alloy is mainly determined by the Al addition other than CaO. However, CaO change affects the recovery rate of elements in the alloy as shown in Fig.13, because of the high reduction rate of oxide components with small composition change of elements in the alloy. The change of recovery rates of Fe and Si is apparent and it shows an increase tendency for Fe and decrease tendency for Si. This phenomenon could be understood by considering interaction between CaO and SiO₂, and CaO and Al₂O₃. Since there exists strong attractive interaction among CaO-SiO₂, and CaO-Al₂O₃ pairs in the liquid phase^[18], increase of CaO in the slag can decrease Al₂O₃ by forming stable calcium aluminide and calcium silicate pairs or compounds. It is further confirmed by the XRD results as shown in Fig.4.

In this series of experiments, relatively high order of distributions of elements is also observed as shown in Fig.14. It seems the effect of CaO addition is not obvious on the distribution of elements.

4.3 Effect of temperature

With changing the temperature shown in Fig.15, the phases of the alloy are mainly Ti₅Si₃, TiAl, and Ti_{0.75}Fe_{0.25}Al₃. It is noticed that the Al₂O₃ phase appears at low temperature and this is probably because the Al₂O₃ inclusion formed during reducing reaction may not dissolve into the slag at low temperatures.

Compositional change of the slag and the alloy at different temperatures are shown in Fig.16 and Fig.17. With the increase of temperature, the content of Al₂O₃ is increased. This increase of Al₂O₃ is consistent with Al increase in the alloy as they can be thermodynamically stable at high temperature. It generally shows an increase tendency for the recovery rate and distribution rate for most reduced elements as shown in Fig.18 and Fig.19.

4.4 Reducibility of slag

Based on the reduction efficiency of aluminothermic reaction, the reducibility of the slag (or reduction rate) was investigated by counting the mass of oxygen in the slag before and after reduction as shown from Eq.(13) to Eq.(15).

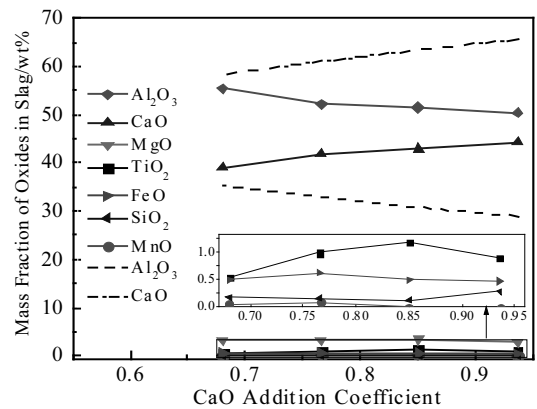


Fig.11 Chemical composition of the slag after reducing reaction

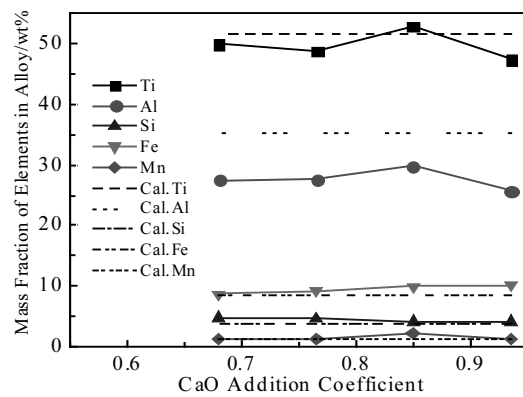


Fig.12 Chemical composition of the alloy after reducing reaction

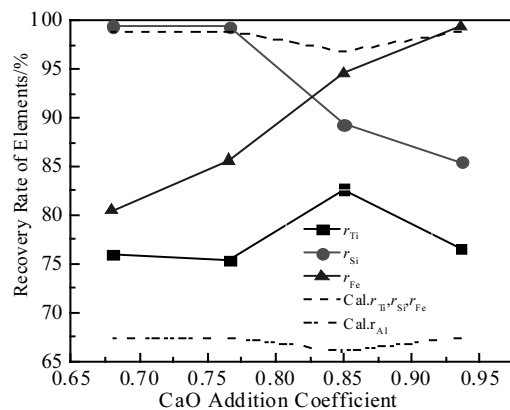


Fig.13 Recovery rate of elements after reduction

$$(W_o)_{initial} = \frac{(W_{slag})_{initial} \cdot M_o}{100} \cdot \left\{ \frac{(\%TiO_2)_{initial} \times 2}{M_{(TiO_2)}} + \frac{(\%MnO)_{initial}}{M_{(MnO)}} + \frac{(\%SiO_2)_{initial}}{M_{(SiO_2)}} + \frac{(\%FeO)_{initial}}{M_{(FeO)}} \right\} \quad (13)$$

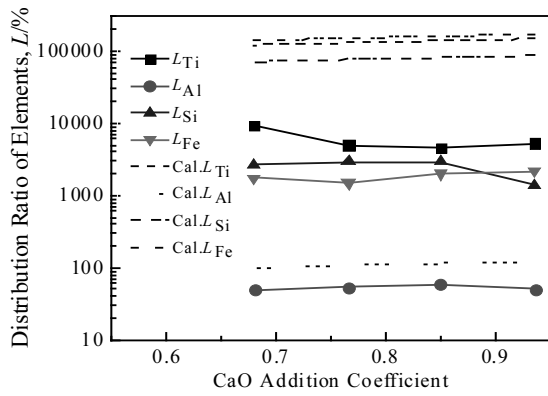


Fig.14 Distribution ratio of elements after reduction

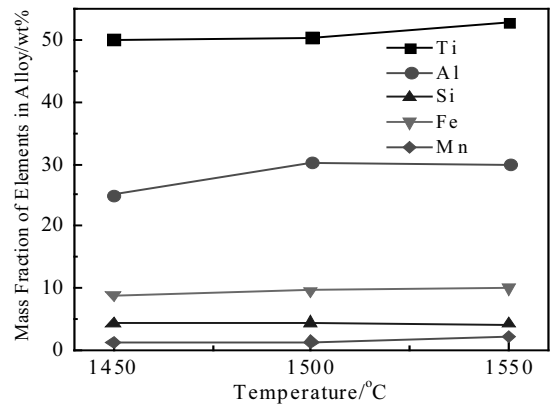


Fig.17 Chemical composition of the alloy after reducing reaction

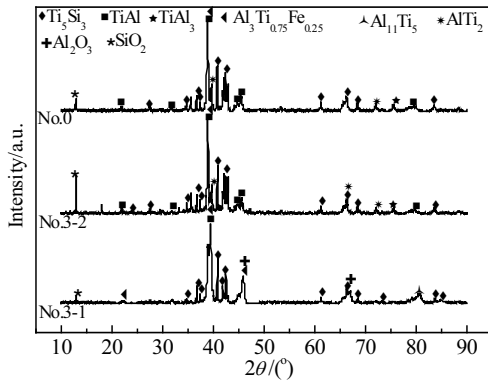


Fig.15 XRD patterns of the alloys reduced at different temperatures

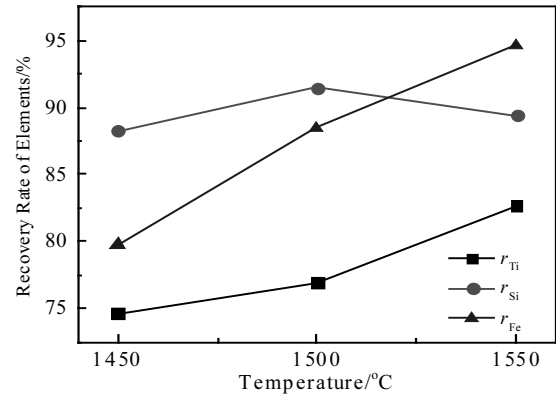


Fig.18 Recovery rate of elements at different temperatures

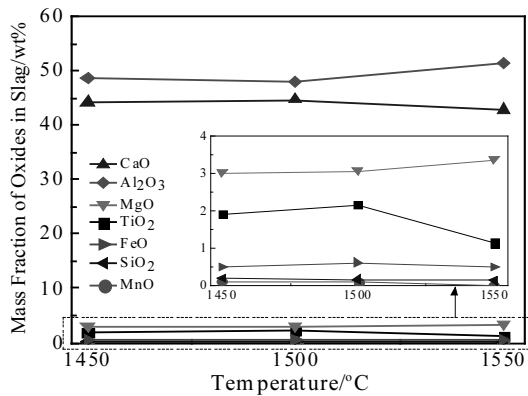


Fig.16 Chemical composition of the slag after reducing reaction

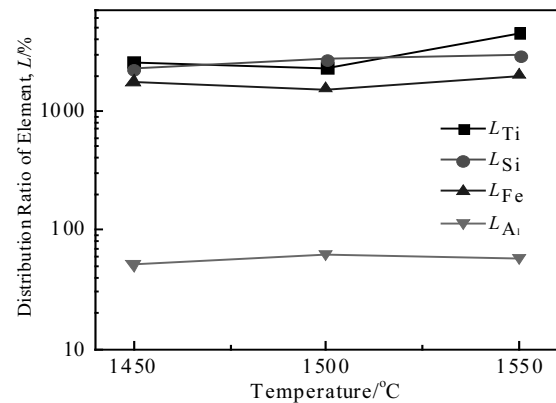


Fig.19 Distribution ratio of elements at different temperatures

$$(W_o)_{final} = \frac{(W_{slag})_{final}}{100} \cdot M_o \cdot \left\{ \frac{(\%TiO_2)_{final}}{M_{(TiO_2)}} \times 2 + \frac{(\%MnO)_{final}}{M_{(MnO)}} + \frac{(\%SiO_2)_{final}}{M_{(SiO_2)}} \times 2 + \frac{(\%FeO)_{final}}{M_{(FeO)}} \right\} \quad (14)$$

$$Reducibility = \frac{(W_o)_{initial} - (W_o)_{final}}{(W_o)_{initial}} \times 100\% \quad (15)$$

Fig.20 to Fig.23 show the results of the reduction rate under different experimental conditions. It can be seen from the results that the reduction rates of the slag for all series of experiments could reach about 95%, implying a high

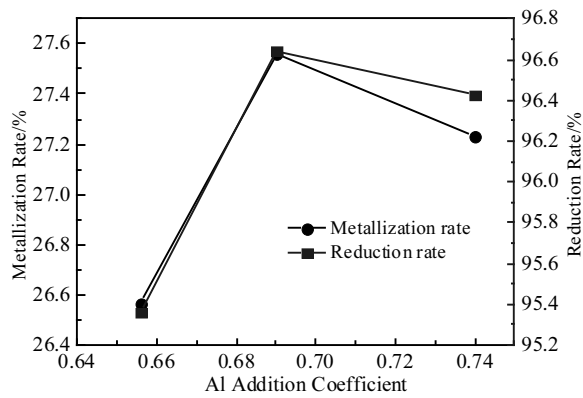


Fig.20 Reduction rate of the slag with different Al additions

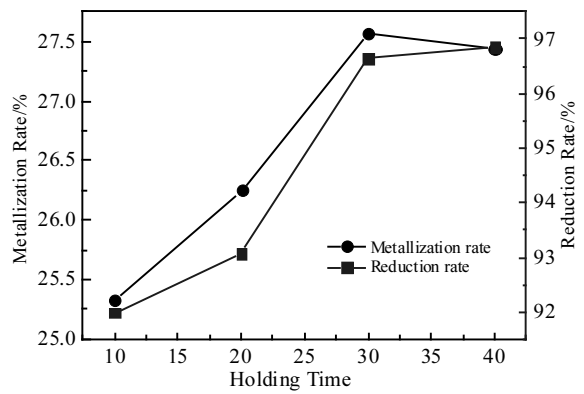


Fig.23 Reduction rate of the slag at different holding times

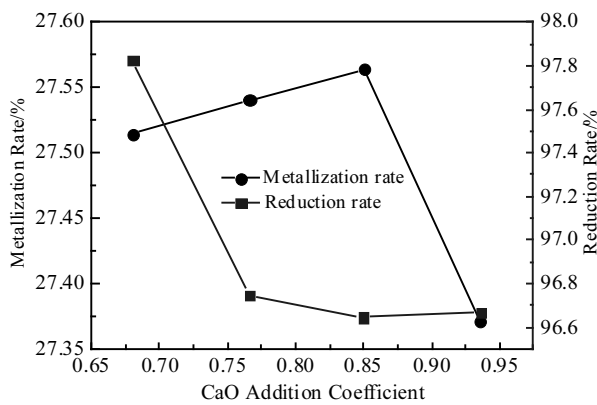


Fig.21 Reduction rate of the slag with different CaO additions

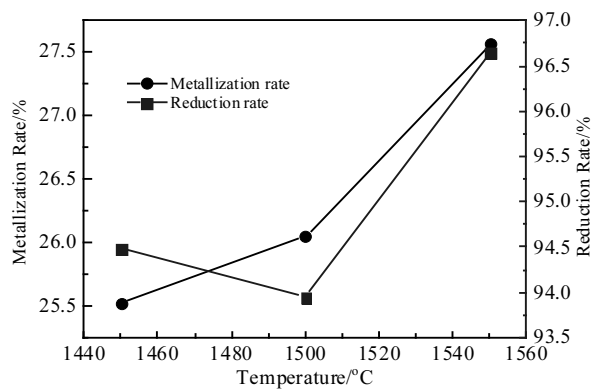


Fig.22 Reduction rate of the slag at different temperatures

reducibility at the present study. Taking the 1wt% of error range of experiments into consideration, the reduction rate at different Al and CaO additions does not change much, while the reduction rate at different temperatures can be increased. Moreover, it is interesting to notice that the behavior of metallization rate (ratio of metal mass to sum of metal and slag mass) has a very similar tendency with the reduction rate of slag. In order to see the effect of heating time on reducibility of oxide, the experiments with different

heating times were also conducted and it is shown in Fig.23. It is clearly seen that the maximum reducibility of slag could be obtained after 30 min.

5 Conclusions

1) The preparation of TiAl intermetallic alloys by the aluminothermic reduction reaction of acid soluble titanium slag (ASTS) is performed for the first time in the present study under a not strictly reduced atmosphere. By considering all possible reduction reactions and materials proportioning calculations of the system, it could successfully produce the TiAl intermetallic alloy.

2) It could make production of TiAl intermetallic alloy with good slag-alloy separation if the phases of the slag after reduction are controlled to be liquid calcium aluminate phases of low melting point. The main phases of the slag are identified mainly as CaAl_2O_4 and $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$, while the main phases of the alloy after reduction are identified as TiAl, $\text{Al}_3\text{Ti}_{0.75}\text{Fe}_{0.25}$ (or TiAl_3 phase) and Ti_5Si_3 .

3) The Al in the raw materials mainly affects the composition of TiAl and it shows the decrease tendency of all species and slight increase of distribution ratio for most reduced elements.

4) The CaO addition mainly influences the slag-alloy separation by varying fluidity of the slag other than the composition of final product of TiAl alloy. Change of CaO the recovery rate of elements in the alloy markedly, and among them the change of recovery rate for Fe and Si is most significant.

5) The temperature can affect the reducing reaction in such a way that it shows increase of recovery rate and distribution ratio for the most reduced elements.

6) The reducibility of slag is about 95% under all the experimental conditions. The behavior of slag reducibility is very similar to the metallization rate after reaction and the increase tendency occurs with the increase of temperature and holding time.

References

- 1 Huang Q Y, Lv X W, Huang R et al. *Canadian Metallurgical Quarterly*[J], 2013, 52(4): 413
- 2 Ashraf Imam M. *JOM*[J], 2016, 68(9): 2492
- 3 Wu X. *Intermetallics*[J], 2006, 14: 1114
- 4 Loria E A. *Intermetallics*[J], 2000, 8: 1339
- 5 Clemens H, Kestler H. *Adv Eng Mater*[J], 2000, 2: 551
- 6 Li Binbin, Yang Shaoli, Zhao Junhui et al. *Metal Materials and Metallurgy Engineering*[J], 2014, 42(6): 3 (in Chinese)
- 7 Hassan-Pour S, Vonderstein C, Achimovičová M et al. *Metall Mater Eng*[J], 2015, 21(2): 101
- 8 Meada Masafumi, Yahata Toshifumi, Mitugi Kei et al. *Material Transactions*[J], 1993, 34(7): 599
- 9 Haidar J, Gnanarajan S, Dunlop J B et al. *Intermetallics*[J], 2009, 17(8): 651
- 10 Babyuk Vitaly, Friendrich Bernd, Sokolov Vladyslav. *World of Metallurgy-Erzmetall*[J], 2007, 60(5): 288
- 11 Li Jun, Yang Shaoli, Wu Enhui et al. *Iron Steel Vanadium Titanium*[J], 2013, 34(6): 21 (in Chinese)
- 12 Yang Huimin, Luo Liangshun, Song Meihui et al. *Chinese Journal of Rare Metals*[J], 2015, 39(6): 498 (in Chinese)
- 13 Novák Pavel, Kríz Jan, Prusa Filip et al. *Intermetallics*[J], 2013, 39: 11
- 14 Lamb H. *Hydrodynamics, 6th ed*[M]. Cambridge: Cambridge University Press, 1994
- 15 Liu Di, Zhang Lijun, Mi Lei et al. *Titanium Industry Progress*[J], 2014, 31: 11 (in Chinese)
- 16 Huang Xu, Li Zhenxi, Gao Fan et al. *Advanced High Temperature Material*[J], 2014, 7: 70 (in Chinese)
- 17 Xie Senlin. *Thesis for Master Degree*[D]. Ganzhou: Jiang Xi University of Science and Technology, 2012
- 18 Piao R, Lee H G, Kang Y B. *Acta Mater*[J], 2013, 61(2): 683

铝热还原酸溶性钛渣制备 TiAl 基多元合金

马 兰¹, 朴荣勋¹, 杨绍利¹, 李彬彬²

(1. 攀枝花学院, 四川 攀枝花 617000)

(2. 西华大学, 四川 成都 610039)

摘要: 对含高钛的酸溶性钛渣进行铝热还原制备钛铝基多元合金。为了控制并了解合金的制备, 讨论了铝和氧化钙的添加和温度的影响。通过考虑材料的配比计算, 可以成功地使合金与渣合金分离。大多数还原元素的回收率表现为高值, 在所有实验条件下均为 95%。铝的添加主要影响合金的成分, 而氧化钙的添加则通过改变渣系成分来影响渣金分离。此外, 系统的温度可以提高大部分还原元素的回收率和分配比。

关键词: 多元TiAl; 铝热还原; 酸溶性钛渣

作者简介: 马 兰, 女, 1972 年生, 副教授, 攀枝花学院材料工程学院, 四川 攀枝花 617000, 电话: 0812-3372090, E-mail: hudie5656@163.com