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(54) **METHOD FOR PREPARING METALLIC TITANIUM BY ELECTROLYZING MOLTEN SALT WITH TITANIUM CIRCULATION**

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(57) **ABSTRACT**

The present invention provides a method for preparing metallic titanium by electrolyzing molten salt with titanium circulation. The method mainly comprises reducing titanium tetrachloride ($TiCl_4$) to at least one of titanium trichloride ($TiCl_3$) and titanium dichloride ($TiCl_2$) in chloride molten salt by metallic titanium (Ti), and electrolyzing the at least one of $TiCl_3$ and $TiCl_2$ in the chloride molten salt to form metallic titanium. According to the method for preparing metallic titanium of the present invention, $TiCl_2$, and/or $TiCl_3$ are prepared and electrolyzed continuously without changing the surrounding medium, thereby simplifying process flow, reducing power consumption, and realizing industrialization.

METHOD FOR PREPARING METALLIC TITANIUM BY ELECTROLYZING MOLTEN SALT WITH TITANIUM CIRCULATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims foreign priority benefits under 35 U.S.C. §119(a)-(d) to CN 200910128311.5, filed on Mar. 30, 2009, which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a technical filed of non-ferrous metal metallurgy, more particularly, to a method for preparing metallic titanium by electrolyzing molten salt.

DESCRIPTION OF RELATED ART

[0003] Titanium (Ti) is a metal with superior performances, and has many advantages such as low specific gravity, high specific strength, good corrosion resistance and the like. Titanium alloy also has various excellent properties, for example, good high/low temperature resistance, nonmagnetic, shape memory characteristics, hydrogen absorption characteristics, superconductivity, and low damping characteristics and the like, thus it is an excellent constructional and/or functional material. Because of numerous advantages of titanium, titanium is called "Metal for outer space", "Marine Metal", "Metal of 21st century", etc. Consequently, in modern society, metallic titanium and its alloy are increasingly applied to national defense, chemical industry, metallurgy, medical treatment, industrial and agriculture production and other fields, especially to high and new technology industries.

[0004] However, it is pretty difficult to extract titanium. Currently, Kroll process is mainly used to produce sponge titanium in the world, and sponge titanium obtained by this process is generally purified by using a method of vacuum arc remelting. In particular, the process of producing sponge titanium by using the Kroll method comprises: firstly preparing titanium tetrachloride ($TiCl_4$) by chloridizing titanium dioxide (TiO_2) with addition of carbon (C) (see the following reaction equation (1)), obtaining sponge titanium by thermally reducing metallic magnesium (see the following reaction equation (2)), and then vacuum distilling the obtained sponge titanium to obtain commercial sponge titanium.

$$TiO_2+2Cl_2+2C \rightarrow TiCl_4+2CO \quad (1)$$

$$2Mg+TiCl_4 \rightarrow 2MgCl_2+Ti \quad (2)$$

[0005] During producing sponge titanium through the Kroll method, metallic Mg is obtained by electrolyzing $MgC\mathbf{1}_2$, and chlorine gas (Cl_2) obtained through electrolysis is used to prepare titanium chloride in turn, thus the whole production process comprises four main steps, i.e. chloridization of TiO_2, thermal reduction with magnesium, vacuum distillation and electrolysis of $MgCl_2$. The method is advantageous in high productivity, is capable of producing sponge titanium with good quality, and facilitates commercialization, thus it seems that this method is irreplaceable so far. On the other hand, the method has disadvantages such as long process flow, excessive steps, high power consumption, and difficulty in achievement of continuous processes, resulting in high manufacturing cost of sponge titanium. For example, the sponge titanium produced by the Kroll method has a price much higher than steel, and has a price per unit weight three times higher than that of metal aluminum. Furthermore, Kroll process has already been a considerably mature process at present, and little improvement in it can be made.

[0006] In this case, it is expected that a method for producing metallic titanium with a lower cost can be developed. At present, representative methods comprise: OS method, FFC process, QIT process, USTB method, PRP method, electrolysis of $TiCl_4$, Hunter method, Armstrong method (reduction with Na), SOM technique, producing Ti in vacuum, etc., but the industrialization has not been realized so far due to various disadvantages thereof.

[0007] Since $TiCl_4$ is used as a raw material in Kroll method, people all conceive of such a method of obtaining metallic titanium by directly electrolyzing $TiCl_4$. As a result, the disadvantage existing in reduction and distillation of Kroll method can be avoided. However, studies have shown that $TiCl_4$, the most common in titanium chlorides, has a pretty high vapor pressure at a temperature of molten salt electrolysis, and has a pretty small solubility (<1%) in melt, thus it is not feasible to use $TiCl_4$ as a raw material for directly electrolysis.

[0008] Studies on electrolysis of titanium chlorides mostly focus on a method of electrolyzing $TiCl_3$. Cordner and Warner from Australia reported their research results at the earliest; in particular, they obtained titanium crystals having a purity of 99% by electrolyzing a mixed molten salt of LiCl—KCl having $TiCl_3$ dissolved therein at a temperature of 550° C. However, it was difficult to realize industrialization of this method due to the following problems: on one hand, there is no available method of preparing $TiCl_3$; on the other hand, there is no proper method to supply $TiCl_3$ to an electrolytic bath. Additionally, $TiCl_3$ is decomposed due to easily absorbing moisture in air, causing pollution to the product.

[0009] In addition, there were other research results reported that metallic titanium was prepared by electrolyzing $TiCl_2$. However, it could not be industrialized yet, since there was not an available method for preparing $TiCl_2$, and it was difficult to add $TiCl_2$ to an electrolytic bath and to store it.

SUMMARY OF THE INVENTION

[0010] An object of the present invention is to overcome the disadvantages such as long process flow, high power consumption or impossibility in realizing industrialization in the conventional method for preparing metallic titanium. Thus, the present invention provides a method for preparing metallic titanium having simple process, low power consumption and being capable of realizing industrialization, by using Ti as a reducing agent to reduce titanium tetrachloride ($TiCl_4$) to titanium trichloride ($TiCl_3$) and/or titanium dichloride ($TiCl_2$).

[0011] The present invention provides a method for preparing metallic titanium by electrolyzing molten salt with titanium circulation comprising: i) reducing titanium tetrachloride ($TiCl_4$) to at least one of titanium trichloride ($TiCl_3$) and titanium dichloride ($TiCl_2$) in chloride molten salt by metallic titanium (Ti); and ii) electrolyzing the at least one of $TiCl_3$ and $TiCl_2$ in the chloride molten salt to form metallic titanium.

[0012] According to the present invention, the metallic titanium used in the step i) is a portion of metallic titanium obtained by electrolyzing the at least one of $TiCl_3$ and $TiCl_2$. A mole ratio of the metallic titanium for reducing to $TiCl_4$ is 1:1 to 1:3. The chloride molten salt is at a temperature higher than the eutectic temperature of the molten salt and lower than

vaporization temperatures and decomposition temperatures of salts for forming the molten salt. According to preferable embodiments of the present invention, the chloride molten salt is formed by melting two or more of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$. The chloride molten salt is at a temperature of 400° C. to 850° C.

[0013] According to the present invention, a small amount of sponge titanium, titanium powder or titanium scrap is added as a titanium source before electrolyzing so as to react with $TiCl_4$, thereby obtaining $TiCl_2$, $TiCl_3$, or a mixture of $TiCl_2$ and $TiCl_3$ used as electrolyte to induce electrolysis.

[0014] According to the present invention, the method further comprises enclosing an anode with a ceramic material article, and collecting Cl_2 liberated at the anode in the step ii).

[0015] According to the present invention, the method further comprises sequentially washing the generated titanium using hydrochloric acid aqueous solution having a concentration of 0.5 wt %-5 wt % and water after obtaining titanium by electrolyzing the at least one of $TiCl_2$ and $TiCl_3$, and drying the acid-washed and water-washed titanium in a vacuum oven.

[0016] According to the method for preparing metallic titanium of the present invention, $TiCl_2$, $TiCl_3$ or a mixture thereof is prepared and electrolyzed continuously without changing the surrounding medium, thus the problems in the preparation and feeding of $TiCl_2$ and/or $TiCl_3$ can be solved, no additional foreign substance is introduced in the electrolysis and the operation can be simplified. In addition, Cl_2 generated at the anode can be recovered and reused as a byproduct.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0017] The present invention provides a method for preparing metallic titanium (Ti). In particular, the present invention provides a method for preparing metallic titanium by electrolyzing titanium trichloride ($TiCl_3$) and/or titanium dichloride ($TiCl_2$) in a molten salt with titanium circulation.

[0018] According to the present invention, the method for preparing metallic titanium comprises the following steps:

[0019] 1) A suitable molten salt system of chloride is selected as an electrolyte, and in the system, $TiCl_3$, $TiCl_2$ or a combination thereof with a certain concentration is prepared by using Ti and $TiCl_4$. In particular, $TiCl_4$ is reduced to $TiCl_3$ and/or $TiCl_2$ by metallic Ti in the molten salt system (see the following reaction equations (3) and (4)).

$$Ti+TiCl_4 \rightarrow 2TiCl_2 \quad (3)$$

$$Ti+3TiCl_4 \rightarrow 4TiCl_3 \quad (4)$$

[0020] In this step, the chloride molten salt system is required to be dried to sufficiently remove various forms of moisture from the electrolyte.

[0021] In the present invention, titanium used at the early stage of electrolysis is the added metallic titanium such as sponge titanium, titanium powder, titanium scrap and the like, so that $TiCl_4$ is reduced to $TiCl_2$, $TiCl_3$ or a combination thereof. Titanium obtained by electrolyzing is used after the electrolysis process is recycled.

[0022] 2) $TiCl_2$, $TiCl_3$ or a combination thereof in the molten salt system is electrolyzed to generate metallic titanium and Cl_2 (see the following reaction equations (5) and (6)).

$$TiCl_2 \rightarrow Ti+Cl_2 \quad (5)$$

$$2TiCl_3 = 2Ti+3Cl_2 \quad (6)$$

[0023] According to the present invention, in the step of electrolyzing $TiCl_2$, $TiCl_3$ or a combination thereof, an anode of the electrolytic bath is made of graphite, and a cathode thereof is made of low carbon steel which is spaced apart from the anode by porous material. Herein, a porous material commonly used in the art can be used to enclose the anode so as to collect chlorine gas liberated from the anode, and can further prevent Ti^{2+}, Ti^{3+} in the molten salt from being oxidized to $TiCl_4$ by Cl_2 at an anode region. It is preferable to enclose the anode using a ceramic material. The conditions of electrolyzing $TiCl_2$ and/or $TiCl_3$ to Ti include a voltage of 2-5V, an anode current density of 0.05-0.6 A/cm^2, and a cathode current density of 0.1-5 A/cm^2.

[0024] 3) The product obtained at the metal cathode is washed by hydrochloric acid having a concentration of 0.5-5 wt %, subsequently by distilled water so that the filtrate contains no chloride ion (Cl^-), and then acid-washed and water-washed titanium is dried in a vacuum oven, thereby obtaining metallic titanium having a relatively high purity.

[0025] In addition, it should be noted that $TiCl_4$ is continuously or discontinuously introduced to the cathode during the electrolysis so that $TiCl_4$ contacts with the titanium at the cathode region. $TiCl_4$ may react with Ti to generate low valence-Ti chloride at a certain electrolysis temperature (i.e. the temperature of chloride molten salt, 400-850° C.), and the amount and velocity of the introduced $TiCl_4$ are controlled to ensure the electrolysis to proceed smoothly.

[0026] The chloride molten salt used in the present invention is a molten salt formed by melting two or more of alkali metal chlorides and alkali-earth metal chlorides, which has a temperature (i.e. electrolysis temperature) higher than the eutectic temperature of the molten salt and lower than vaporization temperatures and decomposition temperatures of the salts for forming the molten salt. In particular, alkali metal chlorides may be one or more of lithium chloride (LiCl), sodium chloride (NaCl) and potassium chloride (KCl), and alkali-earth metal chlorides may be one or more of magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), strontium chloride ($SrCl_2$) and barium chloride ($BaCl_2$). According to the present invention, the temperature of chloride molten salt is preferably in a range of 400° C. to 850° C. For example, in the present invention, KCl—LiCl system may be selected with a mole ratio of 41%:59%, which has an electrolysis temperature of 400V to 600V; NaCl—$CaCl_2$ system may also be selected with a mole ratio of 47.1%:52.9%, which has an electrolysis temperature of 550V to 750° C.; or NaCl—KCl system may also be selected with a mole ratio of 50%:50%, which has an electrolysis temperature of 700° C. to 850° C.

[0027] According to the present invention, $TiCl_3$ and $TiCl_2$ in the molten salt system are electrolyzed to generate metallic titanium at the cathode, a portion of which is used as a reducing agent, and to liberate Cl_2 at the anode, which is used as a byproduct to be recovered and reused.

[0028] In addition, according to the present invention, the concentration of low valence-Ti ion in the electrolyte will be reduced continuously as the electrolysis proceeds, and the concentration of low valence-Ti ion in the electrolyte is required to be controlled within a certain concentration range

in order to carry out the electrolysis process more smoothly, thus a predetermined amount of $TiCl_4$ may be introduced into the chloride molten salt periodically so that it reacts with a portion of titanium generated by electrolyzing to generate $TiCl_3$, $TiCl_2$ or a combination thereof. Low valence-Ti to be consumed by electrolyzing in the electrolyte may be added in time, titanium trichloride and/or titanium dichloride generated in the molten salt continue to be electrolyzed, and the above procedures are repeated, thereby building up a complete process of preparing metallic titanium by electrolyzing molten salt with titanium circulation.

[0029] Furthermore, it should be noted that there is only one molten salt system formed in the whole electrolysis, i.e. the molten salt system of chlorides of alkali metal and/or alkali earth-metal with $TiCl_2/TiCl_3$, such as NaCl—KCl—$TiCl_2/TiCl_3$ or $CaCl_2$—KCl—$TiCl_2/TiCl_3$, since titanium (Ti) is directly used as the reducing agent in the present invention. Therefore, no additional foreign substance is introduced in the electrolysis processes for preparing metallic titanium according to the present invention, and the operation parameters are kept the same in the whole electrolysis, thereby reducing cost and facilitating operation.

[0030] Hereinafter, the present invention will be further explained in connection with embodiments.

Embodiment 1

[0031] A chloride molten salt system was prepared. 117 g of NaCl (analytical reagent) and 149 g of KCl (analytical reagent) were mixed uniformly and dried in an oven at 120° C. for 24 hours, followed by dried in a reactor made of stainless steel under vacuum at 350° C.-450° C. for 48 hours so that various forms of moisture contained in the electrolyte was sufficiently removed.

[0032] In this system, an electrolyte having a Ti^{2+} concentration of 5% was prepared using sponge titanium and $TiCl_4$. The temperature was then increased to 700° C. in an Ar atmosphere to perform constant-current electrolysis. The anode was made of graphite and was spaced apart from the cathode by a porous material (preferably ceramic material) so as to facilitate collecting Cl_2 liberated from the anode, while avoiding the possibility of oxidizing Ti^{2+}, Ti^{3+} in the molten salt to $TiCl_4$ by Cl_2 liberated at the anode region. The cathode was made of low carbon steel. The electrolysis system had an anode current density of 0.3 A/cm^2, a cathode current density of 1.2 A/cm^2, an anode-cathode distance of 6 cm, a current intensity of 10 A, and 7 g of metallic titanium was obtained based on 80% of current efficiency after 1 hr of electrolysis time. At this time, 25 g of $TiCl_4$ was introduced to the cathode region in the molten salt to generate $TiCl_2$, and the generated $TiCl_4$ was electrolyzed for 1 hr under the conditions of a current intensity of 15 A and other parameters (i.e. the anode current density, the cathode current density, and the anode-cathode distance) the same as above.

[0033] After electrolysis, the cathode product was firstly washed by 1 wt % of hydrochloric acid to be colorless, and then washed by distilled water to have no chloride ion, followed by dried in a vacuum oven, thereby obtaining 12.08 g of titanium powder. The results obtained by analyzing a sample were as follows: a Ti content of 99.83%, an oxygen content of 0.085%, a carbon content less than 0.02%, and an iron content less than 0.045% by weight of the product. The current efficiency of $TiCl_2$ electrolysis was calculated as 89.98%.

Embodiment 2

[0034] After **40**g of LiCl, **46**g of NaCl and **22**g of KCl were weighed and mixed uniformly, a chloride molten salt system was prepared through dehydrating process in the same manner as that in Embodiment 1.

[0035] In this system, an electrolyte having a Ti^{3+} concentration of 6% was prepared using sponge titanium and $TiCl_4$. The temperature was then increased to 600° C. in an Ar atmosphere to perform constant-current electrolysis. By using the same anode and cathode devices as those in Embodiment 1, the electrolysis system had an anode current density of 0.5 A/cm^2, a cathode current density of 3 A/cm^2, an anode-cathode distance of 5 cm, and a current intensity of 6 A, and 4.6 g of metallic titanium was obtained based on 85% of current efficiency after 1 hr of electrolysis time. At this time, 55 g of $TiCl_4$ was introduced to the cathode region in the molten salt to generate $TiCl_3$, and the generated $TiCl_3$ was electrolyzed for 2 hr under the conditions of a current intensity of 8 A and other parameters the same as above.

[0036] After electrolysis, the cathode product was firstly washed by 5 wt % hydrochloric acid to be colorless, and then washed by distilled water to have no chloride ion, followed by dried in a vacuum oven, thereby obtaining 12.65 g of titanium powder. The results obtained by analyzing a sample were as follows: a Ti content of 99.72%, an oxygen content of 0.072%, a carbon content less than 0.02%, and an iron content less than 0.060% by weight of the product. The current efficiency of $TiCl_3$ electrolysis was calculated as 88.37%.

Embodiment 3

[0037] After 70 g of $CaCl_2$ and 80 g of KCl were weighed and mixed uniformly, a chloride molten salt system was prepared through dehydrating process in the same manner as that in Embodiment 1.

[0038] In this system, an electrolyte having a combined concentration of Ti^{2+} and Ti^{3+} of 10% was prepared using sponge titanium and $TiCl_4$. The temperature was then increased to 800° C. in an Ar atmosphere to perform constant-current electrolysis. By using the same anode and cathode devices as those in Embodiment 1, the electrolysis system had an anode current density of 0.1 A/cm^2, a cathode current density of 0.5 A/cm^2, an anode-cathode distance of 5 cm, and a current intensity of 12 A, and 8 g of metallic titanium was liberated based on 85% of current efficiency after 1 hr of electrolysis time. At this time, 65 g of $TiCl_4$ was introduced to the cathode region in the molten salt to generate a mixture of $TiCl_2$ and $TiCl_3$, and the generated $TiCl_2$ and $TiCl_3$ were electrolyzed for 2 hr under the conditions of a current intensity of 8 A and other parameters the same as above.

[0039] After electrolysis, the cathode product was firstly washed by 0.5 wt % hydrochloric acid to be colorless, and then washed by distilled water to have no chloride ion, followed by dried in a vacuum oven, thereby obtaining 10.20 g of titanium powder. The results obtained by analyzing a sample were as follows: a Ti content of 99.67%, an oxygen content of 0.09%, a carbon content less than 0.03%, and an iron content less than 0.05% by weight of the product. The current efficiency of $TiCl_2$ and $TiCl_3$ electrolysis in combination was calculated as 78.07%.

[0040] It can be known from the experiment results of Embodiments 1-3 that the contents of Ti in the products were all above 99.6%, which showed that the generated titanium powders have high purity and can be directly cast, and that the current efficiencies in electrolyzing were all above 87%, which showed that the method for preparing metallic titanium according to the present invention can produce metallic titanium with high yield and low power consumption.

[0041] It can be known from the above embodiments that $TiCl_2$, $TiCl_3$ or a mixture thereof is prepared and electrolyzed continuously in the method for preparing metallic titanium according to the present invention, without changing the surrounding medium, thereby solving the problems in the preparation and feeding of $TiCl_2$ and/or $TiCl_3$. In addition, Cl_2 generated at the anode can be recovered and reused as a byproduct. Therefore, compared with the conventional method for preparing metallic titanium by electrolyzing, the method for preparing metallic titanium by electrolyzing molten salt with titanium circulation according to the present invention can simplify preparation process, reduce power consumption, and realize industrialization.

[0042] The above description is only to illustrate some principles of the present invention, and does not limit the present invention to the scope as described above. Therefore, all available corresponding modifications and equivalents fall into the scope claimed in the present invention, without departing from the spirit and scope of the present invention as defined in the claims and their equivalents.

What is claimed is:

1. A method for preparing metallic titanium by electrolyzing molten salt with titanium circulation, comprising:

i) reducing titanium tetrachloride ($TiCl_4$) to at least one of titanium trichloride ($TiCl_3$) and titanium dichloride ($TiCl_2$) in chloride molten salt by metallic titanium (Ti); and

ii) electrolyzing the at least one of $TiCl_3$ and $TiCl_2$ in the chloride molten salt to form metallic titanium.

2. The method of claim **1**, wherein the metallic titanium used in the step i) is a portion of metallic titanium obtained by electrolyzing at least one of $TiCl_3$ and $TiCl_2$.

3. The method of claim **1**, wherein a mole ratio of the metallic titanium for reducing to $TiCl_4$ is 1:1 to 1:3.

4. The method of claim **1**, wherein the chloride molten salt is formed by melting two or more of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$.

5. The method of claim **4**, wherein the chloride molten salt is at a temperature higher than the eutectic temperature of the chloride molten salt and lower than vaporization temperatures and decomposition temperatures of salts for forming the chloride molten salt.

6. The method of claim **5**, wherein the chloride molten salt is at a temperature of 400° C. to 850° C.

7. The method of claim **1**, wherein a small amount of sponge titanium, titanium powder or titanium scrap is added as a titanium source before electrolyzing so as to react with $TiCl_4$, thereby obtaining $TiCl_2$, $TiCl_3$, or a mixture of $TiCl_2$ and $TiCl_3$ as electrolyte to induce electrolysis.

8. The method of claim **1**, further comprising: collecting Cl_2 liberated from an anode in the step ii).

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