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(54) **PRODUCTION OF TITANIUM**

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(57) **ABSTRACT**

A method of producing titanium semi-finished or ready-to-use products from titanium oxide powders and/or pellets is disclosed. The method produces products that are not affected adversely by levels of chlorine that have an impact on performance, particularly weldability, of products made by other methods.

PRODUCTION OF TITANIUM

[0001] This application is a continuation-in-part of and claims priority to PCT application PCT/AU2005/000907 published in English on Jan. 5, 2006 as WO 2006/000025 and to Australian application no. 2004903532 filed Jun. 28, 2004, the entire contents of each are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to the production of titanium metal and titanium metal alloys. The present invention relates particularly, although by no means exclusively, to a method of producing semi-finished or ready-to-use products, such as products in sheet, bar, tube and other forms, of titanium metal (which term includes titanium alloy) from titanium oxide powders and/or pellets.

BACKGROUND OF THE INVENTION

[0003] Currently, the Kroll and Hunter processes are the only commercial processes for producing titanium metal. These processes include chemical reduction of TiCl_4 with molten magnesium or sodium metal in a sealed reactor that has been evacuated and back-filled with an inert gas. In one process route, after reduction has been completed the material in the hot reactor is vacuum distilled to vaporise magnesium and sodium metal and chlorides. The reactor is allowed to cool and the solid material, i.e. titanium sponge, is then recovered from the reactor.

[0004] The titanium sponge may be processed by two process routes. One process route, a remelting route, includes melting the sponge in an inert atmosphere and forming ingots from the melt. Thereafter, the ingots are then converted into semi-finished or ready-to-use products, such as sheet, bar, tube and other forms, by hot working techniques such as forging, rolling and extrusion.

[0005] The other process route, a direct compaction route, includes crushing the sponge into particulate form, typically powders, and directly compacting particles into semi-finished or ready-to-use products using standard powder metallurgy processing, such as roll compaction.

[0006] One of the disadvantages of Kroll and Hunter products formed by the direct compaction route is poor weldability when welded using arc welding technology. The poor weldability has been attributed to high levels of chlorine, typically 1000-1500 ppm, in the products reacting with tungsten electrodes causing unstable arcs when arc welding the products. Poor weldability is not an issue with Kroll and Hunter products formed by the remelting route because the remelted products have substantially lower concentrations of chlorine. However, the remelting route is a more expensive processing route than the direct compaction route.

[0007] During the 1950s and 1960s E I Du Pont Nemours & Company developed: (a) technology for producing titanium metal powders that were suitable for the direct compaction route by powder metallurgical processing to form titanium metal products in semi-finished or ready-to-use forms, such as sheet, bar, tube and other forms; and (b) titanium metal powder processing technology for producing these end products.

[0008] The Du Pont technology is described in a number of US patents, including U.S. Pat. Nos. 2,984,6560, 3,072,

347, 3,478,136, and 3,084,042. The Kroll process was the source technology for the titanium sponge used by Du Pont in the Du Pont technology. Du Pont found that it could produce a friable titanium metal sponge that, when ground in the presence of a salt, produced a high purity acicular powder. Du Pont also found that the powder was well suited to be compacted directly in the nip of a rolling mill to produce sheet. In addition, Du Pont found that the powder was well suited to be compacted into billets which could then be processed in an extruder to produce semi-finished or ready-to-use products, such as bar, tube and other shapes.

[0009] However, Du Pont found that the Du Pont products had poor weldability. As is the case with conventionally produced directly compacted Kroll products, the poor weldability of the Du Pont products has been attributed to chlorine in the products. Du Pont has reported finding that the chlorine in the Kroll products volatilised rapidly during welding and caused a build-up of salts on tungsten welding electrodes that resulted in an unstable arc and consequently poor weldability. The chlorine was present in amounts greater than 50 ppm. Du Pont was not able to reduce the concentration of chlorine in the titanium metal or otherwise solve the poor weldability problem caused by the chlorine and consequently Du Pont did not commercialise the technology.

[0010] The applicant has been carrying out extensive research into an electrochemical method for reducing metal oxides, such as titania. The electrochemical method of the applicant is described, by way of example, in International application PCT/AU03/00306 in the name of the applicant. The disclosure in the International application is incorporated herein by cross-reference.

[0011] The electrochemical method of the applicant is an alternative technology to the Kroll and Hunter processes. The electrochemical method of the applicant, as described in the International application, is concerned with reducing a metal oxide in a solid state in an electrolytic cell of the type that includes an anode, a cathode, and a molten electrolyte that includes cations of a metal that is capable of chemically reducing the metal oxide.

[0012] The International application focuses particularly on reducing titanium oxides, such as titania, to titanium metal. The electrochemical method of the applicant, as described in the International application, is characterised by a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide can deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

[0013] The applicant has found surprisingly that, whilst the electrochemical method of the applicant produces titanium metal (which term includes titanium alloy) powders and/or pellets with high concentrations of chlorine, the chlorine does not have the same adverse impact on weldability of products made from the powders and/or pellets as is the case with chlorine in Kroll and Hunter products formed by the direct compaction route.

[0014] Experimental work carried out by the applicant indicates that products made from titanium metal produced by the electrochemical method of the applicant that has comparable chlorine concentrations to that of Kroll and

Hunter products formed by the direct compaction route, typically 1000-1500 ppm, has considerably better weldability than these Kroll products.

[0015] The applicant believes that the forms of the chlorine in the Kroll and Hunter products formed by the direct compaction route (predominantly magnesium and sodium chlorides) and in the applicant's products (predominantly calcium chlorides) is a relevant factor in the comparatively minor impact of chlorine concentration on weldability of the applicant's products. Specifically, the chlorine in the Kroll and Hunter products formed by the direct compaction route appears to be in a more volatile form that readily reacts with tungsten welding electrodes and makes the arcs unstable.

[0016] On the other hand, the chlorine in the applicant's products appears to be less volatile. This is a significant finding because it means that it may no longer be necessary to carry out extensive post-cell treatment of titanium metal powders and/or pellets made by the electrochemical method of the applicant to lower the chlorine concentration to levels, typically less than 50 ppm. These chlorine concentrations were thought to be necessary to achieve acceptable weldability of semi-finished or ready-to-use products made from titanium metal powders and/or pellets given the experience with Kroll and Hunter products made by the direct compaction route. Thus, in situations where weldability is important, the applicant's products may be a lower cost alternative to Kroll and Hunter products formed by the remelting processing route.

SUMMARY OF THE INVENTION

[0017] According to the present invention there is provided a method of producing titanium metal (which term includes titanium alloy) semi-finished or ready-to-use products from titanium oxide powders and/or pellets.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0018] The method according to the present invention includes the steps of: (a) electrochemically reducing titanium oxide powders and/or pellets in an electrolytic cell and producing titanium metal powders and/or pellets, which electrolytic cell includes an anode, a cathode, and a molten electrolyte that includes cations of a metal that is capable of chemically reducing titanium oxide and chloride anions; and (b) processing the titanium metal powders and/or pellets produced in step (a) and forming semi-finished or ready-to-use products having a concentration of chlorine of at least 100 ppm.

[0019] The chlorine concentration of the semi-finished or ready-to-use products produced by step (b) may be at least 200 ppm, typically may be at least 500 ppm, and more typically may be at least 1000 ppm without affecting adversely the weldability of the products. Typically, the chlorine concentration of the semi-finished or ready-to-use products is less than 2000 ppm.

[0020] Preferably, the titanium oxide powders and/or pellets have a size of 3.5 mm or less in a minor dimension of the powders and/or pellets. In a situation in which the powders and/or pellets are generally spherical, the "minor" dimension will be the diameter of the powders and/or pellets and the reference to "minor" dimension is not significant.

However, in a situation in which the powders and/or pellets are formed into selected shapes, such as discs, and have different dimensions, the reference to "minor" dimension is significant. For example, in a situation in which the pellet is disc shaped with a cylindrical side wall and flat top and bottom walls and a diameter of 20 mm and a thickness of 2 mm, identifying the dimension to be measured as the minimum dimension is an important consideration.

[0021] More preferably, the size of the titanium oxide powders and/or pellets is less than 2.5 mm. More preferably, the size of the powders and pellets is 1-2 mm.

[0022] Preferably, step (a) includes electrochemically reducing titanium oxide to titanium metal having a concentration of oxygen that is no more than 0.5% by weight. More preferably, the oxygen concentration is no more than 0.3% by weight. More preferably, the oxygen concentration is no more than 0.1% by weight.

[0023] Preferably, the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents. Preferably, step (a) includes maintaining the cell potential above the decomposition potential for CaO . Preferably, step (a) includes maintaining the cell potential below the decomposition potential for CaCl_2 .

[0024] Step (a) may be carried out on a batch, continuous, or semi-continuous basis. By way of example, step (a) may be carried out on a continuous or semi-continuous basis as described in International application PCT/AU03/001657 in the name of the applicant. The disclosure in the International application is incorporated herein by cross reference.

[0025] Preferably, step (b) includes processing the titanium metal powders and/or pellets produced in step (a) by quenching the titanium metal powders and/or pellets from an elevated temperature to a lower temperature at which there is a comparatively low rate of oxidation of titanium metal in air. Preferably, the lower temperature is ambient temperature.

[0026] Preferably, step (b) includes quenching the titanium metal powders and/or pellets with water. Step (b) may include processing the titanium metal powders and/or pellets produced in step (a) by compacting titanium metal powders and/or pellets into semi-finished or ready-to-use products.

[0027] In a situation in which the semi-finished or ready-to-use product is sheet, step (b) may include the steps of roll compacting the titanium metal powders and/or pellets into strip, sintering the strip to increase the mechanical properties of the strip, and cold rolling the sintered strip into sheet. Alternatively, step (b) may include processing the titanium metal powders and/or pellets produced in step (a) by powder metallurgically processing the titanium metal powders and/or pellets into semi-finished or ready-to-use products other than by roll compacting the powders and/or pellets.

[0028] Preferably, step (b) includes compacting the titanium metal powders and/or pellets to form semi-finished or ready-to-use products, such as products in sheet, bar, tube and other forms.

[0029] According to the present invention there is also provided a titanium metal semi-finished or ready-to-use product having a concentration of chlorine of at least 100 ppm produced by the above-described method.

[0030] As is indicated above, the chlorine concentration of the semi-finished or ready-to-use products may be at least 200 ppm, typically may be at least 500 ppm, and more typically may be at least 1000 ppm without affecting adversely the weldability of the products. Typically, the chlorine concentration of the semi-finished or ready-to-use products is less than 2000 ppm.

[0031] As is indicated above, the present invention is based on experimental work carried out by the applicant. The experimental work is summarised below.

[0032] The experimental work evaluated the weldability of:

[0033] (a) 15-20 mm×10 mm×2 mm titanium metal strips formed by the applicant from titanium metal pellets produced in accordance with the method described in International application PCT/AU03/00306 (samples NTC(1) NTC(3)),

[0034] (b) 45×15 mm×2 mm titanium metal strips formed by the applicant from commercially available Grade 2 titanium strip having a chlorine concentration of less than 20 ppm produced from Kroll and Hunter products formed by the remelting route (samples WM(1) and WM(2)), and

[0035] (c) 45×15 mm×2 mm titanium metal strips formed by the applicant from titanium metal sponge having a chlorine concentration of 1000-1500 ppm produced from Kroll and Hunter products formed by the direct compaction route (Samples WK(1) to WK (4)).

[0036] The NTC samples were prepared by the following procedure. The titanium metal pellets produced in accordance with the method described in International application PCT/AU03/0030 were of the order of 15 mm. The pellets were washed to remove retained electrolyte and thereafter processed to remove carbides adhered to the surface of the pellets. The pellets were then crushed to a particle size of 1-1.5 mm and washed again to remove further retained electrolyte. The particles were then die compacted to a density of 80-85% and thereafter sintered to increase the density to 85-90%. The particles were then cold rolled to form fully dense strips, i.e. strips having a density of at least 98%, and cut into the strips of the above-mentioned size.

[0037] The WM samples were formed by cutting small strips of the above-mentioned size from titanium strip having a chlorine concentration of less than 20 ppm produced from Kroll or Hunter products formed by the remelting route.

[0038] The WK samples were made from commercially available Kroll or Hunter powders formed by the direct compaction route into fully dense strips by the same sequence of die compacting, sintering, and cold rolling steps described above in relation to the NTC samples and then cut into the strips of the above-mentioned size.

[0039] In order to assess the weldability of the strips a state of the art GTAW welding power source (Migatronic Navigator 400 AC/DC) was used and a special inert gas shielding chamber and backing plate were constructed. A stepper motor drive was used to effect linear workpiece motion under the torch. The electrical parameters (voltage and current) were monitored using a computer based data acquisition system (AMC Weld check™). Arc appearance was monitored with an analogue CCD camera (Panasonic

F15) and high quality VHS(S) video recorder. The welding parameters are summarized in the following table.

Welding Parameters		
Power Source	Migatronic Navigator	400 AC/DC
Polarity	DCEN	
Shielding gas	Argon	12 L/min
Chamber gas	Argon	18 L/min
Chamber purge time		1 minute
Electrode Diameter		3.2 mm
Electrode Vertex Angle		120 deg
Arc length		2 mm
Travel speed		40 mm/min

[0040] An initial weld run was made on an austenitic stainless steel strip with approximately the same dimensions as the titanium metal strips to establish the welding parameters and shielding effectiveness.

[0041] The titanium metal strips (Samples NTC (1) to NTC(3), WM(1), WM(2), and WK (1) to WK(4)) were then butt welded at a nominal current of 25 amps.

[0042] Current and voltage were automatically recorded at 1 second intervals and video recordings of the arc were made using a macro telephoto lens and appropriate welding filters. The electrode tip condition was monitored directly from the video and by visual examination and grinding spark appearance after weld completion.

[0043] The results of the trials are summarized in the following table.

Sample Number	Comment
NTC(1)	Stable arc, less evidence of arc oscillation and voltage variation and better weld bead appearance than the WK samples.
NTC(2)	Same as NTC(1).
NTC(3)	Same as NTC(1).
WM(1)	Very stable arc, insignificant voltage variation, excellent weld bead appearance, and slight under penetration due to sample thickness.
WM(2)	Very stable arc, insignificant voltage variation, excellent weld bead appearance and consistent penetration.
WK(1)	Noticeable visible arc oscillation, confirmed by arc voltage variation, probable electrode contamination, pronounced ripple in weld bead appearance.
WK(2)	Severe arc oscillation, electrode contamination and melting, very poor weld appearance. Electrode reground before each trial, contamination apparent during grinding.
WK(3)	Same as WK(2).
WK(4)	Same as WK(2).

[0044] The titanium metal strips were welded using standard practice for titanium in an inert gas enclosure using GTAW.

[0045] Although it was originally intended to assess the weldability on the basis of porosity and embrittlement it was found that the samples provided could be clearly differen-

tiated by arc performance and electrode contamination. In the worst case, these effects would render the materials "unweldable" even before porosity is considered.

[0046] The samples NTC(1) TO NTC(3) produced in accordance with the present invention were weldable with good arc stability and good weld bead appearance.

[0047] The samples WM(1) and WM(2) made from commercially available low chlorine Grade 2 strip had excellent arc stability and weld bead appearance.

[0048] The samples WK(1) to WK(4) made from Kroll/Hunter powders and pellets having 1000-1500 ppm chlorine were easily identified by arc instability, unacceptable weld beads and severe electrode erosion. In addition, samples WK(1) and WK(2) showed pronounced weld bead ripple and some electrode erosion whilst samples WK(3) and WK(4) displayed more severe electrode erosion and instability.

[0049] Many modifications may be made to the preferred embodiment described above without departing from the spirit and scope of the present invention.

[0050] Since modifications within the spirit and scope of the invention may readily be effected by persons skilled within the art, it is to be understood that this invention is not limited to the particular embodiment described by way of example hereinabove.

1. A method of producing titanium products comprising:

(a) electrochemically reducing titanium oxide in an electrolytic cell that includes an anode, a cathode, and a molten electrolyte that includes cations of a metal that is capable of chemically reducing titanium oxide and chloride anions; and

(b) processing the titanium product of step (a) and forming one of a semi-finished or ready-to-use product having a concentration of chlorine of at least 100 ppm.

2. The method defined in claim 1 wherein the titanium oxide is in the form of a powder or pellet.

3. The method defined in claim 2 wherein the titanium oxide powder or pellet has a size of 3.5 mm or less in a minor dimension of the powder or pellet.

4. The method defined in claim 2 wherein the size of the titanium oxide powder or pellet is less than 2.5 mm in the minor dimension of the powder or pellet.

5. The method defined in claim 2 wherein the size of the powder or pellet is 1-2 mm in the minor dimension of the powder or pellet.

6. The method defined in claim 1 wherein step (a) includes electrochemically reducing titanium oxide to titanium metal having a concentration of oxygen that is no more than 0.5% by weight.

7. The method defined in claim 6 wherein the oxygen concentration is no more than 0.3% by weight.

8. The method defined in claim 6 wherein the oxygen concentration is no more than 0.1% by weight.

9. The method defined in claim 1 wherein the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents.

10. The method defined in claim 1 wherein the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents and step (a) includes maintaining the cell potential above the decomposition potential for CaO .

11. The method defined in claim 1 wherein the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents and step (a) includes maintaining the cell potential below the decomposition potential for CaCl_2 .

12. The method defined in claim 1 wherein step (a) is carried out on a batch, continuous, or semi-continuous basis.

13. The method defined in claim 1 wherein the processing in step (b) includes quenching from an elevated temperature to a lower temperature at which there is a comparatively low rate of oxidation of titanium metal in air.

14. The method defined in claim 13 wherein the lower temperature is ambient temperature.

15. The method defined in claim 13 wherein the quenching is conducted with water.

16. The method defined in claim 2 wherein the forming includes compacting the titanium metal powder or pellet into a semi-finished or a ready-to-use product.

17. The method defined in claim 16 wherein, in a situation in which the semi-finished or ready-to-use product is a sheet, step (b) includes the steps of roll compacting the titanium metal powders or pellet into a strip, sintering the strip to increase the mechanical properties of the strip, and cold rolling the sintered strip into a sheet.

18. The method defined in claim 2 wherein step (b) includes processing the powder or pellet produced in step (a) by powder metallurgically processing the metal powder or pellet into a semi-finished or a ready-to-use product other than by roll compacting the powder or pellet.

19. The method defined in claim 1 wherein the semi-finished or ready-to-use product includes products in sheet, bar, or tube forms.

20. A titanium metal semi-finished or ready-to-use product having a concentration of chlorine of at least 100 ppm produced by the method defined in claim 1.

21. The titanium metal semi-finished or ready-to-use product defined in claim 20 wherein the chlorine concentration is at least 200 ppm.

22. The titanium metal semi-finished or ready-to-use product defined in claim 20 wherein the chlorine concentration is at least 500 ppm.

23. The titanium metal semi-finished or ready-to-use product defined in claim 20 wherein the chlorine concentration is at least 1000 ppm.

24. The titanium metal semi-finished or ready-to-use product defined in claim 20 wherein the chlorine concentration is less than 2000 ppm.

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