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METHOD OF PRODUCING TITANIUM AND TITANIUM ALLOYS

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The present invention relates to a method of producing titanium and titanium alloys, and more particularly it relates to a method of producing iron-free titanium alloys from iron-containing raw materials.

It is known to produce titanium-containing aluminum alloys by electrolysis of a molten mass. As starting material for this process titanium dioxide is used, which together with aluminum oxide is introduced into the electrolyte. The composition of the electrolyte corresponds substantially to the composition of cryolite. Throughout this application the term "cryolite" is used to denote any material having substantially the same composition as cryolite. With the above described method it is possible to obtain aluminum-titanium alloys having a titanium content of up to about 1%. However, it is not possible according to the method described above to produce aluminum-titanium alloys with a titanium content which is substantially higher than 1%.

It is therefore an object of the present invention to provide a method for the production of aluminum-titanium alloys of any desired titanium content.

It is another object of the present invention to provide a method for the production of iron-free aluminum-titanium alloys from iron-containing raw materials.

It is a further object of the present invention to provide a method of producing aluminum-titanium alloys or also titanium metal in a simple and economical manner.

It is yet another object of the present invention to provide a method of separating in a raw material containing titanium dioxide and also containing iron or iron compounds, the titanium dioxide from iron.

Other objects and advantages of the present invention will become apparent from a further reading of the description and the appended claims.

With the above and other objects in view, the present invention mainly comprises in a method of separating titanium dioxide from iron in a raw material containing both, the steps of forming a molten mixture of cryolite and a raw material containing iron and titanium dioxide whereby the titanium dioxide dissolves in the cryolite forming a molten solution while the iron does not dissolve in the solution, and separating the solution from the undissolved iron.

The present invention also includes in a method of producing an alloy of aluminum and titanium the steps of forming a molten mixture including cryolite, titanium dioxide and aluminum, the amount of aluminum in the molten mixture being greater than the amount necessary to reduce all of the titanium dioxide, so as to reduce substantially all of the titanium dioxide to titanium by reaction with only a portion of the aluminum, thereby forming an alloy of the unreacted aluminum and the formed titanium, and recovering the thus-formed titanium-aluminum alloy.

The present invention also contemplates a method of producing an alloy of aluminum and titanium comprising the steps of forming a molten mixture of cryolite

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and a raw material containing iron and titanium dioxide whereby the titanium dioxide dissolves in the cryolite forming a molten solution while the iron does not dissolve in the solution, separating the molten solution from the undissolved iron, adding aluminum to the molten solution, the amount of aluminum added to the molten solution being greater than the amount necessary to reduce all of the titanium dioxide therein, so as to reduce substantially all of the titanium dioxide to titanium by reaction with only a portion of the aluminum, thereby forming an alloy of the unreacted aluminum and the formed titanium, and recovering the thus-formed titanium-aluminum alloy.

According to the present invention it is possible to produce titanium-aluminum alloys of any desired aluminum content as well as to produce titanium metal and to produce such titanium metal or titanium-aluminum alloys free of iron.

Titanium dioxide-containing raw materials such as bauxite, rutile, or ilmenite are preferably used as starting materials for the method of the present invention. While other titanium dioxide-containing raw materials may also be used, the above mentioned are usually of greatest commercial importance and in order to further illustrate the method of the present invention the usual composition of these materials is given in the following Table I.

TABLE I

30	Bauxite:	
	Ignition loss-----	11-13%.
	Al ₂ O ₃ -----	44-55%.
	Fe ₂ O ₃ -----	16-30%.
	SiO ₂ -----	1-5%.
35	TiO ₂ -----	2-4% (sometimes up to 10%).
	CaO-----	0.2-5%.
	P ₂ O ₅ , V ₂ O ₅ , Cr ₂ O ₃ , MnO ₂ , ZnO -----	less than 1%.
	Rutile:	
40	TiO ₂ -----	80-90%.
	Fe ₂ O ₃ -----	1-10%.
	Nb ₂ O ₅ -----	Sometimes in varying amounts.
	Ilmenite:	
45	TiO ₂ -----	45-52%.
	Fe ₂ O ₃ -----	up to 8%.
	FeO-----	depending on the percentage of TiO ₂ in the stoichiometric amount corresponding to the formula FeO.TiO ₂ .
50	MgO-----	up to 1%.

As can be seen from Table I, all of the customarily used raw materials contain iron oxides. Bauxite also contains water of hydration, as indicated by the ignition loss.

Raw materials containing water of hydration, such as bauxite, have first to be calcined in order to remove the water. The ignition loss of calcined material should be less than 0.5%.

It is also sometimes desirable, and especially in the case of ilmenite as raw material it is important to reduce at least a portion of the iron oxides in the raw material. When for instance bauxite is calcined in the presence of carbon-containing material, about 50% of the iron oxides are reduced to metallic iron and about 50% of the zinc oxides are reduced and volatilized. Rutile as raw material requires neither calcination nor reduction. In the case of ilmenite calcination is not necessary, however in order to separate the FeO of the ilmenite, the same is preferably molten in the presence of carbon-containing materials so as to reduce the iron oxides, whereby a very pure iron

ball containing about 96% iron and about 4% carbon is obtained.

The raw material after preliminary calcination or reducing treatment, if required, is then molten together with cryolite at a temperature of about 1,000° C.

In the molten mixture of cryolite and the raw material, practically all of the oxides present except Fe_2O_3 are dissolved. Since Fe_2O_3 is soluble in cryolite only to a very small extent, the iron oxide is separated from the molten mixture. In this manner a nearly complete separation between titanium dioxide which is dissolved in the molten cryolite, and iron which is present in the form of Fe_2O_3 is achieved. Thus, according to the present invention, it is possible in a simple and economical manner to completely separate titanium dioxide from iron contained in the raw material, by first reducing iron present in a form other than Fe_2O_3 to metallic iron which is separated from the molten raw material, and by then dissolving the Fe_2O_3 -containing raw material in molten cryolite whereby titanium dioxide and oxides of other metals except iron are dissolved in the molten cryolite, while Fe_2O_3 is not soluble therein to any substantial extent.

The titanium dioxide-containing cryolite is preferably then transferred from the furnace in which the same has been produced into another furnace in which an aluminothermic reaction takes place at a temperature of about 1,000° C. by introduction of metallic aluminum in the form of shavings, scrap or the like. The aluminum which is thus introduced into the molten cryolite containing dissolved titanium dioxide reduces titanium dioxide to metallic titanium which forms a metal sump at the bottom of the reaction vessel, while simultaneously an equivalent amount of aluminum is oxidized and dissolved in the molten cryolite in the form of aluminum oxide. In this manner it is possible to remove substantially all of the titanium from the molten cryolite, while for instance silicon dioxide originating from the raw material and also dissolved in the molten cryolite remains in the same.

By using an induction furnace for aluminothermic reduction of the titanium dioxide in the molten cryolite, it is also possible to agitate the metal sump which forms at the bottom of the furnace and which consists of titanium and usually also aluminum, by utilizing the electromagnetic pinch effect. The length of time during which the metal sump is to be electromagnetically agitated and the length of time for which the metals are to remain in the metal sump on the bottom of the induction furnace before being removed therefrom depends on the size of the furnace, respectively on the quantity of the molten material therein. It is important to avoid overheating of the bath which might cause excessive convection. It is also important to prevent the temperature from rising above about 1,000° C.

The maximum solubility of titanium dioxide in molten cryolite having a temperature of about 1,000° C. amounts to about 5% titanium dioxides. Consequently, depending on the titanium dioxide content of the raw materials, approximately 100 parts by weight of bauxite may be used to form a molten mixture with 100 parts by weight of cryolite, while in the case of rutile approximately 5 parts by weight, and in the case of ilmenite approximately 10 parts by weight of raw materials may be used to form a molten mixture with 100 parts by weight of cryolite.

When a raw material is used which, for instance like bauxite, contains a considerable quantity of impurities, all other metals which are present and which are more electro-positive than aluminum are also separated in the metal sump during the aluminothermic reaction. Surprisingly it has been found that contrary to theoretical expectations, due to the free reaction enthalpies of the oxides, also silicon dioxide is separated from titanium dioxide. While the titanium dioxide is nearly quantitatively reduced and thus removed from the molten solu-

tion, only a small portion of the silicon dioxide is thereby reduced.

Depending on the amount of metallic aluminum in relation to the amount of titanium dioxide contained in the molten cryolite, the metal sump on the bottom of the furnace is formed either of metallic titanium alone or of an alloy-forming mixture of titanium and aluminum. If metallic aluminum is introduced in an amount sufficient to reduce the titanium dioxide, substantially only metallic titanium is obtained, when the amount of aluminum which is introduced into the titanium dioxide-containing molten cryolite is increased to an amount greater than the amount necessary to reduce all of the dissolved titanium dioxide, then the aluminum which is not reacted with titanium dioxide also becomes part of the metal sump.

The metal sump is removed from time to time from the reaction vessel in which the aluminothermic reaction takes place. After tapping the metal sump, the relative amount of titanium in the aluminum-titanium alloy can be further increased by heating the metal to a temperature of at least 1,000° C. or even higher and by subsequent cooling whereby by liquation the alloy compound Al_3Ti having a titanium content of 37.2% or more is obtained. Those skilled in the art may easily understand from the known diagram of the binary alloy AlTi that the compound Al_3Ti precipitates in solid form under the given working conditions, and thus the more the cooling of the molten metal proceeds.

If care is taken that the temperature of the molten metal does not essentially fall below 900° C. the precipitated crystals of the compound Al_3Ti may be separated from the liquid melt by filtering, centrifuging or similar known methods.

The utilization of this knowledge for the present process is new.

By performing the liquation process and the heating of the metals to a temperature of higher than 1,000° C. after the metals have been removed from the reaction vessel in which the aluminothermic reaction takes place, evaporation losses of cryolite due to heating of the same above 1,000° C. are avoided.

The molten cryolite into which the titanium dioxide-containing raw material is introduced, as well as the molten cryolite having titanium dioxide dissolved therein to which aluminum is added for execution of the aluminothermic reaction with the dissolved titanium dioxide is preferably kept at a temperature of between 1,000 and 1,050° C. and it is generally advisable that the temperature of the molten cryolite should not be below 950° C. and not above 1,100° C. By reducing the temperature of the molten mass below the above indicated minimum figures, the molten cryolite may eventually solidify. In any event, even prior to solidification of the molten cryolite, the reduction of FeO contained in the raw material which may be effected by adding carbon-containing materials to the raw material and the molten cryolite, will be incomplete if the temperature falls below 950° C. By exceeding a temperature of 1,100° C., an uneconomically great loss of cryolite due to evaporation of the same is experienced.

It is also within the scope of the present invention to use the cryolite from which titanium dioxide has been removed by an aluminothermic reaction and which contains aluminum oxide, i.e. the cryolite which has been employed in the production of metallic titanium or titanium aluminum alloy, for forming the molten mixture of titanium dioxide-containing raw material and cryolite. Furthermore, the cryolite which, due to the aluminothermic reaction contains a considerable amount of aluminum oxide, may also be used for recovering metallic aluminum therefrom in a customary aluminum-producing electrolytic cell.

The following examples are given as illustrative of the method of the present invention only, the present in-

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vention however not being limited to the specific details of the examples.

Example 1

Bauxite of Greek origin containing 18% of Fe_2O_3 , 56% of alumina and 3.2% of titanium dioxide is first calcined under addition of coke in a rotary furnace. The thus-prepared bauxite which has lost its water of hydration and part of the iron oxide of which has been reduced, is then introduced into a bath of molten cryolite which is kept at 1,000° C. Equal amounts of cryolite and bauxite are thus mixed under stirring. The molten mixture remains for 20 minutes at a temperature of 1,000° C. Thereafter, the molten titanium dioxide-containing cryolite is tapped and removed to a second reaction vessel, preferably an induction furnace. After removal of the titanium dioxide-containing molten cryolite, there remains on the bottom of the vessel a body containing about 95% of the originally present Fe_2O_3 mainly in the form of Fe, as well as 16% of the originally present silicon dioxide. The material is free of titanium and titanium dioxide. Consequently all of the titanium dioxide contained in the raw material has been dissolved in the molten cryolite.

The molten cryolite which now contains about 5% titanium dioxide is then treated in a reduction furnace with a quantity of metallic aluminum, sufficient to reduce all of the titanium dioxide to metallic titanium, and to form with the metallic titanium an aluminum-titanium alloy of desired proportions of aluminum and titanium. During the aluminothermic reaction a temperature of between 950° C. and 1,000° C., preferably of 1,000° C. is maintained.

Example 2

The process of the present invention is executed with rutile as raw material substantially as described in Example 1. However calcination and carbon reduction of the raw material are omitted. In view of the higher percentage amount of titanium dioxide contained in rutile and in view of the maximum solubility of titanium dioxide in molten cryolite at 1,000° C. of about 5%, approximately 5 parts by weight of rutile are introduced into 100 parts by weight of molten cryolite.

Example 3

When ilmenite is used as raw material for the process of the present invention, calcination for removal of water of hydration is not required, however the ilmenite has first to be reduced with a carbon containing material in order to remove the FeO. Ilmenite is molten with a sufficient quantity of carbon containing material so as to effect this reduction, whereby an iron ball containing about 96% iron and about 4% carbon is formed. The raw material which is thus freed from FeO is then introduced into molten cryolite, the titanium dioxide of the raw material dissolved in the molten cryolite and the process of the present invention is further executed as described in Example 1.

Example 4

After the reducing melting of bauxite and cryolite the melt contained 0.56% TiO_2 . 50 kilograms of an aluminum alloy were added to 500 kilograms of the liquid melt. This melt was then stirred for ten minutes and let stand for sixty minutes at a temperature between 950 and 1000° C. After this time the melt contained only 0.01% of TiO_2 . Thus the titanium was reduced and alloyed with the aluminum down to this content.

In another case 15 kilograms of pure aluminum were added to 750 kilograms of melt. Thereby the content of TiO_2 in the melt was lowered beneath 0.006%.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this in-

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vention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. In a method of separating titanium dioxide from iron in a raw material containing titanium dioxide and at least one substance selected from the group consisting of metallic iron and iron compounds the steps of forming a mixture of a predetermined quantity of cryolite and said raw material at a predetermined temperature above the melting point of said cryolite so as to melt the same, said predetermined quantity of cryolite in relation to the quantity of titanium dioxide in said raw material, and said predetermined temperature of said molten mixture being chosen in such a manner as to substantially completely dissolve all of said titanium dioxide of said raw material in said molten cryolite, while said substance does not dissolve in the thus-formed solution; and separating said iron-free, titanium-dioxide containing solution from the remainder of said mixture.

2. In a method of separating titanium dioxide from iron in a raw material containing titanium dioxide and at least one substance selected from the group consisting of metallic iron and iron compounds and also containing water of hydration, the steps of calcining said raw material thereby removing said water of hydration; forming a mixture of a predetermined quantity of cryolite and of said calcined raw material, the quantity of cryolite being at least equal to about 20 times the quantity of titanium dioxide present in said raw material, and the temperature of up to 1000° C. also being higher than the melting point of cryolite and sufficiently high so that substantially all of the titanium dioxide will be dissolved in said molten cryolite forming a molten solution, while said substance does not dissolve in said solution; and separating said iron-free, titanium-dioxide containing solution from the remainder of said mixture.

3. In a method of separating titanium dioxide from iron in a raw material containing titanium dioxide and an iron-containing compound, the steps of melting said raw material in the presence of a carbon-containing material thereby reducing at least a portion of said iron-containing compound to iron; forming a mixture having a temperature of up to 1000° C. of a predetermined quantity of molten cryolite and of said raw material containing iron and titanium dioxide, said predetermined quantity of cryolite being so chosen in relation to the quantity of titanium dioxide in said raw material as to cause substantially complete dissolution of all of said titanium dioxide in said molten cryolite and to form a molten solution of said titanium dioxide in said cryolite, while said iron-containing compound and iron do not dissolve in said solution; and separating said iron-free, titanium-dioxide containing solution from the remainder of said mixture.

4. A method of producing an alloy of aluminum and titanium from a raw material containing titanium dioxide and at least one substance selected from the group consisting of metallic iron and iron compounds, comprising the steps of forming a mixture of a predetermined quantity of cryolite and of said raw material at a predetermined temperature above the melting point of said cryolite so as to melt the same, said predetermined quantity of cryolite in relation to the quantity of titanium dioxide in said raw material, and said predetermined temperature of said molten mixture being chosen in such a manner as to substantially completely dissolve all of said titanium dioxide of said raw material in said molten cryolite, while said substance does not dissolve in the thus-formed solution; separating said molten iron-free, titanium dioxide-containing solution from the remainder of said mixture; adding aluminum to said molten iron-free solution, the amount of aluminum added to said molten solution being greater than the amount necessary to reduce all of the

titanium dioxide therein, so as to reduce substantially all of said titanium dioxide to titanium by reaction with only a portion of said aluminum, thereby forming an alloy of the unreacted aluminum and the formed titanium; and recovering the thus-formed titanium-aluminum alloy.

5. A method of producing an alloy of aluminum and titanium from a raw material containing titanium dioxide and at least one substance selected from the group consisting of metallic iron and iron compounds, comprising the steps of calcining a raw material containing said substance, titanium dioxide and also containing water of hydration thereby removing said water of hydration; forming a mixture having a temperature of up to 1000° C. of a predetermined quantity of cryolite and said calcined raw material at a predetermined temperature above the melting point of said cryolite so as to melt the same, said predetermined quantity of cryolite in relation to the quantity of titanium dioxide in said raw material, and said predetermined temperature of said molten mixture being chosen in such a manner as to substantially completely dissolve all of said titanium dioxide of said raw material in said molten cryolite while said substance does not dissolve in the thus-formed solution; separating said molten iron-free, titanium dioxide-containing solution from said undissolved substance; adding in an induction furnace aluminum to said iron-free solution, the amount of aluminum added to said molten solution being greater than the amount necessary to reduce all of the titanium dioxide therein, so as to reduce substantially all of said titanium dioxide to titanium by reaction with only a portion of said aluminum, thereby forming below the molten mixture in said induction furnace a metal sump comprising the unreacted aluminum and the formed titanium, while simultaneously electromagnetically agitating said metal sump; recovering said metal sump from said induction furnace; adjusting the temperature of said recovered metal sump to about 1000° C.; slowly cooling

said metal sump, thereby forming by liquation an aluminum-titanium alloy of high titanium content; and recovering the thus-formed titanium-aluminum alloy.

6. A method of producing titanium from a raw material containing titanium dioxide and at least one substance selected from the group consisting of metallic iron and iron compounds, comprising the steps of forming a mixture of a predetermined quantity of cryolite and said raw material at a predetermined temperature above the melting point of said cryolite so as to melt the same, said predetermined quantity of cryolite in relation to the quantity of titanium dioxide in said raw material, and said predetermined temperature of said molten mixture being chosen in such a manner as to substantially completely dissolve all of said titanium dioxide of said raw material in said molten cryolite while said substance remains substantially undissolved in the thus-formed solution; separating said molten, iron-free, titanium dioxide-containing solution from said undissolved substance; adding aluminum to said iron-free, molten solution, the amount of aluminum added being substantially equal to the amount necessary to reduce all of said dissolved titanium dioxide to titanium, so as to transform substantially all of said titanium dioxide into titanium; and separating the thus-formed titanium from the remainder of the molten solution.

References Cited in the file of this patent

UNITED STATES PATENTS

451,405	Langley	Apr. 28, 1891
778,345	Weber	Dec. 27, 1904
1,533,505	Lowbowski	Apr. 14, 1925
2,439,216	McLellan	Apr. 6, 1948
2,451,490	Johnson	Oct. 19, 1948
2,451,492	Johnson	Oct. 19, 1948