A New Two-Stage Aluminothermic Reduction Process for Preparation of Ti/Ti-Al Alloys

Kun Zhao and Naixiang Feng

Abstract This work presents a two-stage aluminothermic reduction process for preparing Ti and Ti-Al alloys using Na_2TiF_6. Al-Ti master alloy and pure cryolite as co-products could be obtained. After the first stage reduction, O content of the metal production (particle size of less than 74 μm) was below about 0.35 wt%. Ti (IV), Ti (III) and Ti (0) existed in the Ti-containing cryolite, and the content was about 3 to ~10 wt%. After secondary reduction, Ti content of the clean cryolite was reduced to 0.002 wt%. The Al-Ti master alloy obtained by secondary reduction was composed of Al and $TiAl_3$. A cyclical production process is founded by Al-Ti master alloy returned to the next first and secondary reduction process as reductant, in which Ti and Al are almost 100% recyclable.

Keywords Titanium · Ti-Al alloys · Aluminothermic reduction · Cryolite · Cyclical production

Introduction

Titanium and titanium alloys, as important structural materials besides steel and aluminum, have attracted increasing attentions owing to their superior performances such as light weight, high strength, and high corrosion resistance [1–3]. In recent years, Ti-Al alloys have been considered as top candidate for excellent engineering materials used in aerospace and automotive fields due to their high specific strength and stiffness, high strength retention and high creep resistance at high temperature [4–6].

Currently, Ti metal is produced by a mature commercial technology named as Kroll process, and Ti alloys are usually prepared by blending of pure titanium and metallic elements under high temperature. Kroll process mainly involves the problems of the high-temperature chlorination of rutile or ilmenite, the purification of

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$TiCl_4$, the reduction of $TiCl_4$ with magnesium and the retreating of $MgCl_2$ melt to magnesium, etc., is a cumbersome process with heavy environmental burdens [7–11]. Therefore, Ti metal and its alloys are relatively expensive, restricting their applications in different fields.

In short, developing a shorter, simpler and higher economic benefit process for preparing titanium and titanium alloys is a significant class in the field of metallurgy as before.

To date, the existing approaches on producing titanium mainly focus on two methods, metallothermic reduction and electrochemical reduction. Depending on its short process flow and low pollution, electro-deoxidation process is the key research direction in the field of titanium metallurgy in the past two decades, in which titanium powder is obtained as the product usually. Nevertheless, electro-deoxidation processes exhibit a common problem on the poor efficiency and troublesome subsequent treatment [12–16]. Besides, aluminothermic reduction method has been reported to recovery of titanium from TiO_2, K_2TiF_6 and Na_2TiF_6 [17–20]. Most of these methods also attributing to low product quality (≤ 97.01 wt %) and high cost, embodied in the low recovery and the polluted by-product due to the generated of lower valency compound of titanium.

The aim of this study is to introduce a high productivity and pollution-free recycling metallurgical two-stage reduction process for preparing Ti and Ti-Al alloys (e.g. Ti_3Al, TiAl and $TiAl_3$) using industrial Na_2TiF_6 and aluminum powder. Clean cryolite, which can be used in aluminum electrolysis production, as co-product can be obtained after reduction process.

Experimental

Raw Materials

The main raw materials of experiment are Na_2TiF_6 ($\geq 98\%$, particle size of less than 74 μm), aluminum powder ($\geq 99.9\%$, particle size of less than 74 μm). The oxygen content of Na_2TiF_6 and Al powders is 0.34 and 0.09 wt% respectively.

Experimental Apparatus and Methods

In the first stage, the general reactions for synthesizing Ti/Ti-Al alloys (Ti_3Al, TiAl and $TiAl_3$) are as follows:

$$12Na_2TiF_6 + 16Al = 12Ti + 3Na_3AlF_6 + 3Na_5Al_3F_{14} + 4AlF_3 \quad (1)$$

$$12Na_2TiF_6 + 20Al = 4Ti_3Al + 3Na_3AlF_6 + 3Na_5Al_3F_{14} + 4AlF_3 \quad (2)$$

$$12Na_2TiF_6 + 28Al = 12TiAl + 3Na_3AlF_6 + 3Na_5Al_3F_{14} + 4AlF_3 \quad (3)$$

$$12Na_2TiF_6 + 52Al = 12TiAl_3 + 3Na_3AlF_6 + 3Na_5Al_3F_{14} + 4AlF_3 \quad (4)$$

In order to make a more uniform composition, Na_2TiF_6 and Al powder were mixed 12 h by high-energy ball milling under a rotation speed of 250 r/min. Then the mixture was uniaxially pressed in a hydraulic press with 40 MPa to make piece with 20 mm in diameter and 40 mm in thickness. The pieces were sintered 2 h at 1100 °C under high pure argon atmosphere, and then, the distillation process started and lasted 2 h in a vacuum of $\sim$0.1 Pa. After cooling to room temperature, the product was taken out from the crucible, and the crystallized product was collected from the condenser.

In the second stage, the said distillated product was mixed with Al powder under a mass radio to be 10:3. The mixture was sintered for 2 h at 1100 °C in an argon protection environment to complete the second stage reduction. Finally, several characterization methods were applied to describe the phases and structures of the different products.

Analysis Methods

The crystal structures of reduction products were identified using X-ray diffraction (XRD) measurements with a Cu-Kα characteristic ray and energy-dispersive spectrometry (EDS). The morphologies of the reduction products were observed using scanning electron microscopy (SEM). X-ray photoelectron spectroscopy (XPS) was used to characterize the form of Ti ions existence in the crystallized product. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to examine the impurities contents in the final product and co-product.

Results and Discussion

Characterization of the Products Obtained by the First Stage Reduction

Figure 1a shows the original form picture of the reduction product, exhibiting a structure of gray-black sponge foam. Figure 1b illustrates XRD profiles of the different reduction products obtained with different proportions of raw materials.

After the first reduction, the single phase of Ti, Ti_3Al, TiAl, and $TiAl_3$ are identified under different proportions of raw materials. O content of the product in powder (particle size of less than 74 μm) is about 0.19–0.35 wt%. Different intermetallic phases have formed due to the different Al proportions. The SEM

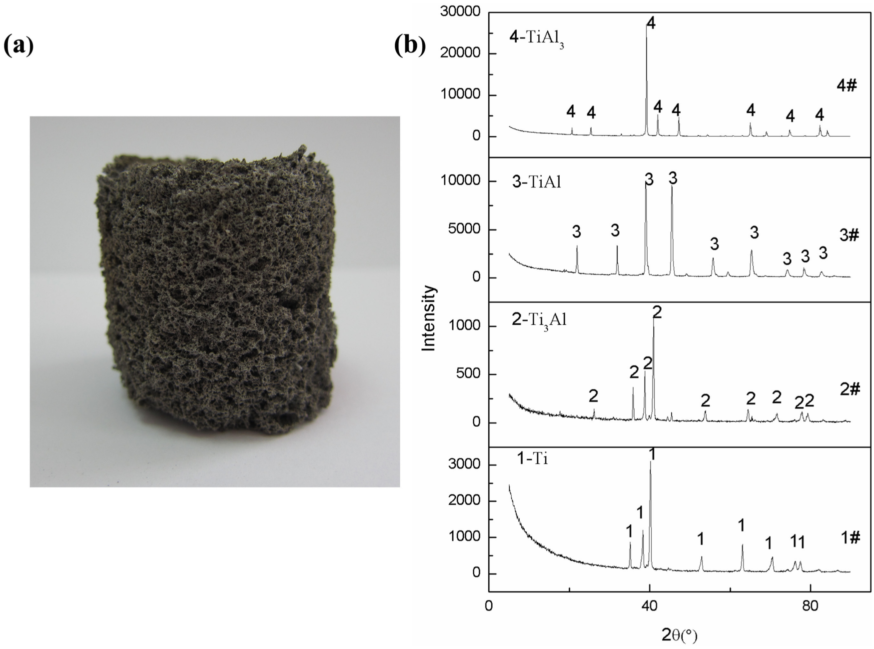

Fig. 1 The original form picture (**a**) of the reduction product, and XRD patterns (**b**) of reduction products prepared with different ratio of Al (Al: Na_2TiF_6 is 1#—4:3, 2#—5:3, 3#—7:3, 4#—13:3)

micrographs of different metal products are shown in Fig. 2. It can seen that the metal product displays a loose sponge-like structure.

The component result analyzed by EDS is shown in Table 1, which illustrates that Ti and Al contents in metal products are close to the target product. In addition, O content analyzed by an oxygen-nitrogen analyzer of Ti, Ti_3Al, TiAl and $TiAl_3$ product (particle size of less than 74 μm) obtained by this method was about 0.35, 0.24, 0.13, 0.22 wt%, respectively.

Figure 3 shows Ti 2p photoelectron spectra of the distillated product. It reveals that Ti presented in the distillated product as three kinds of valence state, which was Ti (0), Ti (IV) and Ti (III) respectively. The inset of Fig. 3 evidenced that the distillated product was black.

Titanium element contained should be the major reason for the blackened distillated product obtained after the first stage reduction process. For convenience, the black distillated product is defined as Ti-containing cryolite.

Table 2 shows the chemical compositions of the Ti-containing cryolite fabricated by the first reduction. The mainly elements were F, Na and Al contained in the distillated product. Besides those, a little O, Fe, Si and S also can be found from it, which is come from the raw material. It is worth noticed that Ti was detected approximately 5.29 wt%.

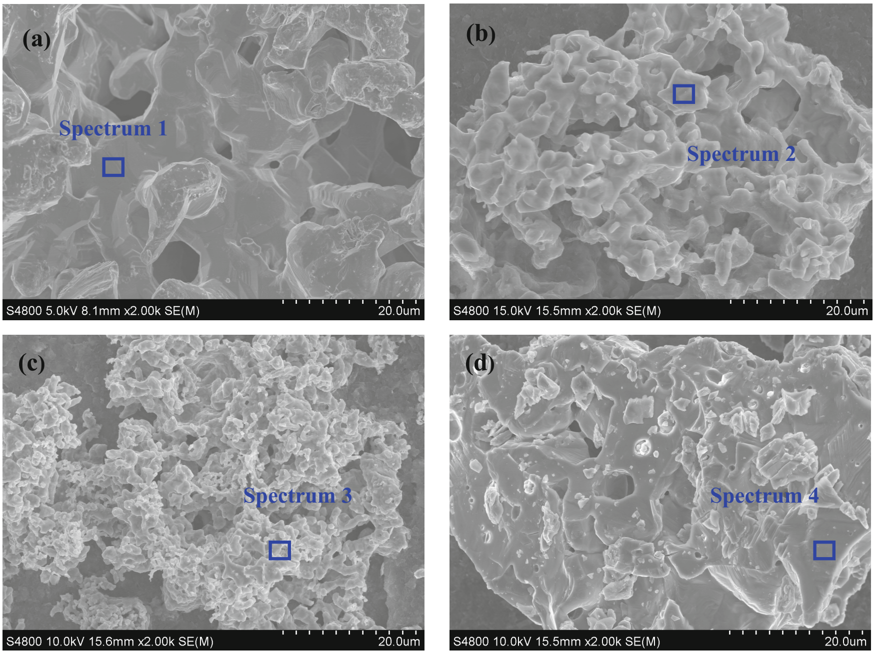

Fig. 2 The SEM micrographs of different metal products after the first stage reduction (**a** Ti, **b** Ti_3Al, **c** TiAl, **d** $TiAl_3$)

Table 1 The component result analyzed by EDS

Mass percent	Ti element	A-element
1	99.48	0.52
2	84.61	15.39
3	65.08	34.92
4	36.89	63.11

Characterization of the Products Obtained by the Second Stage Reduction

As seen from the picture shown in Fig. 4, Ti-containing cryolite was bleached, and a metal ingot was obtained after the secondary reduction. Ti content of the bleached cryolite measured by ICP-AES was merely 0.002 wt%.

Figure 5a shows the micrograph of the metal ingot obtained from the secondary reduction. It demonstrates that there are new phase in two shapes existed in matrix, granular and slender needles likes. An evident boundary can be seen between the new phases in different shapes. The EDS patterns of the new phases and matrix are shown in Fig. 5b, indicating that the new phases in granular and slender needles likes are all $TiAl_3$, and the matrix is associated to Al phase. For convenience, the metal ingot is named as Al-Ti master alloy.

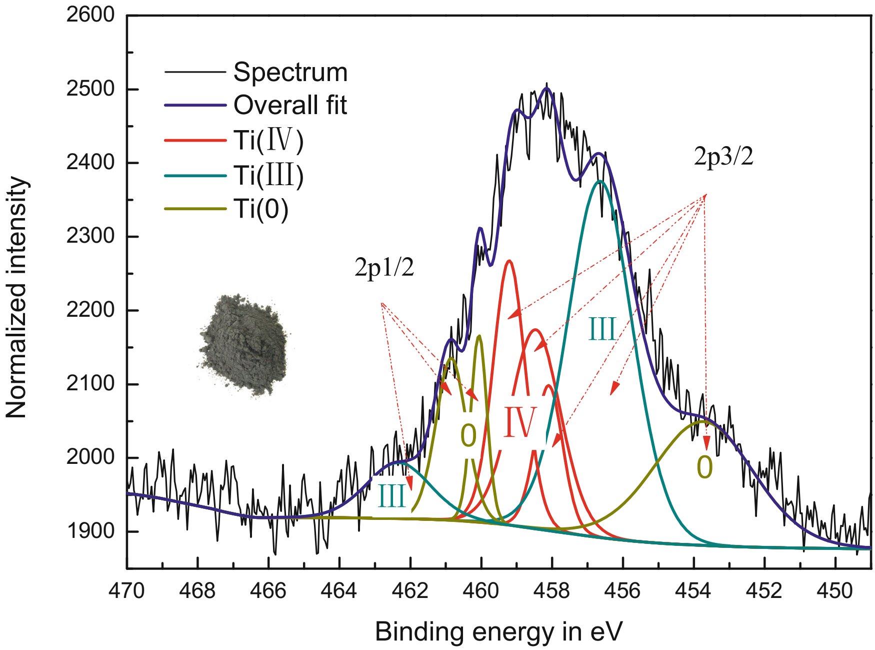

Fig. 3 The XPS trace of the distillated product, and the inset displays its original form photo

Table 2 XRF data of the product attached on the condenser

Element	F	Na	Al	Ti	O	Fe	Si	S	Other
Mass %	52.65	24.38	15.03	5.29	2.33	0.08	0.12	0.02	0.10

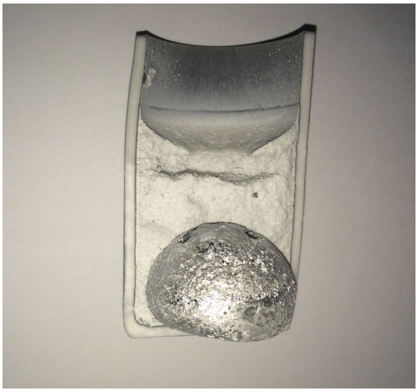

Fig. 4 The photo of the crucible section obtained after the secondary reduction

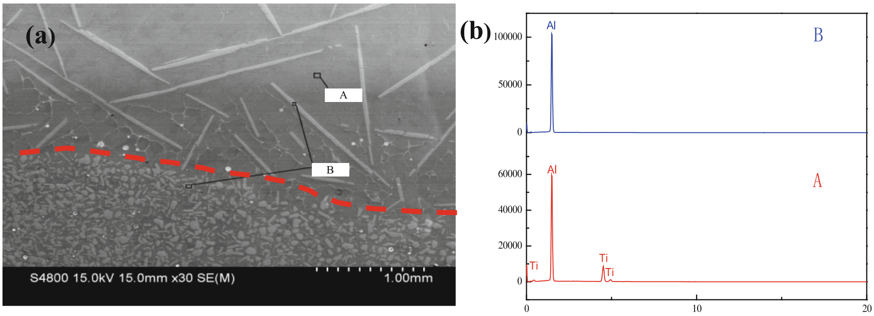

Fig. 5 The SEM image (**a**) and EDS maps (**b**) of the metal ingot obtained after the secondary reduction

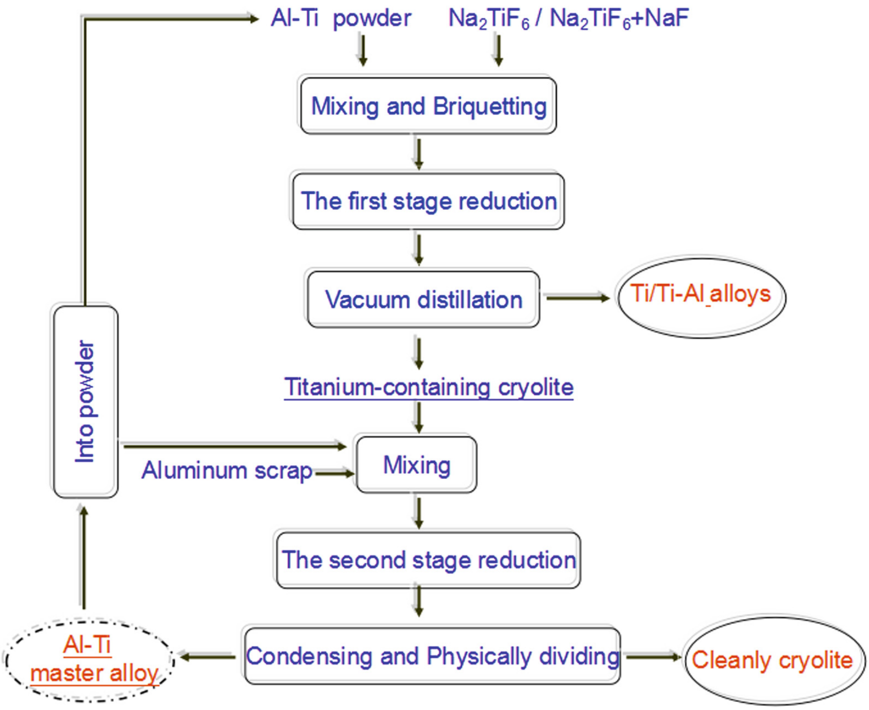

Fig. 6 The flow of the two-stage reduction process

At last, the two-stage reduction process was completed with Ti/Ti-Al alloys, cleanly cryolite, and Al-Ti master alloy as final products. It's worth mentioning that Al-Ti master alloy can be returned to the next first and secondary reduction process and used as reductant. As a result, a cyclical production process is founded without any pollutions and useless products. The flow of this consecutive two-stage reduction process is shown in Fig. 6.

Conclusion

In summary, a two-stage aluminothermic reduction process for preparing Ti/Ti-Al alloys was introduced in this paper. Cleanly cryolite and Al-Ti master alloy could be obtained as co-products. A cyclical production process is founded by Al-Ti master alloy returned to the next first and secondary reduction process as reductant. The new route for production Ti/Ti-Al alloys can be regarded as an environment-friendly metallurgy process, which also brings an exceedingly positive forecast for widespread use of Ti/Ti alloys.

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