METHOD FOR PREPARING TITANIUM OR TITANIUM ALUMINUM ALLOY AND BYPRODUCT-TITANIUM-FREE CRYOLITE THROUGH TWO-STAGE ALUMINOTHERMIC REDUCTION

The present invention relates to a method for preparing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts. The method comprises the following steps: (1) using sodium fluoride and sodium fluotitanate as raw materials, or using sodium fluotitanate as raw materials, and using titanium aluminum alloy powder as a reducing agent; (2) mixing and pressing into pellets, and carrying out first-stage aluminothermic reduction and vacuum distillation; (3) finely grinding after taking out titanium-containing cryolite, mixing with the reducing agent and briquetting, and carrying out second-stage aluminothermic reduction; and (4) separating low-titanium titanium aluminum alloys from high-titanium titanium aluminum alloys, making the low-titanium titanium aluminum alloys and the high-titanium titanium aluminum alloys into powder and returning to the two-stage aluminothermic reduction as the reducing agent; or after the alloys are molten, making the alloys into powder for the two-stage aluminothermic reduction.
Description

Technical Field

[0001] The present invention belongs to the technical field of metallurgy and particularly relates to a method for producing titanium and titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts.

Background

[0002] Titanium is a light rare metal material and is widely applied in the technical fields of aviation, aerospace and chemical engineering. At present, titanium is produced by a method for reducing titanium tetrachloride (TiCl₄) with magnesium at high temperature, and the titanium produced by the method is spongy. The titanium can also be produced by a method for reducing titanium tetrachloride (TiCl₄) with sodium at high temperature. The method for producing titanium by reducing the titanium tetrachloride (TiCl₄) with the magnesium or the sodium is high in cost. In addition, Cl₂ is a raw material during production of the TiCl₄, and the byproduct in reduction process is chloride. Since Cl₂ and the chloride are strong corrosive to equipment, the operation conditions are complicated and extreme. Therefore, people also continuously explore other smelting methods for producing titanium, such as fused salt electrolysis of TiCl₄, and electro-deoxidization fused salt electrolysis of TiO₂ which is used as a negative pole, but the methods are still in a laboratory research stage and do not succeed in the industry. Additionally, methods for producing the titanium by using sodium fluoritanate or potassium fluoritanate or titanium trifluoride as a raw material and using Al-Zn, Al-Mg, and Al-Zn-Mg alloys as well as pure Al, pure Mg and pure Na as reducing agents, also exist (see US Pub, NO:US 2010/0173170A1, CN102534263A, CN102560153A and CN102534260A). According to the methods of producing titanium, the purity of titanium can be 70.7% or above, and the maximum purity can be 99.5%.

[0003] The reduction reactions are all performed at the temperature of 900-1000 °C, but the methods still cannot be applied in the industry. The methods have the disadvantages and problems as follows:

1. The reduction process is comparatively complicated; in the methods disclosed by the patents, the reducing agents are mixed and fused firstly, and then the mixed and fused compound reducing agents are added or dropped into the raw material needed to reduce; and the reaction material needs to be stirred in the reaction process, and finally products should be separated out;
2. when the reduction agent is Al-Zn alloys, Zn does not participate in the reduction reaction, so that Zn needs to be separated out the purification technology is complicated, and the production cost is greatly increased; and
3. in the technical methods disclosed by the patents, the byproducts mainly Na₃AlF₆ and AlF₃ separated out from products are black or grey-black and contain a lot of titanium compounds, so that the loss of titanium is caused.

[0004] With the development of aviation and aerospace techniques and requirements for some high-temperature corrosion-resistant materials in the chemical engineering field, the development of Ti-Al alloys or Ti-Al-based high-performance alloys doped with some other metal elements is extensively concerned in various countries of the world. However, raw metals of the alloys are all produced by the method of smelting pure metal aluminum and sponge titanium which are produced by magnesiothermic reduction for TiCl₄, and the production technology is comparatively complicated.

Summary of Invention

[0005] For the problems existing in the production technique of titanium, the present invention provides a method for producing titanium and titanium aluminum alloys through two-stage aluminothermic reduction and producing titanium-free cryolite as byproducts; the titanium-free cryolite containing the extremely low content of titanium can be used for electrolytic aluminum industry. The two-stage aluminothermic reduction method consists of a first-stage aluminothermic reduction process and a second-stage aluminothermic reduction process. In the first-stage aluminothermic reduction process, the titanium or the titanium aluminum alloys are the to-be-produced products, and sodium fluoride and sodium fluoritanate are used as raw materials, or sodium fluoritanate is used as raw material, and powder made of the Al-Ti alloys produced by the second-stage aluminothermic reduction process is used as reducing agent. The titanium or the titanium aluminum alloys are produced by the first-stage aluminothermic reduction. In the first-stage aluminothermic reduction process, the materials and the reducing agent participating in the reduction reaction are mixed and pressed into lumps, and the lumps are heated to 900-1300 °C under the vacuum or argon protection condition for aluminothermic reduction. Then, the reduction product is separated through vacuum distillation at the temperature of 900-1300 °C, so as to obtain titanium-containing cryolite and the titanium or the titanium aluminum alloys. In the second-stage aluminothermic reduction process, the titanium-containing cryolite produced by the first-stage aluminothermic reduction is used...
as a raw material, and aluminum powder is used as reducing agent. The titanium-containing cryolite and the reducing agent are mixed and pressed into lumps, and the lumps are reduced under the argon protection condition at the temperature of 900-1300 °C, so as to obtain the titanium-free cryolite and the aluminum titanium alloys. In the second-stage aluminothermic reduction process, the feeding quantity of the reducing agent follows a rule that the melting point of the aluminum titanium alloys produced after the second-stage reduction process is lower than the temperature of the reduction reaction. In the second-stage aluminothermic reduction process, the aluminum titanium alloys and the titanium-free cryolite are mutually insoluble, so that the aluminum titanium alloy melt and the titanium-free cryolite melt can be well separated out in the molten state. The titanium in the aluminum titanium alloys produced by the second-stage aluminothermic reduction mainly exist in the form of TiAl3 metallic compound, and most of TiAl3 metallic compound settle at the bottom of the alloy melt in a slow cooling process, therefore, low-titanium aluminum titanium alloys with lower content of titanium are formed at the upper part, and high-titanium aluminum titanium alloys with higher content of titanium are formed at the lower part. When the second-stage reduction reaction completed and the reduction product cooled, the solid titanium-free cryolite can be separated from the aluminum titanium alloys. The aluminum titanium alloys separated out in the second-stage aluminothermic reduction process are remolten and made into powder to be used as the reducing agent of the first-stage aluminothermic reduction. The aluminum titanium alloys produced in the second-stage aluminothermic reduction can also be separated out by adopting one of the following two methods: 1, separating the low-titanium aluminum titanium alloys from the high-titanium Al-Ti alloys by a mechanical method. 2, putting the aluminum titanium alloys obtained by the second-stage aluminothermic reduction into a tiltable induction furnace for remelting, after standing for a period of time, firstly pouring out the low-titanium aluminum titanium alloys at the upper part, and then digging out the high-titanium aluminum titanium alloys at the bottom, so that the purpose of separating the high-titanium aluminum titanium alloys from the low-titanium aluminum titanium alloys is realized. The low-titanium aluminum titanium alloys which are divided out or separated are made into powder, and the powder is used as the reducing agent of the first-stage aluminothermic reduction, and the high-titanium aluminum titanium alloys with higher content of titanium are sold as commodities.

The method provided by the present invention comprises the following steps:

1. using sodium fluotitanate as the raw material, or using sodium fluoride and sodium fluotitanate as the raw materials, when the titanium and the titanium aluminum alloys are produced and manufactured, using the aluminum titanium alloy powder produced in the second-stage aluminothermic reduction as the reducing agent. In addition, designing the proportion of all the materials according to the to-be-produced product, wherein the reaction formulas of the production proportion are shown as follows:

$$3Na_2TiF_6 + 2NaF + (3x+4)Al = 3TiAl_{x} + Na_3AlF_6 + Na_5Al_3F_{14}, \quad 10 \geq x \geq 0 \quad (1)$$

$$Ti + xAl = TiAl_{x}, \quad x = 0 - 10 \quad (2);$$

or,

$$12Na_2TiF_6 + (12x+16)Al = 12TiAl_{x} + 3Na_3AlF_6 + 3Na_5Al_3F_{14} + 4AlF_3, \quad 10 \geq x \geq 0 \quad (3);$$

and,

$$Ti + xAl = TiAl_{x}, \quad x = 0 - 10 \quad (4);$$

2. uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under the vacuum condition or in the argon atmosphere, performing the first-stage aluminothermic reduction, and separating the reduction product by vacuum distillation at the temperature of 900-1300 °C; coagulating the titanium-containing cryolite distilled out on a crystallizer at the low-temperature end of the vacuum reduction furnace, wherein the product mainly comprises Na2AlF6, Na5Al3F14, AlF3 and titanium-containing sub-fluoride, the residual product which is not distilled out in the reduction furnace is the metal Ti or the titanium aluminum alloys. Because of containing some unreacted sodium fluotitanate and titanium-containing sub-fluoride produced by a side reaction, the product distilled out after the first-stage aluminothermic reduction is black-grey, so that the product
Brief Description of Drawings

[0012] Fig. 1 is a flow diagram of the method for producing titanium or titanium aluminum alloys by two-stage aluminothermic reduction process and producing titanium-free cryolite as byproducts in the second-stage aluminothermic reduction process, wherein the aluminum titanium alloys produced in the second-stage aluminothermic reduction are remolten and then made into alloy powder, and the alloy powder is used as a reducing agent in the first-stage aluminothermic reduction process; Fig. 2 is a flow diagram of the method for producing titanium or titanium aluminum alloys by two-stage aluminothermic reduction process and producing titanium-free cryolite as byproducts in the second-stage aluminothermic reduction process, wherein the aluminum titanium alloys produced in the second-stage aluminothermic reduction are divided into two parts of low-titanium aluminum titanium alloys and high-titanium aluminum titanium alloys, the high-titanium aluminum titanium alloys are sold as commodities, and the low-titanium aluminum titanium alloys are used as the reducing agent in the first-stage aluminothermic reduction process; Fig. 3 is an XRD phase analysis diagram of a Ti₃Al alloy product obtained in an embodiment 1 of the present invention; Fig. 4 is an XRD phase analysis diagram of titanium-containing cryolite in an embodiment 1 of the present invention; Fig. 5 is an XRD phase analysis diagram of a distillation product obtained in an embodiment 2 of the present invention;
Fig. 6 is an XRD phase analysis diagram of a TiAl3 alloy product obtained in an embodiment 3 of the present invention; Fig. 7 is an XRD phase analysis diagram of a TiAl alloy product obtained in an embodiment 5 of the present invention; Fig. 8 is an XRD phase analysis diagram of a metal Ti product obtained in an embodiment 7 of the present invention; Fig. 9 is an XRD phase analysis diagram of titanium-free cryolite (Na3AlF6) obtained in an embodiment 9 of the present invention; Fig. 10 is an SEM (scanning electron microscope) morphology analysis diagram of a layered interface of an aluminum titanium alloy product obtained in an embodiment 9 of the present invention; and Fig. 11 is an EDS (energy dispersive spectrum) detection result diagram of the aluminum titanium alloy product obtained in the embodiment 9 of the present invention, wherein an upper diagram and a lower diagram respectively correspond to the position A and the position B of Fig. 10.

Embodiments

[0013] XRD phase analysis equipment adopted in an embodiment of the present invention is an X’ Pert Pro type X-ray diffractometer.

[0014] SEM morphology analysis equipment adopted in an embodiment of the present invention is an S-4800 type cold field emission scanning electron microscope.

[0015] EDS detection equipment adopted in an embodiment of the present invention is an accessory X-ray energy spectrometer of the S-4800 type scanning electron microscope.

[0016] Metal aluminum powder adopted in an embodiment of the present invention is a product purchased on the market, and the purity of the metal aluminum powder is greater than or equal to 99%.

[0017] Sodium fluoride adopted in an embodiment of the present invention is a powder product purchased on the market, and the purity of the sodium fluoride is greater than or equal to 98%.

[0018] Sodium fluotitanate adopted in an embodiment of the present invention is a powder product purchased on the market, and the purity of the sodium fluotitanate is greater than or equal to 98%.

[0019] A reduction furnace adopted in an embodiment of the present invention is a vacuum reduction furnace with a crystallizer.

Embodiment 1

[0020]

1. Sodium fluoride and sodium fluotitanate are used as raw materials, and 100g of aluminum titanium alloy powder containing 4.21wt% of titanium is used as reducing agent; when Ti2Al alloys (x=1/3 in the formula (1)) are produced, the reaction formulas of the production proportion of all the materials are shown as follows:

\[ 3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + 5\text{Al} = \text{Ti}_3\text{Al} + \text{Na}_3\text{AlF}_6 + \text{Na}_5\text{Al}_3\text{F}_{14} \]  \hspace{1cm} (5)

and,

\[ 3\text{Ti} + \text{Al} = \text{Ti}_3\text{Al} \]  \hspace{1cm} (6);

according to the chemical reaction formulas (5) and (6), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 4.21g of Ti, namely the content of Ti2Al is 5g, Al powder participating into the reduction reaction is 95g, the content of Na2TiF6 required by the reaction is 439.11g, and the content of NaF required by the reaction is 59.11g; therefore, the actual production materials of the embodiment comprise 439.11g of Na2TiF6, 59.11g of NaF and 100g of the aluminum titanium alloy powder containing 4.21wt% of titanium;

2. the production materials are uniformly mixed and then are pressed into lumps, the lumps are placed into a vacuum reduction furnace, the reduction furnace is vacuumized to 10Pa or below, argon is inflated into the reduction furnace to realize normal pressure, and the reduction furnace is heated to 1100 °C under the argon atmosphere condition, so that a first-stage aluminothermic reduction reaction is completed; and

3. after the reduction reaction is ended, the reduction furnace is vacuumized to 10Pa or below, a product of the reduction reaction is distilled for 2h under the vacuum condition at the temperature of 1100 °C, a distillation product on a crystallizer at the low-temperature end in the vacuum reduction furnace is titanium-containing cryolite, and an
alloy product is reserved in a reactor in a loose spongy form; an XRD phase analysis result of the alloy product is shown in Fig. 3, and an XRD phase analysis result of the titanium-containing cryolite is shown in Fig. 4.

**Embodiment 2**

[0021]

1. Sodium fluotitanate is used as raw materials, and 100g of titanium aluminum alloy powder containing 4.21wt% of titanium is used as reducing agent; when the produced product is Ti₃Al alloys (x=1/3 in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:

\[
12\text{Na}_2\text{TiF}_6 + 20\text{Al} = 4\text{Ti}_3\text{Al} + 3\text{Na}_3\text{AlF}_6^+ + 3\text{Na}_5\text{Al}_3\text{F}_{14} + 4\text{AlF}_3
\] (7)

and,

\[
3\text{Ti} + \text{Al} = \text{Ti}_3\text{Al}
\] (8);

according to the chemical reaction formulas (7) and (8), it can be obtained that 100g of the reducing agent (titanium aluminum alloy powder) contains 4.21g of Ti, namely the content of Ti₃Al is 5g, Al powder participating into the reduction reaction is 95g, the content of Na₂TiF₆ required by the reaction is 439.11g; therefore, the actual production materials of the embodiment comprise 439.11g of Na₂TiF₆ and 100g of the titanium aluminum alloy powder containing 4.21wt% of titanium;

2. the production materials are uniformly mixed and then are pressed into lumps, the lumps are placed into a vacuum reduction furnace, the reduction furnace is vacuumized to 10Pa or below, and the reduction furnace is heated to 1100 °C under the argon atmosphere condition, so that a first-stage aluminothermic reduction reaction is completed; and

3. after the reduction reaction is ended, the reduction furnace is vacuumized to 10Pa or below, a product of the reduction reaction is distilled for 2h under the vacuum condition at the temperature of 1100 °C, the distillation product on the crystallizer at the low-temperature end in the vacuum reduction furnace is a mixture of the titanium-containing cryolite and aluminium fluoride, and an alloy product is reserved in a reactor in a loose spongy form; an XRD phase analysis result of the alloys is shown in embodiment 1; and an XRD phase analysis result of the distillation product is shown in Fig. 5.

**Embodiment 3**

[0022] A method in an embodiment 3 is the same as the method in the embodiment 1, but differs from it in that 100g of aluminum titanium alloy powder containing 1.86wt% of titanium is used as reducing agent for production of TiAl₃ alloys:

1. according to the produced product TiAl₃ (x=3 in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:

\[
3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + 13\text{Al} = 3\text{Ti}_3\text{Al} + \text{Na}_3\text{AlF}_6^+ + \text{Na}_5\text{Al}_3\text{F}_{14}
\] (9)

and,

\[
\text{Ti} + 3\text{Al} = \text{Ti}_3\text{Al}
\] (10);

according to the chemical reaction formulas (9) and (10), it can be obtained that 100g of the reducing agent (titanium aluminum alloy powder) contains 1.86g of Ti, namely the content of TiAl₃ is 5g, Al powder participating in the reduction reaction is 95g, the content of Na₂TiF₆ required by the reaction is 168.89g, and the mass of NaF required by the reaction is 22.74g; therefore, the actual production materials of the embodiment 3 comprise 168.89g of Na₂TiF₆, 22.74g of NaF and 100g of titanium aluminum alloy powder containing 1.86wt% of titanium;
2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and
3. distillation is performed for 2h at the temperature of 1100 °C; after cooling, the residual metal in a reduction furnace is the TiAl₃ alloys, and an XRD phase analysis result of the TiAl₃ alloys is shown in Fig. 6.

**Embodiment 4**

**[0023]** A method in an embodiment 4 is the same as the method in the embodiment 2 and differs from it in that 100g of aluminum titanium alloy powder containing 1.86wt% of titanium is used as reducing agent for production of TiAl₃ alloys:

1. according to the produced product TiAl₃ (x=3 in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:

   \[
   12\text{Na}_2\text{TiF}_6 + 52\text{Al} = 12\text{TiAl}_3 + 3\text{Na}_3\text{AlF}_6 + 3\text{Na}_5\text{Al}_3\text{F}_{14} + 4\text{AlF}_3
   \]  

   (11)

   and,

   \[
   \text{Ti} + 3\text{Al} = \text{TiAl}_3
   \]  

   (12);

   and therefore, it can be obtained that from the reaction equations (11) and (12) the actual production materials of the embodiment comprise 168.89 g of Na₂TiF₆ and 100g of aluminum titanium alloy powder containing 1.86wt% of titanium;

2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for the first-stage aluminothermic reduction; and
3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in a reduction furnace is the TiAl₃ alloys, and an XRD phase analysis result of the TiAl₃ alloys is the same as that in embodiment 3.

**Embodiment 5**

**[0024]** A method in an embodiment 5 is the same as the method in the embodiment 1 and differs from it in that 100g of titanium aluminum alloy powder containing 3.2wt% of titanium is used as reducing agent for production of TiAl alloys.

1. according to the produced product TiAl (x=1 in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:

   \[
   3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + 7\text{Al} = 3\text{TiAl} + \text{Na}_3\text{AlF}_6 + \text{Na}_5\text{Al}_3\text{F}_{14}
   \]  

   (13)

   and,

   \[
   \text{Ti} + \text{Al} = \text{TiAl}
   \]  

   (14);

   according to the chemical reaction formulas (13) and (14), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 3.2g of Ti, namely the content of TiAl is 5g, Al powder participating in the reduction reaction is 95g, the content of Na₂TiF₆ required by the reaction is 313.65g, and the content of NaF required is 42.22g;

   therefore, the actual production materials of the embodiment 5 comprise 313.65g of Na₂TiF₆, 42.22g of NaF and 100g of aluminum titanium alloy powder containing 3.2wt% of titanium;

2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and
3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the reduction furnace is the TiAl alloys, and an XRD phase analysis result of the TiAl alloys is shown in Fig. 7.
Embodiment 6

[0025] A method in an embodiment 6 is the same as the method in the embodiment 2 and differs from the embodiment 2 in that 100g of aluminum titanium alloy powder containing 3.2wt% of titanium is used as reducing agent for production of TiAl alloys.

1. according to the produced product TiAl(x=1 in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:

\[12\text{Na}_2\text{TiF}_6 + 28\text{Al} = 12\text{TiAl} + 3\text{Na}_3\text{AlF}_6 + 3\text{Na}_5\text{Al}_3\text{F}_{14} + 4\text{AlF}_3 \] (15)

and,

\[\text{Ti} + \text{Al} = \text{TiAl} \] (16);

and therefore, it can be obtained that from the reaction equations (15) and (16) the actual production materials of the embodiment comprise 313.65 g of Na₂TiF₆ and 100g of the aluminum titanium alloy powder containing 3.2wt% of titanium;
2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and
3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in a reduction furnace is the TiAl alloys, and an XRD phase analysis result of the TiAl alloys is shown in embodiment 5.

Embodiment 7

[0026] A method in an embodiment 7 is the same as the method in the embodiment 1 and differs from the embodiment 1 in that 100g of titanium aluminum alloy powder containing 3wt% of titanium is used as reducing agent for production of pure titanium:

1. according to the produced product Ti (x=0 in the formula (1)), the reaction formulas of the production proportion of all the materials are shown as follows:

\[3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + 4\text{Al} = 3\text{Ti} + \text{Na}_3\text{AlF}_6 + \text{Na}_5\text{Al}_3\text{F}_{14} \] (17);

according to the chemical reaction formula (17), it can be obtained that 100g of the reducing agent(aluminum titanium alloy powder contains 3g of Ti), Al powder participating in the reduction reaction is 97g, the content of Na₂TiF₆ required by the reaction is 560.44g, and the content of NaF added is 75.44g; therefore, the actual production materials of the embodiment 7 comprise 560.44g of Na₂TiF₆,75.44g of NaF and 100g of aluminum titanium alloy powder containing 3wt% of titanium;
2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and
3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the reduction furnace is the Ti, and an XRD phase analysis result of the Ti is shown in Fig. 8.

Embodiment 8

[0027] A method in an embodiment 8 is the same as the method in the embodiment 2 and differs from the embodiment 2 in that 100g of aluminum titanium alloy powder containing 3wt% of titanium is used as reducing agent for production of pure titanium:

1. according to the produced product Ti (x=0 in the formula (3)), the reaction formulas of the production proportion of all the materials are shown as follows:
it can be obtained through the chemical reaction formula (18), the actual production materials of the embodiment comprise 560.44g of Na₂TiF₆ and 100g of the aluminum titanium alloy powder containing 3wt% of titanium;  
2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and  
3. distillation is performed at the temperature of 1100 °C for 2h; after cooling, the residual metal in the reduction furnace is the metal Ti, and an XRD phase analysis result of the Ti is shown in embodiment 7.

Embodiment 9

[0028] A method in an embodiment 9 is the same as the method in the embodiment 1 and differs from the embodiment 1 in that 100g of aluminum titanium alloy powder containing 2.13wt% of titanium is used as reducing agent for production of titanium aluminum alloys containing 42.55% of titanium.

1. The titanium aluminum alloys containing 42.55wt% of titanium are the same as the product TiAl₂.₄ alloys (x=2.4 in the formula (1)), and therefore, the reaction formulas of the production proportion of all the materials in the embodiment 9 are shown as follows:

\[ 3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + 11.2\text{Al} = 3\text{TiAl}_{2.4} + 3\text{Na}_3\text{AlF}_6 + \text{Na}_5\text{Al}_3\text{F}_{14} \]  (19)

And

\[ \text{Ti} + 2.4\text{Al} = \text{TiAl}_{2.4} \]  (20)

according to the chemical reaction formulas (19) and (20), it can be obtained that 100g of the reducing agent (aluminum titanium alloy powder) contains 2.13g of Ti, namely the content of TiAl₂.₄ is 5g, Al powder participating in the reduction reaction is 95g, the content of Na₂TiF₆ required by the reaction is 196.03g, and the mass of NaF added is 26.39g; therefore, the actual production materials of the embodiment 9 comprise 196.03g of Na₂TiF₆, 26.39g of NaF and 100g of aluminum titanium alloy powder containing 2.13wt% of titanium;  
2. all the materials are heated to 1100 °C under the argon atmosphere condition, and the temperature is preserved for 2h for first-stage aluminothermic reduction; and  
3. distillation is performed for 2h at the temperature of 1100 °C; after cooling, the residual metal in a reduction furnace is the TiAl₂.₄ alloys, and an chemical component analysis result of the TiAl₂.₄ alloys is shown in Table 1.

| Table 1 |
|------------------|--------|--------|--------|--------|
| **Chemical components** | **Al** | **Ti** | **Ca** | **Si** |
| **Percentage by mass(%)** | 57.4963 | 42.0368 | 0.0537 | 0.0152 | 0.0044 |

Embodiment 10

[0029] Titanium-free cryolite and aluminum titanium alloys are produced through vacuum reduction by using the titanium-containing cryolite distilled out through the first-stage aluminothermic reduction in the embodiment 7 as a raw material and aluminum powder as reducing agent.

1. after the first-stage aluminothermic reduction process, 427.78g of the titanium-containing cryolite is grinded until the particle size is lower than 1.0mm, wherein the content of titanium is 12.84g; 100g of aluminum powder is used as reducing agent; the grinded titanium-containing cryolite and the aluminum powder are uniformly mixed and then are pressed into lumps; the lumps are placed into the vacuum reduction furnace, the vacuum reduction furnace is vacuumized to 10Pa or below, argon is inflated into the vacuum reduction furnace to normal pressure, the lumps are heated to 1200 DEG C under the argon atmosphere condition, and the temperature is preserved for 2h for the
second-stage aluminothermic reduction; and
2. after the materials in the reduction furnace are cooled to normal temperature, a product is taken out and separated out, so as to obtain the white titanium-free cryolite and the aluminum titanium alloys with the forming amounts of 414.94g and 112.84g respectively in theory; the aluminum titanium alloys can be used as reducing agent for the next first-stage aluminothermic reduction process to produce metal titanium, and the cycle continues; an XRD phase analysis result of the white titanium-free cryolite is shown in Fig. 9, and an XRF component analysis result is listed in Table 2;

<table>
<thead>
<tr>
<th>Chemical components</th>
<th>F</th>
<th>Na</th>
<th>Al</th>
<th>Mg</th>
<th>Ca</th>
<th>Si</th>
<th>Fe</th>
<th>K</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage by mass(%)</td>
<td>59.8487</td>
<td>22.7601</td>
<td>16.6017</td>
<td>0.7133</td>
<td>0.0254</td>
<td>0.0177</td>
<td>0.0058</td>
<td>0.0043</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

[0030] It can be seen from Table 2 that the cryolite produced in the embodiment 10 completely conforms with the national standard GB/T 4291-1999 ‘cryolite’ and can be directly applied in the aluminum electrolysis industry. Low-titanium aluminum titanium alloys are formed at the upper layer of the aluminum titanium alloy product, and high-titanium aluminum titanium alloys are formed at the lower layer of the aluminum titanium alloy product. An SEM image and an energy spectrum analysis result of the aluminum titanium alloy product are respectively shown in Fig. 10 and Fig. 11.

[0031] The titanium-containing cryolite obtained in the first-stage aluminothermic reduction of the embodiments 1-9 can be further treated by the method shown in the embodiment 10, the aluminum powder is adopted for performing the second-stage vacuum aluminothermic reduction, the obtained white titanium-free cryolite can be applied in the aluminum electrolysis industry, and the aluminum titanium alloys can fully returns to the next first-stage aluminothermic reduction process as the reducing agent.

Claims

1. A method for producing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, characterized by comprising the following steps:

   (1) using sodium fluoride and sodium fluotitanate as raw materials, and using aluminum titanium alloy powder obtained through second-stage aluminothermic reduction as a reducing agent, wherein the reaction formulas of the production proportion of all the materials are shown as follows:

   \[ 12\text{Na}_2\text{TiF}_6 + (12x+16)\text{Al} = 12\text{TiAl}_x + 3\text{Na}_3\text{AlF}_6 + 3\text{Na}_5\text{Al}_3\text{F}_{14} + 4\text{AlF}_3 \]  \quad (1)

   and,

   \[ \text{Ti} + x\text{Al} = \text{TiAl}_x \]  \quad (2);

   wherein \( x=0-10 \);

   (2) uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under the vacuum condition or in the argon atmosphere, and performing the first-stage aluminothermic reduction and vacuum distillation; coagulating a titanium-containing cryolite distilled out on a crystallizer at the low-temperature end of the vacuum reduction furnace, wherein the product mainly comprises \( \text{Na}_2\text{AlF}_6, \text{Na}_5\text{Al}_3\text{F}_{14}, \text{AlF}_3 \) and titanium-containing sub-fluoride, and the residual product in the reduction furnace is TiAl_x;

   (3) taking out the titanium-containing cryolite, grinding the titanium-containing cryolite until the particle size is lower than 1.0mm, using the aluminum powder as the reducing agent, uniformly mixing the grinded titanium-containing cryolite with the aluminum powder to obtain a mixture, and pressing the mixture into lumps, wherein the feeding amount of the aluminum powder follows the rule that the melting point of the Al-Ti alloys produced by the second-stage aluminothermic reduction is lower than or equal to the temperature of the second-stage aluminothermic reduction temperature; placing the lumps into the reduction furnace, heating the placed lumps to 900-1300 °C in the argon atmosphere and preserving the temperature for 0.5-2h for the second-stage alu-
minothermic reduction, wherein according to the products obtained after the reduction reaction is ended and the temperature in the furnace body is reduced to normal temperature, white titanium-free cryolite is formed at the upper parts of the products and the aluminum titanium alloys are formed at the bottoms of the products, wherein alloys with low content of titanium are formed at the upper parts of the aluminum titanium alloys, which are called as the low-titanium titanium aluminum alloys; the aluminum titanium alloys with comparatively high content of titanium are formed at the lower parts of the aluminum titanium alloys, which are called as the high-titanium titanium aluminum alloys; and

(4) dividing or separating the low-titanium aluminum titanium alloys and the high-titanium aluminum titanium alloys with a mechanical division method or a remelting and dumping method of the induction furnace, making the low-titanium aluminum titanium alloys divided out or separated out into powder as the reducing agent of the first-stage minothermic reduction, or remelting the aluminum titanium alloy produced by the second-stage minothermic reduction to make powder, and returning the powder back to the first-stage minothermic reduction as the reducing agent for use.

2. The method for producing titanium or titanium aluminum alloys through two-stage minothermic reduction and obtaining titanium-free cryolite as byproducts, characterized by comprising the following steps:

(1) using sodium fluotitanate as raw materials, and using aluminum titanium alloy powder obtained through second-stage minothermic reduction as a reducing agent, wherein the reaction formulas of the production proportion of all the materials are shown as follows:

$$3\text{Na}_2\text{TiF}_6 + 2\text{NaF} + (3x+4)\text{Al} = 3\text{TiAl}_x + \text{Na}_5\text{AlF}_{14} + \text{Na}_3\text{AlF}_6$$  (3)

and,

$$\text{Ti} + x\text{Al} = \text{TiAl}_x$$  (4);

wherein $x=0-10$;

(2) uniformly mixing the raw materials with the reducing agent to obtain a mixture, pressing the mixture into lumps, placing the lumps into a vacuum reduction furnace, heating the placed lumps to 900-1300 °C under the vacuum condition or in the argon atmosphere, and performing the first-stage minothermic reduction and vacuum distillation; coagulating titanium-containing cryolite distilled out on a crystallizer at the low-temperature end of the vacuum reduction furnace, wherein the product comprises the main components of a mixture of Na$_5$AlF$_{14}$, Na$_3$AlF$_6$, AlF$_3$, and titanium-containing sub-fluoride, the residual product in the reduction furnace is TiAl$_x$;

(3) taking out the titanium-containing cryolite, grinding the titanium-containing cryolite until the particle size is lower than 1.0mm, using the aluminum powder as the reducing agent, uniformly mixing the ground titanium-containing cryolite with the aluminum powder to obtain a mixture, and pressing the mixture into lumps, wherein the feeding amount of the aluminum powder follows the rule that the melting point of the Al-Ti alloys produced by the second-stage minothermic reduction is less than or equal to the temperature of the second-stage minothermic reduction; placing the lumps in the reduction furnace, heating the placed lumps to 900-1300 °C in the argon atmosphere and preserving the temperature for 0.5-2h for the second-stage minothermic reduction, wherein according to the products obtained after the reduction reaction is ended and the temperature in the furnace body is reduced to normal temperature, white titanium-free cryolite is formed at the upper parts of the products and the aluminum titanium alloys are formed at the bottoms of the products, wherein the low-titanium aluminum titanium alloys are formed at the upper parts of the aluminum titanium alloys, which are called as the low-titanium aluminum titanium alloys; the aluminum titanium alloys with comparatively high content of titanium are formed at the lower parts of the aluminum titanium alloys, which are called as the high-titanium aluminum alloys; and

(4) dividing or separating the low-titanium aluminum titanium alloys and the high-titanium aluminum titanium alloys with a mechanical division method or a remelting and dumping method of the induction furnace, making the low-titanium aluminum titanium alloys divided out or separated out into powder as the reducing agent of the first-stage minothermic reduction, or remelting the aluminum titanium alloys produced by the second-stage minothermic reduction to make powder, and returning the powder back to the first-stage minothermic...
3. The method for producing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, according to claim 1 or 2, characterized in that when the first-stage aluminothermic reduction is performed for the first time, metal aluminum powder is used as a reducing agent, and the production proportion of the using dosage of the reducing agent is shown in the reaction formula in step (1).

4. The method for producing titanium or titanium aluminum alloys through two-stage aluminothermic reduction and obtaining titanium-free cryolite as byproducts, according to claim 1 or 2, characterized in that the vacuum distillation lies in that the reduction furnace is vacuumized to 10Pa or below, and distillation is performed for 1h or above under the condition that the temperature is 900-1300 °C.
titanium aluminum alloys (powder) \( \text{Na}_2\text{TiF}_6 / \text{Na}_2\text{TiF}_8, \text{NaF} \)

pressing the mixture into a lump

first-stage aluminothermic reduction

vacuum distillation \( \rightarrow \) metal titanium/titanium aluminum alloys

titanium-containing cryolite

aluminum (powder) \( \rightarrow \) mixing materials

pressing the mixture into a lump

second-stage aluminothermic reduction

titanium-free cryolite, titanium aluminum alloys

physical separation \( \rightarrow \) titanium-free cryolite

preparing titanium aluminum alloys to obtain powder

Fig. 1
Fig. 2
Fig. 3

- 1-Ti₃Al

Fig. 4

- 1-Na₃AlF₆
- 2-Na₅AlF₁₄
- 3-TiF₃
Fig. 5

Fig. 6
Fig. 9

Fig. 10
Fig. 11
## INTERNATIONAL SEARCH REPORT

### A. CLASSIFICATION OF SUBJECT MATTER

C22B 34/12 (2006.01) i; C22B 5/04 (2006.01) i; C22C 1/04 (2006.01) i; C22C 14/00 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22B 34, C22B 5, C22C 1, C22C 14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI, SPOAABS, VEN, CN-PAT, CNKI: fluoroaluminic acid, fluoritanic acid, thermite, cryolite, aluminum fluoride, reduc+

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CN 102534263 A (SHENZHEN SUNXING LIGHT ALLOY MATERIALS CO., LTD.), 04 July 2012 (04.07.2012), the whole document</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>CN 102560153 A (SHENZHEN SUNXING LIGHT ALLOY MATERIALS CO., LTD.), 11 July 2012 (11.07.2012), the whole document</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>CN 102818670 A (NORTHEASTERN UNIVERSITY), 14 September 2011 (14.09.2011), the whole document</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>CN 101967531 A (NORTHEASTERN UNIVERSITY), 09 February 2011 (09.02.2011), the whole document</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>JP H03243732 A (NIPPON MINING CO.), 30 October 1991 (30.10.1991), the whole document</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>US 5482691 A (UNIV. MELBOURNE), 09 January 1996 (09.01.1996), the whole document</td>
<td>1-4</td>
</tr>
</tbody>
</table>

* Special categories of cited documents:
  - “A” document defining the general state of the art which is not considered to be of particular relevance
  - “E” earlier application or patent but published on or after the international filing date
  - “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - “O” document referring to an oral disclosure, use, exhibition or other means
  - “P” document published prior to the international filing date but later than the priority date claimed
  - “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - “&” document member of the same patent family

- Further documents are listed in the continuation of Box C.

- See patent family annex.

Date of the actual completion of the international search:
24 March 2016 (24.03.2016)

Date of mailing of the international search report:
20 April 2016 (20.04.2016)

Name and mailing address of the ISA/CN:
State Intellectual Property Office of the P. R. China
No. 6, Xinxing Road, Jieminqiao
Haidian District, Beijing 100088, China
Facsimile No.: (86-10) 62019451

Authorized officer:
DANG, Xing

Telephone No.: (86-10) 62084417

Form PCT/ISA/210 (second sheet) (July 2009)
<table>
<thead>
<tr>
<th>Patent Documents referred in the Report</th>
<th>Publication Date</th>
<th>Patent Family</th>
<th>Publication Date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>US 2012304826 A1</td>
<td>06 December 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2617845 B1</td>
<td>03 September 2014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2498609 A</td>
<td>24 July 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 102534263 B</td>
<td>05 June 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2498609 B</td>
<td>04 March 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2525103 T3</td>
<td>17 December 2014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2013107111 A1</td>
<td>25 July 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 8864874 B2</td>
<td>21 October 2014</td>
</tr>
<tr>
<td>CN 102560153 A</td>
<td>11 July 2012</td>
<td>GB 2498611 B</td>
<td>03 June 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2617843 A1</td>
<td>24 July 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES 2534188 T3</td>
<td>20 April 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 2617843 B1</td>
<td>21 January 2015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 8864873 B2</td>
<td>21 October 2014</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 2013107108 A1</td>
<td>25 July 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 102560153 B</td>
<td>10 April 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB 2498611 A</td>
<td>24 July 2013</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 2012304823 A1</td>
<td>06 December 2012</td>
</tr>
<tr>
<td>CN 102181670 A</td>
<td>14 September 2011</td>
<td>CN 102181670 B</td>
<td>30 January 2013</td>
</tr>
<tr>
<td>CN 101967531 A</td>
<td>09 February 2011</td>
<td>CN 101967531 B</td>
<td>04 July 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5397375 A</td>
<td>14 March 1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 9214851 A1</td>
<td>03 September 1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 1274192 A</td>
<td>15 September 1992</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 650724 B</td>
<td>30 June 1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 6183894 A</td>
<td>21 July 1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AU 667432 B</td>
<td>21 March 1996</td>
</tr>
</tbody>
</table>

Form PCT/ISA/210 (patent family annex) (July 2009)
REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 20100173170 A1 [0002]
- CN 102534263 A [0002]
- CN 102560153 A [0002]
- CN 102534260 A [0002]