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(54) PRODUCING TITANIUM ALLOY MATERIALS THROUGH REDUCTION OF TITANIUM TETRACHLORIDE

HERSTELLUNG VON MATERIALIEN AUS TITANLEGIERUNG DURCH REDUKTION VON TITANTETRACHLORID

PRODUCTION DE MATÉRIAUX EN ALLIAGE DE TITANE PAR RÉDUCTION DE TÉTRACHLORURE DE TITANE

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(73) Proprietor: **General Electric Company**
Evendale, Ohio 45215 (US)

(72) Inventors:
- **COPLAND, Evan H.**
  Clayton
  Victoria 3168 (AU)
- **STELLA, Albert Santo**
  Niskayuna
  New York 12309 (US)
- **OTT, Eric Allen**
  Cincinnati
  Ohio 45215 (US)
- **WOODFIELD, Andrew Philip**
  Cincinnati
  Ohio 45215 (US)
- **PRENTICE, Leon Hugh**
  Clayton
  Victoria 3168 (AU)

(74) Representative: **Openshaw & Co.**
8 Castle Street
Farnham, Surrey GU9 7HR (GB)

(56) References cited:
WO-A1-2009/129570 **WO-A1-2011/072338**
US-A- 2 745 735

- **HAIDAR J ET AL: "Direct production of alloys based on titanium aluminides", INTERMETALLICS, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 17, no. 8, 1 August 2009 (2009-08-01), pages 651 - 656, XP026042996, ISSN: 0966-9795, [retrieved on 20090306], DOI: 10.1016/J.INTERMET.2009.02.005**
- **OKABE T H ET AL: "Reaction pathways during metallothermic reduction of TiCl4 by utilizing chemical potential diagrams", TITANIUM EXTRACTION AND PROCES, XX, XX, 1 January 1997 (1997-01-01), pages 133 - 151, XP008087398**

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Description

PRIORITY INFORMATION

[0001] The present application claims priority to U.S. Provisional Patent Application Serial No. 62/411,205 filed on October 21, 2016.

FIELD OF THE INVENTION

[0002] The present invention relates generally to methods for producing titanium alloy materials through reduction of titanium tetrachloride ($TiCl_4$) in an $AlCl_3$-based reaction media. More particularly, the titanium alloy materials are formed through reducing the Ti^{4+} in the $TiCl_4$ to a lower valence form of titanium (e.g., Ti^{3+} and Ti^{2+}), followed by a disproportionation reaction of Ti^{2+}. Optionally, other alloying elements may also be formed from a salt to the alloy in a reduction and/or disproportionation process.

BACKGROUND OF THE INVENTION

[0003] Titanium alloy materials that include aluminum, such as titanium-aluminum (Ti-Al) based alloys and alloys based on titanium-aluminum (Ti-Al) inter-metallic compounds, are very valuable materials. However, they can be difficult and expensive to prepare, particularly in a powder form, and there are certain alloys inaccessible by traditional melt processes. This expense of preparation limits wide use of these materials, even though they have highly desirable properties for use in aerospace, automotive and other industries.

[0004] Reactors and methods for forming titanium-aluminum based alloys and inter-metallic compounds have been disclosed. For example, WO 2007/109847 teaches a stepwise method for the production of titanium-aluminum based alloys and inter-metallic compounds via a two stage reduction process, based on the reduction of titanium tetrachloride with aluminum. WO 2009/129570 discloses a reactor adapted to address one of the problems associated with the reactors and methods disclosed in WO 2007/109847, when such are used under the conditions that would be required to form low-aluminum titanium-aluminum based alloys.

[0005] However, the discussion of the chemical processes that actually occur in the processes described by WO 2007/109847 and WO 2009/129570 do not represent a complete understanding of the actual reactions occurring to form the metal alloy from metal halide precursors. WO 2011/072338 relates to a method for producing a titanium-aluminum alloy containing less than about 15wt% aluminum.

[0006] In view of these teachings, a need exists for a better understanding of the chemical processes for producing titanium aluminum alloys through reduction of titanium tetrachloride $TiCl_4$, as well as improved processing techniques for such reactions.

[0007] The above references to the background art do not constitute an admission that such art forms a part of the common general knowledge of a person of ordinary skill in the art.

BRIEF DESCRIPTION OF THE INVENTION

[0008] Aspects and advantages of the invention will be set forth in part in the following description, or may be obvious from the description, or may be learned through practice of the invention. The present invention is defined in the accompanying claims.

[0009] A process is generally provided for producing a titanium alloy material, such as a titanium aluminum alloy. In one embodiment, the process includes adding $TiCl_4$ to an input mixture at a first reaction temperature such that at least a portion of the Ti^{4+} in the $TiCl_4$ is reduced to Ti^{3+} to form a first reaction product. The input mixture may include aluminum, and, optionally $AlCl_3$ and/or optionally one or more alloying element halides. After $TiCl_4$ addition is stopped, the first reaction product may be heated at drying conditions to complete reduction of Ti^{4+} or to remove substantially all of any remaining $TiCl_4$ to form a first intermediate mixture that is an $AlCl_3$-based salt solution that includes Ti^{3+}. The first intermediate mixture may then be heated to a second reaction temperature such that at least a portion of the Ti^{3+} is reduced to a second intermediate mixture that is an $AlCl_3$-based salt solution that includes Ti^{2+}. The second intermediate mixture is then further heated to a third reaction temperature such that the Ti^{2+} forms the titanium alloy material via a disproportionation reaction.

[0010] In one embodiment, the process for producing a titanium alloy material, may include: reducing an amount of $TiCl_4$ with an amount of aluminum, $AlCl_3$ and at least one metal chloride at a temperature below 180 °C to form a first intermediate product comprising Ti^{3+}; and reducing the first intermediate product to a temperature below 900 °C to form a titanium aluminum alloy.

[0011] In one embodiment, the process for producing a titanium-containing material may include: mixing Al particles, $AlCl_3$ particles, and, optionally, particles of at least one other alloy element chloride to form an input mixture; adding $TiCl_4$ to the input mixture; reducing Ti^{4+} in the $TiCl_4$ in the presence of the input mixture at a first reaction temperature (e.g., lower than about 180 °C) to form a first intermediate mixture comprising Ti^{3+}.

[0012] These and other features, aspects and advantages of the present invention will become better understood with reference to the following description and appended claims. The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the description, serve to explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth in the specification, which makes reference to the appended Figs., in which:

FIG. 1 shows a diagram of an exemplary process according to one embodiment of the present disclosure;

FIG. 2 shows a schematic of one exemplary embodiment of the stage 1 reaction of the exemplary process of FIG. 1;

FIG. 3 shows a schematic of one exemplary embodiment of the stage 2 reactions and post-processing of the resulting titanium alloy material of the exemplary process of FIG. 1; and

FIG. 4 shows an equilibrium stability diagram (Gibbs energy per mole of Cl_2 vs. absolute *T*) for Ti-Cl and Al-Cl systems overlaid to show reducing potential of metallic Al. Only pure elements (Ti, Al and Cl_2) and pure salt compounds ($TiCl_4$, $TiCl_3$, $TiCl_2$ and $AlCl_3$) are considered because there is no assessed thermodynamic data for salt solution phases ($TiCl_4(AlCl_3)_x$, $TiCl_3(AlCl_3)_x$, $TiCl_2(AlCl_3)_x$).

[0014] Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0015] Reference now will be made in detail to embodiments of the invention, one or more examples of which are illustrated in the drawings. Each example is provided by way of explanation of the invention, not limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment can be used with another embodiment to yield a still further embodiment. Thus, it is intended that the present invention covers such modifications and variations as come within the scope of the appended claims and their equivalents.

[0016] As used herein, the terms "first", "second", and "third" may be used interchangeably to distinguish one component from another and are not intended to signify location or importance of the individual components.

[0017] Chemical elements are discussed in the present disclosure using their common chemical abbreviation, such as commonly found on a periodic table of elements. For example, hydrogen is represented by its common chemical abbreviation H; helium is represented by its common chemical abbreviation He; and so forth.

[0018] As used herein, the term "titanium alloy material", or the like, is to be understood to encompass an alloy based on titanium or an alloy based on a titanium intermetallic compound and optionally other additional alloying elements in addition to Ti and Al. Similarly, the term "titanium-aluminum alloy", or the like, is to be understood to encompass an alloy based on titanium-aluminum or an alloy based on titanium-aluminum intermetallic compounds and optionally other additional alloying elements in addition to Ti and Al.

[0019] As used herein, the term "aluminum chlorides" is to be understood to refer to aluminum chloride species or a mixture of such aluminum chloride species, including $AlCl_3$ (solid, liquid, or vapor) or any other Al-Cl compounds or ion species (e.g., AlCl, $AlCl_2$, $(AlCl_4)^-$, Al_2Cl_6 and (Al_2Cl_7)). The use of $AlCl_x$ refers to the term "aluminum chlorides" and is to be understood to refer to such aluminum chloride species or a mixture of such aluminum chloride species, no matter the stoichiometric ratio.

[0020] As used herein, the term "titanium chloride" is to be understood to refer to titanium trichloride ($TiCl_3$) and/or titanium dichloride ($TiCl_2$), or other, combinations of titanium and chlorine, but not to $TiCl_4$, which is referred to herein as titanium tetrachloride. In some sections of the specification, the more general term "$TiCl_x$" may be used, which is to be understood to refer to titanium chloride species and forms of titanium tetrachloride ($TiCl_4$), titanium trichloride ($TiCl_3$), titanium dichloride ($TiCl_2$) and/or other combinations of titanium and chlorine in solid, liquid or vapor forms. Since various solution phases and titanium chloride complexes also exist, the specific oxidation state of the Ti ion (e.g., Ti^{2+}, Ti^{3+}, and Ti^{4+}) in a general phase (i.e., salt mixture) is referred to herein rather than any specific chemical compounds.

[0021] As used herein, the term "alloying element halides" refers to an alloying element ion coupled with a halide (e.g., a chloride, a fluoride, a bromide, an iodide, or an astatide). The alloying element can be any element that would be included within the final titanium alloy material, such as metals and other elements. The "alloying element halide" can be represented by MX_x, where M is the alloying element ion and X is a halide (i.e., a halogen ion), no matter the stoichiometric ratio (represented by x). For example, an alloying element chloride can be represented by MCl_x.

[0022] Processes are generally provided for producing titanium alloy materials (e.g., titanium aluminum alloys) through reduction of $TiCl_4$, which includes a titanium ion (Ti^{4+}). More particularly, the titanium alloy materials are formed through reducing the Ti^{4+} in the $TiCl_4$ to a lower valence form of titanium (e.g., Ti^{3+} and Ti^{2+}), followed by a disproportionation reaction of Ti^{2+} to form the titanium alloy material. It is noted that the valence form of titanium (e.g., Ti^{4+}, Ti^{3+}, and/or Ti^{2+}) may be present in the reaction and/or intermediate materials as a complex with other species in the mixture (e.g., chlorine, other elements, and/or other species such as chloro-aluminates, metal halo aluminates, etc.), and may not necessarily be present in pure form of $TiCl_4$, $TiCl_3$, and $TiCl_2$, respec-

tively. For example, metal halide aluminates can be formed by MX_x complexed with $AlCl_3$ in these intermediates, such as described below. Generally, $AlCl_3$ provides the reaction media that the reactive species (e.g., Ti^{4+}, Ti^{3+}, Ti^{2+}, Al, Al^{+}, Al^{2+}, Al^{3+}, also alloying element ions) for all reactions. Without wishing to be bound by any particular theory, it is believed that the existence of salt solutions in the stage 1 and stage 2 reactions allows for the Ti^{4+} reduction to Ti^{3+} and for the Ti^{3+} reduction to Ti^{2+} to occur in the condensed state (e.g., solid and liquid), such as at temperatures of about 700 °C or less (e.g., about 300 °C or less).

[0023] Fig. 1 shows a general flow diagram of one exemplary process 100 that reduces $TiCl_4$ to a titanium alloy material. The process 100 is generally shown in sequential stages: reaction precursors at 101 (including forming an input mixture at 102), a stage 1 reaction at 104, a stage 2 reaction at 106, and post processing at 108.

I. Reaction Precursors

[0024] The reaction precursors for the stage 1 reaction 104 in the process 100 of FIG. 1 include, at a minimum, $TiCl_4$ and an input mixture that includes aluminum (Al), either alone or with additional chloride components. In one embodiment, the reaction precursors include an input mixture as a solid material at ambient conditions (e.g., about 25 °C and 1 atm), and $TiCl_4$ in liquid form. Additional materials (e.g., $AlCl_3$ and/or other alloying element halides) may be included in the reaction precursors at various stages of process 100, such as included within the input mixture, within the $TiCl_4$, and/or as a separate input into the stage 1 and/or stage 2 reactions. That is, one or more alloying element chlorides can optionally be inputted into the stage 1 reaction materials (e.g., into the input mixture if a solid, into the $TiCl_4$ if a liquid or a soluble solid material, and/or directly into the stage 1 reaction vessel independently), dissolved into another component of the input materials, and/or may optionally be inputted into the Stage 2 reaction materials. In certain embodiments, particularly where the alloying element halide is added to liquid $TiCl_4$ (e.g., soluble within), the liquid $TiCl_4$ may be filtered so as to remove any particulate within the liquid stream. Such a filter may, in particular embodiments, refine the liquid stream by removing oxygen species from the liquid, since the solubility of oxygen and oxygenated species is extremely low. As such, filtering of the $TiCl_4$ liquid (with or without any alloying element halide dissolved therein) may tailor the chemistry of the liquid and remove oxygen species therefrom.

[0025] For example, the reaction precursors can include some or all alloy elements to achieve a desired chemistry in the titanium alloy material. In one embodiment, the alloying element halide (MX_x) may be an alloying element chloride (MCl_x). Particularly suitable alloying elements (M) include, but are not limited to, vanadium, chromium, niobium, iron, yttrium, boron, manganese, molybdenum, tin, zirconium, silicon, carbon, nickel, copper, tungsten, beryllium, zinc, germanium, lithium, magnesium, scandium, lead, gallium, erbium, cerium, tantalum, osmium, rhenium, antimony, uranium, iridium, and combinations thereof.

[0026] As shown in FIG. 1 at 102, the input mixture is formed from aluminum (Al), optionally an aluminum chloride (e.g., $AlCl_3$), and optionally one or more alloying element chloride. Without wishing to be bound by any particular theory, it is presently believed that $AlCl_3$ is useful as a component in the input mixture, but is not necessarily required if there is an alloying element chloride that is soluble or miscible in the $TiCl_4$ at the stage 1 reaction conditions to form $AlCl_x$ in situ from the alloying element chloride and aluminum. In one embodiment, $AlCl_3$ is included as a material in the input mixture. However, in another embodiment, the input mixture may be substantially free from $AlCl_3$. As used herein, the term "substantially free" means no more than an insignificant trace amount present and encompasses "completely free" (e.g., "substantially free" may be 0 atomic % up to 0.2 atomic %). If $AlCl_3$ is not present in the input mixture, then Al and other metal chlorides are present and utilized to form $AlCl_3$ such that the stage 1 reaction can proceed.

[0027] If in a solid state at ambient conditions, one or more alloying element chlorides (MCl_x) can optionally be included into the input mixture to form the input mixture. Particularly suitable alloying element chlorides in a solid state to be included with the aluminum and optional $AlCl_3$ include, but are not limited to, VCl_3, $CrCl_2$, $CrCl_3$, $NbCl_5$, $FeCl_2$, $FeCl_3$, YCl_3, BCl_3, $MnCl_2$, $MoCl_3$, $MoCl_5$, $SnCl_2$, $ZrCl_4$, $NiCl_2$, CuCl, $CuCl_2$, WCl_4, WCl_6, $BeCl_2$, $ZnCl_2$, LiCl, $MgCl_2$, $ScCl_3$, $PbCl_2$, Ga_2Cl_4, $GaCl_3$, $ErCl_3$, $CeCl_3$, and mixtures thereof. One or more of these alloy element chlorides can also be included at other stages in the process including, but not limited to, titanium tetrachloride and/or after Stage 1.

[0028] In one embodiment, the input mixture is in the form of a plurality of particles (i.e., in powder form). For example, the input mixture is formed by milling a mixture of the aluminum (Al), optionally an aluminum chloride (e.g., $AlCl_3$), and optionally one or more alloying element halides (e.g., alloying element chlorides). The material of the input mixture can be combined as solid materials and milled together to form the plurality of particles having a mixed composition. In one embodiment, a mixture of aluminum particles, optionally aluminum chloride particles, and optionally particles of one or more alloying element chlorides is mixed and resized (e.g., milled) together to form the plurality of particles of the input mixture. For example, the aluminum particles can be aluminum particles that have a pure aluminum core with an aluminum oxide layer formed on the surface of the particles. Alternatively, the aluminum particles can include a core of aluminum and at least one other alloying element or a master alloy of aluminum and an alloying

element. The aluminum particles may have any suitable morphology, including a flake like shape, substantially spherical shape, etc.

[0029] Since the aluminum particles generally form a layer of aluminum oxide on the surface of the particles, the milling process is performed in an atmosphere that is substantially free of oxygen to inhibit the formation of any additional aluminum oxides within the input mixture. For example, the milling process can be performed in an inert atmosphere, such as an argon atmosphere, having a pressure of about 93.3 kPa (700 torr) to about 506.6 kPa (3800 torr). Without wishing to be bound by any particular theory, it is believed that a reaction between $AlCl_3$ and surface Al_2O_3 during milling of Al(s) such that $AlCl_3$ converts Al_2O_3 to AlOCl (e.g., via $Al_2O_3 + AlCl_3 \rightarrow 3AlOCl$). The Al_2O_3 surface layer protects the underlying Al(s), and then converting this Al_2O_3 surface layer to AlOCl during milling allows Al to dissolve and diffuse into the salt, as Al^+ of Al^{2+}. Without wishing to be bound by any particular theory, it is believed that having a partial pressure of oxygen below that required to stabilize Al_2O_3 (i.e., in an inert atmosphere) allows for these reactions to convert Al_2O_3, which is otherwise very stable in oxygen. As such, the resulting particles are an "activated" Al powder.

[0030] Additionally, reducing the size of the particles allows the surface area of the particles to increase to expand the availability of aluminum surface area in the subsequent reduction reactions. The plurality of particles may have any suitable morphology, including a flake like shape, substantially spherical shape, etc. In particular embodiments, the plurality of particles of the input mixture have a minimum particle dimension on average of about 0.5 μm to about 25 μm (e.g., about 1 μm to about 20 μm), which is calculated by averaging the minimum dimension of the particles. For example, in one embodiment, the flake may define a planar particle having dimensions in an x-y plane, and a thickness in a z-dimension with the minimum dimension on average of about 0.5 μm to about 25 μm (e.g., about 1 μm to about 20 μm), while the x- and y-dimensions having larger average sizes. In one embodiment, milling is performed at a milling temperature of about 40 °C or less to inhibit Al particle agglomeration.

[0031] Milling can be achieved using a high intensity process or a low intensity process to produce the plurality of particles of the input mixture, such as using a ball milling processes, grinding processes, or other size reduction methods.

II. Stage 1 Reaction (reduction of Ti^{4+} to Ti^{3+})

[0032] As stated, the reaction precursors include, at a minimum, $TiCl_4$ in liquid or vapor form and an input mixture in powder form that includes aluminum (Al), and may include additional materials (e.g., $AlCl_3$ and/or other alloying element chlorides). The $TiCl_4$ may be a pure liquid of $TiCl_4$ or liquid mixed with other alloy chlorides. Mixtures of $TiCl_4$ and another alloy chloride(s) may be heated, in certain embodiments, to ensure that the resulting solution is not saturated, which could result in components precipitating out of the solution. An example of mixed liquid precursors includes a mixture of $TiCl_4$ and VCl_4 to form a vanadium containing titanium alloy. Various metal chlorides (i.e., $AlCl_3$, VCl_4, VCl_3, MCl_x, etc) may be dissolved into $TiCl_4$(l), which can be represented by $(TiCl_4)_x(AlCl_3)_y(MCl_x)_z$ where M is any suitable metal, as discussed herein, and x, y, and z are the mole fraction of the particular components of the salt solution. Such a salt solution can be generally defined in short hand as [Ti^{4+}:salt], with the brackets [ ] represent the material as a solution phase having Ti^{4+} as the major species of solvent and "salt" represents all of the minor species or alloying elements.

[0033] These reaction precursors are added together for reduction of the Ti^{4+} to Ti^{3+} at the stage 1 reaction 104. For the stage 1 reaction, the reaction precursors are heated to a first reaction temperature that is high enough to cause the chemical reduction but low enough to inhibit liquid $TiCl_4$ from forming. For example, the stage one reaction may be performed with the reaction precursors heated to a first reaction temperature that is about 165 °C or less (e.g., about 100 °C to about 165 °C, such as about 140 °C to about 160 °C). In one embodiment, the input mixture is heated to the first reaction temperature prior to adding the $TiCl_4$ to the input mixture. Alternatively or additionally, the $TiCl_4$ can be added to the input mixture simultaneously with heating the input mixture to the first reaction temperature.

[0034] Without wishing to be bound by any particular theory, it is believed that the aluminum (e.g., in a form of metallic aluminum or a salt of aluminum such as $AlCl_3$ and/or $AlCl_x$) present the input mixture reduces the Ti^{4+} in the $TiCl_4$ to Ti^{3+} by an alumino-thermic process at the first reaction temperature, where $AlCl_3$ serves as the reaction media in the form of a $AlCl_3$ salt solution. Additionally, it is believed that Ti^{4+} and Al dissolve in $AlCl_3$ and in $TiCl_3(AlCl_3)_x$ formed from the input mixture reaction products, such that the Ti^{4+} and Al can react. It is also believed that Al dissolves in the salt as Al^+ or Al^{2+}, and that these Al species diffuse to the Ti^{4+} and react to form new $TiCl_3(AlCl_3)_x$ reaction product. Finally, it is believed that Al(s) dissolves into the salt solution through an $AlCl_3$ or AlOCl surface layer on the Al(s). For example, without wishing to be bound by any particular theory, it is believed that the Ti^{4+} in the $TiCl_4$ is reduced to Ti^{3+} in the form of $TiCl_3$ complexed with metal chloride(s), such as $TiCl_3(AlCl_3)_x$ with x being greater than 0, such as greater than 0 to 10 (e.g., x being 1 to 5), which is either a continuous solid solution between $TiCl_3$ and $AlCl_3$ or two solutions $TiCl_3$-rich $TiCl_3(AlCl_3)_x$ and $AlCl_3$-rich $AlCl_3(TiCl_3)_x$ where both solutions have similar crystal structures. Thus, it is believed that substantially all of the Ti^{3+} species formed are in the form of such a metal chloride complex, instead of pure $TiCl_3$.

[0035] As such, the resulting reaction product is an

$AlCl_3$-based salt solution that includes the Ti^{3+} species. Similar to the [Ti^{4+}:salt] discussion above, various metal chlorides (i.e., $AlCl_3$, VCl_4, VCl_3, MCl_x, etc.) dissolve in $TiCl_3$ (solid or liquid), which may be represented by $(TiCl_3)_x(AlCl_3)_y(MCl_x)_z$ where M is any suitable metal and x, y, and z represent the mole fraction of the salt solution. $TiCl_3(AlCl_3)_x$ is a sub-set of the larger solution phase, even though all of the alloying element chlorides, MCl_x, dissolve into this solution phase. Additionally, Ti^{4+} also dissolves into this solution phases, which can be described as the Cl-rich side of the phase field. As $TiCl_4$ is added into the reaction mixture, at some point there may be more $TiCl_4/TiCl_3$ than $AlCl_3$, making the salt $TiCl_3$-rich. Such a salt solution can be generally defined in short hand as [Ti^{3+}:salt], with the brackets [ ] represent the material as a solution phase having Ti^{3+} as the major species of solvent and "salt" represents all of the minor species or alloying elements.

[0036] This reaction can be performed as $TiCl_4$ is added in a controlled manner to the input mixture at the first reaction temperature. For example, the $TiCl_4$ can be added continuously or in a semi batch manner. In one embodiment, excess Al is included in the reaction to ensure substantially complete reduction of Ti^{4+} to Ti^{3+} and for subsequent reductions. As such, $TiCl_4$ may be added to obtain a desired Ti/Al ratio to produce a desired salt composition.

[0037] During the reaction, the input mixture can substantially remain a solid at the first reaction conditions (e.g., the first reaction temperature and the first reaction pressure). In particular embodiments, the stage 1 reaction is performed in a plow reactor, a ribbon blender, or another liquid/solid/vapor reactor. For example, the Ti^{4+} reduction reaction can be performed in an apparatus to reflux during the reaction phase and/or to distill after the reaction phase any unreacted $TiCl_4$ vapor for continued reduction and/or to prevent loss of $TiCl_4$ (g) during the reaction.

[0038] The stage 1 reaction is performed in an inert atmosphere (e.g., comprising argon). As such, the uptake of oxygen (O_2), water vapor (H_2O), nitrogen (N_2), carbon oxides (e.g., CO, CO_2, etc.) and/or hydrocarbons (e.g., CH_4, etc.) by aluminum and/or other compounds can be avoided during the reduction reaction. The inert atmosphere has a pressure of 1 atmosphere (e.g., about 101 kPa (760 torr)) and about 5 atmospheres (e.g., about 506.6 kPa (3800 torr)), such as about 101 kPa (760 torr) to about 199.9 kPa (1500 torr). Although pressures less than about 101kPa (760 torr) could be utilized in certain embodiments, it is not desirable in most embodiments due to possible oxygen, water, carbon oxide and/or nitrogen ingress at such lower pressures. For example, the inert atmosphere has a pressure of 0.92 atmosphere (e.g., about 93.3 kPa (700 torr)) and about 5 atmospheres (e.g., about 506.6 kPa (3800 torr)), such as about 93.3 kPa (700 torr) to about 199.9 kPa (1500 torr).

[0039] Following the stage 1 reaction reducing Ti^{4+} to Ti^{3+}, the first reaction product can be dried at drying conditions to remove substantially all of any remaining unreacted $TiCl_4$ (due to kinetic limitations) to form an intermediate mixture. For example, the first reaction product can be dried by heating and/or vacuum conditions. In one embodiment, any entrained $TiCl_4$ is removed from the first reaction product by heating to a temperature that is above the boiling point of $TiCl_4$ (e.g., about 136 °C) but below the temperature where Ti^{3+} is further reduced (e.g., over about 180 °C), such as a drying temperature of about 160 °C to about 180 °C (e.g., about 160 °C to about 170 °C).

[0040] However, it is noted that Al is capable of reducing Ti^{4+} to Ti^{3+} and Ti^{3+} to Ti^{2+} at all temperatures, including below 20 °C. The temperatures identified above are due to kinetic limitations and/or solid state transport in the reaction products. Also, without wishing to be bound by any particular theory, it is believed that the Ti^{3+} to Ti^{2+} reduction cannot occur while Ti^{4+} exists in the stage 1 reaction products due to the Gibbs phase rule and phase equilibria of the Ti-Al-Cl-O system. That is, Al oxidation can drive both reduction steps at the same temperature, but the sequential aspect of these reactions is due to the present belief that Ti^{4+} and Ti^{2+} cannot exist at the same time in the same location of an isolated system. Thus, the reactions are sequentially performed such that substantially all of the Ti^{4+} is reduced to Ti^{3+} prior to the formation of Ti^{2+} in the system. Thus, the reduction process is performed by the presently disclosed methods in a sequential nature.

[0041] After drying the first reaction mixture and before heating the intermediate mixture to the second reaction temperature for the stage 2 reaction described below, the intermediate mixture containing the [Ti^{3+}:salt] can be stored, such as in an inert atmosphere prior to further reaction. In one embodiment, the intermediate mixture containing the Ti^{3+} complexes can be cooled to a temperature below about 100 °C, such below about 50°C, or below about 25 °C, for storage.

[0042] Referring to FIG. 2, a process schematic 200 of one exemplary embodiment of the reaction precursors at 101 (including forming an input mixture at 102) and the stage 1 reaction at 104 of the exemplary process 100 of FIG. 1. In the embodiment shown, a first liquid storage tank 202 and an optional second liquid storage tank 204 are in liquid communication with a liquid mixing apparatus 206 so as to supply liquid reaction precursors thereto via supply line 208. Generally, the first liquid storage tank 202 includes liquid 201 of $TiCl_4$, as a pure liquid of $TiCl_4$ or liquid mixed with other alloying element chlorides. Valve 210 and pump 212 control flow of liquid 201 from the liquid storage tank 202 into the liquid mixing apparatus 206. Similarly, the second liquid storage tank 204 is in liquid communication with the liquid mixing apparatus 206 so as to supply liquid reaction precursors thereto via supply line 214. The second liquid storage tank 204 includes, in one embodiment, a liquid 205 of at least one alloying element chloride. Valve 216 and pump 218 control flow of liquid 205 from the liquid storage tank 204 into the liquid

mixing apparatus 206.

[0043] Also as shown in FIG. 2, solid reaction precursors are supplied to the ball milling apparatus 220 from an Al storage apparatus 222, an optional aluminum chloride (e.g., $AlCl_3$) storage apparatus 224, and optionally one or more alloying element chloride storage apparatus 226. Although shown as a ball milling apparatus 220, any suitable size reduction apparatus (e.g., a milling apparatus) can be utilized in accordance with this process. As shown, the aluminum chloride storage apparatus 224 and the one or more alloying element chloride storage apparatus 226 are supplied via an optional mixing apparatus 228 to the milling apparatus 220. From the milling apparatus 220, an input mixture 221 is provided to the stage 1 reaction apparatus 230 via a hopper 232. Additionally, the mixed liquid from the liquid mixer 206 is added to the stage 1 reaction apparatus 230 in a controlled manner via supply tube 234 with the flow of the mixed liquid controlled by the pump 236 and valve 238. Optionally, the aluminum chloride storage apparatus 224 and the one or more alloying element chloride storage apparatus 226 can be supplied via an optional mixing apparatus 228 directly to the hopper 232.

[0044] Within the stage 1 reaction apparatus 230, the Ti^{4+} is reduced to Ti^{3+} at the conditions described above to form a first reaction product. The first reaction product can be dried at the end of the stage 1 reaction apparatus 230, such as in a drying zone 229 having drying conditions, such as discussed above, to remove substantially all of any remaining $TiCl_4$ via condenser 231 to form an intermediate mixture (including Ti^{3+}, such as in the form of $TiCl_3$ complexed with metal chloride(s), such as $TiCl_3(AlCl_3)_x$) supplied to product line 244 for further reduction of titanium. As shown, any remaining $TiCl_4$ or liquid mixture can be evaporated and optionally recycled (e.g., via a distillation process, not shown) in recycle loop line 246. In alternative embodiments, the size reduction apparatus can be integrated within the stage 1 reaction apparatus 230. In one embodiment, the conditions of the stage 1 reaction apparatus 230 during reaction keep liquid in reactor or condense vapor to return to stage 1 reactor. Then, during drying the condenser is heated to a temperature above the boiling point of the liquid mixture to allow for drying.

[0045] The intermediate mixture (including Ti^{3+}, such as in the form of $TiCl_3$ complexed with other materials) can be stored after drying but before further reduction processes. In one embodiment, the intermediate mixture is stored in an inert atmosphere to inhibit and prevent the formation of any aluminum oxides, other oxide complexes, or oxy-chloride complexes within the intermediate mixture.

III. Stage 2 Reactions (Ti^{3+} to Ti^{2+} and Ti^{2+} to Ti alloy)

[0046] At the stage 2 reactions at 106 in the process 100, the Ti^{3+} and any alloying elements halides MX_x of the intermediate mixture are reduced to Ti^{2+} and M sub-halides by heating to a second reaction temperature and reacting with Al present as solid Al or as an Al species dissolved in a complex, and then the Ti^{2+} is reduced to Ti alloy via an endothermic disproportionation reaction at a third reaction temperature that is greater than the second reaction temperature. The metal sub-halides are also reduced via Al reduction to form base alloying metal M at temperatures within the range of the stage 2 process. In one embodiment, these reactions can be performed in sequential reactions at different temperatures in a single step reaction or as separate steps as a two-step process or more (e.g., in stages as the temperature is increased).

[0047] Without wishing to be bound by any particular theory, it is believed that the aluminum (e.g., in a form of metallic aluminum or a salt of aluminum such as $AlCl_3$ and/or $AlCl_x$) present the intermediate mixture reduces the Ti^{3+} in the $TiCl_3$ complexed with metal chloride(s), such as $TiCl_3(AlCl_3)_x$, to Ti^{2+} at the second reaction temperature. For instance, without wishing to be bound by any particular theory, it is believed that the reaction may form Ti^{2+} in a $TiCl_2$ complexed with metal chloride(s), to form salt solutions based on titanium aluminum chloride complexes, such as $TiAlCl_5$, $Ti(AlCl_4)_2$), or a mixture thereof, with optionally additionally alloying elements or element halides, or element chloro-aluminates.

[0048] Without wishing to be bound by any particular theory, it is generally believed that there are three forms of $TiCl_2$ possible: (1) substantially pure $TiCl_2$ that only dissolves a small amount of anything, (2) $TiAlCl_5$(s) that also does not dissolve much of anything else and is probably only stable up to about 200 °C, and (3) $\{Ti(AlCl_4)_2\}n$ that is likely an inorganic polymeric material existing as a liquid or gas, glassy material and fine powder (long chain molecules). That is, $\{Ti(AlCl_4)_2\}_n$ has a large composition range (e.g., n can be 2 to about 500, such as 2 to about 100, such as 2 to about 50, such as 2 to about 10) and dissolves all the alloy element chlorides. In one particular embodiment, the gaseous $\{Ti(AlCl_4)_2\}_n$ helps remove unreacted salt from the Ti-alloy particles (e.g., at a low temperature in a later stage of the reaction). As a result, the reaction product comprising Ti^{2+} is a phase based on the complex between $TiCl_2$ and $AlCl_3$ (e.g., $Ti(AlCl_4)_2$, etc.). Such a complex can be a salt solution defined in short hand as [Ti^{2+}:salt], with the brackets [ ] represent the material as a solution phase having $AlCl_3$ as the major species of solvent, Ti^{2+} and "salt" represents all of the minor species or alloying elements.

[0049] The reduction of Ti^{3+} to Ti^{2+} is performed at second reaction temperature of about 180 °C to about 250 °C . Without wishing to be bound by any particular theory, it is believed that at least a portion of the Ti^{2+} is in the form of $TiCl_2$ complexed with metal chloride(s).

[0050] Without wishing to be bound by any particular theory, it is believed that $AlCl_3$ is chemically bound in $TiCl_3(AlCl_3)_x$, $TiAlCl_5$, and $\{Ti(AlCl_4)_2\}_n$ in this process. Due to its significant chemical activity (e.g., < 1), $AlCl_3$ does not evaporate as would be expected for pure $AlCl_3$, and there is no significant $AlCl_3$ evaporation until reaction tempera-

tures reach or exceed about 600 °C. Thus, $AlCl_3$ provides the reactor medium to allow the reaction to take place, and $AlCl_3$ provides the chemical environment that stabilizes the Ti^{2+} ion and allows conversion of Ti^{3+} to Ti^{2+} at reaction temperatures less than about 250 °C (e.g., about 180 °C to about 250 °C).

[0051] After the Ti^{3+} of the $TiCl_3$ complexed with metal chloride(s) (e.g., in the form of $TiCl_3$-$(AlCl_3)_x$ and/or $TiAlCl_6$ (g)) is reduced to Ti^{2+} (e.g., in the form of $TiCl_2$ complexed with metal chloride(s)), the Ti^{2+} can be converted to Ti alloy via a disproportionation reaction. In one embodiment, $TiAlCl_6$ (g) may be present to help remove Ti^{3+} by-products from the Ti-alloy formation and/or recycling Ti^{3+} within the reaction chamber. The third reaction temperature has an upper temperature limit of about 900 °C. The Ti^{2+} is reduced to Ti alloy via a disproportionation reaction at a third reaction temperature of about 300 °C up to about 900 °C (e.g., about 300 °C to about 900 °C, such as about 500 °C to about 900 °C). Without wishing to be bound by any particular theory, it is believed that keeping the third reaction temperature below about 900 °C ensures that any oxygen contaminants present in the reaction chamber remain stable volatile species that can be driven off so as to limit oxygen in the resulting Ti alloy product. On the other hand, at reaction temperatures above 900 °C, the oxygen contaminants are no longer in the form of volatile species making it more difficult to reduce residual oxygen. Any other volatile species, such as oxychlorides, chlorides, and/or oxides containing carbon, can be removed by thermal distillation.

[0052] Generally, this reaction of Ti alloy formation can be separated into an alloy formation stage via disproportionation reaction (e.g., at a disproportionation reaction temperature about 250 °C to about 650°C) and a distillation stage (e.g., at a distillation temperature of about 650 °C to about 1000 °C).

[0053] For example, the Ti alloy formation can be divided into two processes: nucleation and particle growth (which may also be referred to as particle coarsening). During nucleation, the first Ti alloy forms from the [Ti^{2+}:SALT] at lower temperatures (e.g., about 250 °C to about 400 °C). The local composition of the salt (component activities), surface energy, and kinetics of disproportionation determine the resulting Ti alloy composition. Then, the particle growth occurs where the Ti alloy continues to grow from the [Ti^{2+}:SALT] at higher temperatures (e.g., about 400 °C to about 700 °C) in the condensed state and at temperatures of greater than 700 °C (e.g., about 700 °C to about 1000 °C) in as a gas solid reaction. These higher temperature reactions (e.g., greater than about 700 °C) can also be described as a distillation process where Cl is removed from the Ti alloy product, which is occurring simultaneously with the Ti alloy particle grown. Both of these processes are based on a disproportionation reaction, but could produce Ti alloys of different compositions. It is also noted that there is a disproportionation reaction for both Ti and Al in the reaction process: Ti^{2+} = 1/3[Ti] + 2/3Ti^{3+} and Al^{+} = 2/3[Al] + 1/3Al^{3+}. The equipment design for this process may be configured for independent control of the residence time at each temperature (e.g., thermal zone), which may help control the process.

[0054] In one embodiment, the intermediate mixture having the Ti^{2+} is maintained at the third reaction temperature until substantially all of the Ti^{2+} is reacted to the titanium alloy material. In the reaction, any Ti^{3+} formed during the disproportionation reaction can be internally recycled to be reduced to Ti^{2+} by thermos alumic reduction and further reacted in a disproportionation reaction. Additionally, Ti^{4+} (e.g., in the form of $TiCl_4$) may be formed by a competing Ti disproportionation reaction, which can be evacuated out of the reaction system as a gas by-product for continued reaction (e.g., reducing back to Ti^{3+} then to Ti^{2+}) or as a take-off by-product (e.g. carried out via an inert gas counter flow).

[0055] The stage 2 reactions (e.g., Ti^{3+} to Ti^{2+} and/or Ti^{2+} to Ti alloy) are performed in an inert atmosphere, such as comprising argon and/or substantially free of oxygen, nitrogen, moisture, hydrocarbons, and other impurities. In particular embodiments, the inert atmosphere has a pressure between about 1 atmosphere (e.g., about 101 kPa (760 torr)) and about 5 atmospheres (e.g., about 506.6 kPa (3800 torr)), such as about 101 kPa (760 torr) to about 199.9 kPa (1500 torr). As shown in FIG. 1, an inert gas can be introduced as a counter flow to regulate the reaction atmosphere, and to carry gaseous titanium chloride complexes and $AlCl_x$ away from the titanium alloy material and back into the reflux reaction zone of Ti^{3+} to Ti^{2+} and/or Ti^{2+} to Ti alloy. Additionally or alternatively, any $TiCl_4$ produced during the reaction may be carried out of the reactor as a take-off by-product. Thus, the reaction can be performed efficiently without any significant waste of Ti materials.

[0056] For example, the Ti is formed in a Ti-Al based alloy from the Ti^{2+} in salt solution (condensed and vapor) by disproportionation and the formation of Ti^{3+} in a salt solution (condensed and vapor), as described above (Ti^{2+} = 1/3[Ti] + 2/3Ti^{3+}). Similar corresponding disproportionation reactions are occurring simultaneously for Al^{+}/Al/Al^{3+} and other alloying elements dissolved in the salt solutions and forming in the Ti-Al based alloys. Thus, pure-Ti products are not formed during these disproportionation reactions. Without wishing to be bound by any particular theory or specific reaction sequence, the Ti-Al alloy formation is believed to occur via an endothermic reaction which involves the input of heat to drive the reaction to towards the Ti-Al alloy products.

[0057] The Ti-Al alloy formed by the reactions above can be in the form of an Ti-Al alloy mixed with other metal materials. Alloying elements may also be included in the titanium chloro-aluminates consumed and formed in the disproportionation reactions above. Through control of the system, fine, uniformly alloyed particulates can be produced of the desired composition through control of at least temperature, heat flux, pressure, gas flowrate,

$Al/AlCl_3$ ratio, and particle size/state of aggregation of the $Ti^{2+}/Al/AlCl_3$ mixture entering the stage 2 reaction.

[0058] As a reaction product of the stage 2 reactions, a titanium alloy material is formed that includes elements from the reaction precursors and any additional alloying elements added during the stage 1 reaction and/or the stage 2 reactions. For example, Ti-6Al-4V (in weight percent), Ti-4822 intermetallic (48Al, 2Cr, and 2Nb in atomic percent) can be formed as the titanium alloy material. In one embodiment, the titanium alloy material is in the form of a titanium alloy powder, such as a titanium aluminide alloy powder (e.g., Ti-6Al-4V, Ti-4822, etc.).

[0059] Referring to FIG. 3, a process schematic 300 of one exemplary embodiment of the stage 2 reaction at 106 and post processing at 108 of the exemplary process of FIG. 1. In the embodiment shown, the intermediate mixture is supplied via line 244 into a stage 2 reaction apparatus 302 after passing through an optional mixing apparatus 306. Within the stage 2 reaction apparatus 302, the Ti^{3+} of the intermediate mixture is reduced to Ti^{2+} by heating to a second reaction temperature, and then the Ti^{2+} is reduced to Ti alloy via a disproportionation reaction at a third reaction temperature that is greater than the second reaction temperature, as described in greater detail above. The exemplary stage 2 reaction apparatus 302 shown is a single stage reactor that includes a zone heating apparatus 304 surrounding a reaction chamber 306. The zone heating apparatus 304 allows for a variable, increasing temperature within the reaction chamber 306 as the intermediate mixture flows through reaction chamber 306. For example, the zone heating apparatus 304 can have a first reaction temperature towards the input end of the reaction chamber 306 (e.g., a first zone 308) and a second reaction temperature at the output end of the reaction chamber 306 (e.g., a second zone 310). The apparatus may also have a gradation in reaction temperature between 2 or more zones. The apparatus may also have a gradation in reaction temperature between 2 or more zones. This process is designed to allow for uniform mixing and continuous flow through the temperature gradient

[0060] Vapor reaction products, such as $AlCl_3$, Al_2Cl_6, $TiCl_4$, $TiAlCl_6$, AlOCl, $TiOCl(AlOCl)_x$, etc., can be removed from the reaction chamber 306 utilizing a counter-flow gas stream of inert gas. For example, an inert gas can be supplied to the second zone 310 of the reaction chamber 306 via a supply tube 312 from an inert gas supply 313. The inert gas can then flow counter to the solid materials progressing through the reaction chamber 306 to carry gaseous titanium chloride complexes away from the titanium alloy material forming in the second zone 310 and back into the lower temperature reaction of Ti^{3+} to Ti^{2+} occurring in the first zone 308. Additionally or alternatively, gaseous titanium chloride complexes produced during the reaction may be carried back in the reaction chamber 306 where they condense at lower temperature, and thus control the Ti stoichiometry of the reacting salts. Any remaining $AlCl_x$ and any $TiCl_4$ formed during disproportionation are removed from the reactor 306 by vent line 315, which may be a heated line to prevent condensation and blockage, and collected in condenser/sublimator 317 (e.g., a single-stage condenser or a multi-stage condenser) for recapture. Thus, the reaction can be performed efficiently without any significant waste of Ti materials.

[0061] The use of a low impurity inert gas (e.g., low impurity argon gas, such as a high purity argon gas) process gas is preferred to minimize the formation of oxychloride phases such as $TiOCl_x$ and $AlOCl_x$ in the process, and to ultimately inhibit the formation of TiO, TiO_2, Al_2O_3, and/or TiO_2-Al_2O_3 mixtures. Other inert gases can also be used, such as helium or other noble gases, which would be inert to the reaction process.

[0062] In-process monitoring can be used to determine reaction completion by measuring the balance, temperature, pressure, process gas chemistry, output product chemistry, and by-product chemistry.

[0063] The titanium alloy material can be collected via 314 to be provided into a post processing apparatus 316, such as described below. The post processing step may be performed in a separate apparatus or may be performed in the same or connected apparatus that is used for the Stage 2 process.

IV. Post Processing of Titanium Alloy

[0064] After formation, the titanium alloy material may be processed at 108. For example, the titanium alloy powder can be processed for coarsening, sintering, direct consolidation, additive manufacturing, bulk melting, or spheroidization. For example, the titanium alloy material may be high temperature processed to purify the Ti alloy by removing residual chlorides and/or allowing diffusion to reduce composition gradients, such as at a processing temperature of about 800 °C or higher (e.g., about 800 °C to about 1,000 °C).

[0065] In one embodiment, the high temperature processing also continues disproportionation reactions to produce Ti alloy from any residual Ti^{2+}.

EXAMPLES

[0066] The process described here can be explained in the most general and simplest terms by inspecting the overlaid stability diagrams (Gibbs energy per mole of Cl_2 vs. absolute T) for the Ti-Cl and Al-Cl systems as shown in Fig. 4.

[0067] While alloy or salt solutions are not considered, it shows the maximum available chemical energy in the Ti-Al-Cl system. At temperatures below 1000K (730°C) Ti^{4+}, as $TiCl_4$(l,g), can be reduced to Ti^{3+}, as $TiCl_3$(s), and subsequently to Ti^{2+}, as$TiCl_2$(s), by the oxidation of Al metal to Al^{3+} (in the form of $AlCl_3$(s), Al_2Cl_6(g) and / or $AlCl_3$(g)), but Ti^{2+} cannot be reduced to metallic Ti by oxidation of metallic Al. In this process, metallic titanium alloyed with Al[Ti] can form in the temperature range 523

to 923K (250 to 650 °C) via disproportionation of Ti^{2+} (Ti^{2+} = 1/3[Ti] + 2/3Ti^{3+}) in a salt solution [Ti^{2+}:salt] producing [Ti] particles and Ti^{3+} as a salt solution [Ti^{3+}:salt] or vapour. Al-driven reduction of Ti^{4+} and Ti^{3+} is an exothermic process and is carried out in the stage one, S1, reactor and low temperature part of stage two, S2, reactor at temperatures below 523K or 250 °C), while Ti^{2+} disproportionation is an endothermic process and is carried out at an intermediate temperature range in the S2 reactor.

[0068] The reduction of Ti^{4+}, Ti^{3+} (and other alloying elements, M^{x+}), oxidation of Al and subsequent disproportionation mean this process is fundamentally an electrochemical process. The process describe here does not rely on electrodes or external electrical circuits, as a result charge neutrality is expected throughout interaction zones. This means that alloy particles can form homogeneously from the [Ti^{2+}:salt] provided the local heat flux and composition supports the endothermic disproportionation reaction. This is a significant advantage this process has over electrochemical deposition and related processes.

[0069] Additionally, without wishing to be bound by any particular theory, it is believed that metallic Al and other alloying elements, M, precipitate from the salt simultaneously with Ti^{2+} and via corresponding disproportionation reactions (i.e., for Al: Al^{+} = 2/3[Al] + 1/3Al^{3+} [9] and for M: M^{x+} = 1/(x+1)[M] + x/(x+1)$M^{(x+1)+}$) and the supply of low oxidation state ions from the salt to the growth front of alloy particles is not hindered. Further, the low temperature nature of this process means that the crystal structure and phase boundaries typically observed with conventional processing routes (i.e., solidification and thermo-mechanical work) do not necessarily form or are even expected.

[0070] Keeping the general / high level features of this process in mind the details of the process will be described. In particular embodiments, the following processes may be performed after ensuring that the starting reactants ($TiCl_4$, $AlCl_3$, and alloy element halides, MX_x) are effectively free of H_2O and O, since all metal halides react strongly with H_2O and once oxygen is introduced it can be difficult to remove form some salts. Additionally, it is believed that oxygen contamination in salt stabilizes Ti^{3+} over Ti^{2+}, which hiders Ti^{2+} formation and thus influences the composition of alloy that forms.

Example 1:

[0071] A chemical reduction reaction of Ti^{4+}, initially in the form of $TiCl_4$(l) to Ti^{3+}, as $TiCl_3(AlCl_3)_x$, was performed in the stage 1 reactor and evaluated in an inert environments. The input mixture included 201.8 g Al flake, 100.5 g $AlCl_3$, 34.3 g $NbCl_5$ and 20.1 g of $CrCl_3$ that was loaded under a high purity argon atmosphere into a sealed ball milled and milled for 16 hours at close to room temperature (multiple ball mills provide feed for each stage 1 run. The milled material was sieved at 150 μm sieve size and 594.1 grams, nominally from two mills, were loaded into a plow mixer reactor, under a high purity argon atmosphere. The reactor was maintained at a pressure of 1.2 bar with a low flow (less than 1 l/min) of high purity argon flowing through the reactor. The reactor and charge was preheated to 130 °C and stabilized before 1164 g of $TiCl_4$(l) was injected at a rate of 6.5 ±2.0 g/min while continuously mixing. During the time $TiCl_4$(l) is injected it initially evaporates, but overtime $TiCl_4$(l) forms as the reactor wall is maintained at about 130 °C, while the bulk free flowing in process charge, {salt + Al}, can reach temperatures up to 145 °C. Following addition of all $TiCl_4$(l) reactor wall temperature is maintained 130 °C for nominally the same time taken for $TiCl_4$ injection, during which the condensed $TiCl_4$(l), was absorbed in the input mixture and reaction product salt, continues to reaction and is reduced. After the majority of condensed $TiCl_4$(l) is reduced (indicated by a reduction in bulk change temperature and gas temperature above the mixed charge) the reactor wall temperature was increased to 160 °C and held. This ensures all the condensed $TiCl_4$(l) at the reactor wall was able to reduced or can be removed. Intermediate material was cooled and removed from the reactor. Representative samples taken from the product of the described process were characterized, provided suitable precautions are taken to stop reaction with air, using XRD, ICP, Cl titration and electron microscopy and EDS analysis to evaluate form of the metal chlorides. The results of this characterization confirmed the product of residual unreacted Al particles with consistent shape and size observed in the milled product loaded into the plough reaction and also the amount consistent with reduction of $TiCl_4$ added. The microstructure observed with SEM show the Al particles were surrounded by a graded layer of product salt, the salt in contact the Al surface is $AlCl_3$-rich and it is common to observe segregation of O at this interface as an oxychloride layer "AlOCl". Further form the surface of the Al particle, the $TiCl_3(AlCl_3)_x$ phase existed and represented the bulk of the product of this reaction. This salt product had poor mechanical properties and easily separated the core Al particle and can exist isolated from Al particles. XRD analysis showed the $TiCl_3(AlCl_3)_x$ salt phase exists as the α phase, hexagonal close packed structure. This crystal structure was consistent with $AlCl_3(TiCl_3)_x$, and there was evidence of a continuous solid solution. The measured composition of the bulk sample composition was consistent with XRD and the observed microstructure.

[0072] Balance of the material was fed into a HED rotary kiln reactor with Ar counter flow gas with 5 zones with zone temperatures of about 250 °C to about 300 °C, about 300 °C to about 650 °C, and about 650 °C to about 1000 °C. After reaction in the rotary kiln through to a maximum temperature of 800 °C, the sample material was collect and analyzed by XRD, ICP, Cl titration and electron microscopy and EDS and showed formation of gamma titanium aluminide metal alloy powder with a size

of < 150μm particle size and with a composition of 32.0 ± 1.0 wt% Al, 61.4 ± 1.7 wt% Ti, 2.6 ± 0.1 wt% Cr, 4.5 ± 0.1 wt% Nb as well as a small amount of residual chlorine content (0.6 wt%).

Example 2:

[0073] A chemical reduction reaction was performed and evaluated in an inert environment. The input mixture includes 250 g Al flake, 62.5 g $AlCl_3$, 42.75 g $NbCl_5$ and 25.0 g of $CrCl_3$ and milled at room temperature for 16 hours. The milled material was sieved at 150 μm sieve size and 714 grams (nominally product from two mills) were loaded into a plow mixer reactor. The reactor was preheated to 130 °C and $TiCl_4$ was injected at a rate of 6.5 g/min while mixing. Following addition of 1541 g of $TiCl_4$, reactor temperature was increased to 160 °C and held to dry/remove excess $TiCl_4$. Intermediate material was cooled and removed from the reactor. The material from 3 similar stage one processes was fed into a HED rotary kiln reactor with Ar counter flow gas with 5 zones with all zone temperatures set to 250 °C. The $\{Al + TiCl_3(AlCl_3)_x\}$ product from the above stage one reaction was feed into the rotary kiln at a constant rate of 1.0 ± 0.2 kg/hr passed through the heated zone at a range of velocities controlled by the rotation speed of the work tube (6 RPM residence time of about 13 min; 4 RPM residence time of about 20 min; 2 RPM residence time of about 40 min). In-process samples were collected throughout the run and were characterized using XRD, ICP, Cl titration and electron microscopy and EDS analysis. Results showed that the starting $\{Al + TiCl_3(AlCl_3)_x\}$ material quickly reacted in the rotary kiln. The Al particles remained in the XRD spectrum and also clearly visible in the microstructure, but the amount was reduced. This was consistent with continued oxidation to reduce Ti^{3+} to Ti^{2+}. The characteristic XRD peaks for α-$TiCl_3(AlCl_3)_x$ disappeared leaving only the peaks for starting Al and alloy. The bulk composition of the sample, microstructure and amount of condensed $AlCl_3$ vapour collected confirms the bulk of the collected sample is salt and this salt does not have a defined crystal structure (i.e., an amorphous, glass or polymeric material), which shows that Al easily reduces Ti^{3+} as $TiCl_3(AlCl_3)_x$ to Ti^{2+} as $Ti(AlCl_4)_2$ at temperatures below 250°C without a significant amount of $AlCl_3$ evaporation. The $Ti(AlCl_4)_2$ phase is known in the literature to be non-crystalline.

[0074] In addition to low temperature reduction of Ti^{3+}, this result shows without an ambiguity that Ti-alloy starts forming at temperatures as low as 250 °C from the salt phase (via a simultaneous disproportionation reaction). The conditions of the reaction described here are not optimized, and a wide range of alloys were formed: α-[Ti], $\alpha 2$-Ti_3Al, γ-TiAl, $TiAl_2$, $TiAl_3$ also containing Nb and Cr. This alloy particles coexist with salt and unreacted Al particles. The wide range of alloy phases is expected to due to a wide range of salt compositions / inhomogeneous. This experimental run was conducted to prove the ease of reducing Ti^{3+} to Ti^{2+} and prove that Ti-Alloy forms via a simultaneous disproportionation process.

[0075] This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to practice the invention, including making and using any devices or systems and performing any incorporated methods. The patentable scope of the invention is defined by the claims.

Claims

1. A process for producing a titanium alloy material, comprising:

   adding $TiCl_4$ to an input mixture at a first reaction temperature such that at least a portion of the Ti^{4+} in the $TiCl_4$ is reduced to Ti^{3+} to form a first reaction product, wherein the input mixture comprises aluminum, and, optionally $AlCl_3$ and/or optionally one or more alloying element halides; wherein adding the $TiCl_4$ to the input mixture is performed in an inert atmosphere having a pressure of 101 kPa (760 torr) to 199.98 kPa (1500 torr) and at a first reaction temperature of 100 °C to 165 °C;
   after $TiCl_4$ addition is stopped, heating the first reaction product at drying conditions to complete reduction of Ti^{4+} or to remove all of any remaining $TiCl_4$ to form a first intermediate mixture, wherein the first intermediate mixture is an $AlCl_3$-based salt solution that includes Ti^{3+};
   heating the first intermediate mixture to a second reaction temperature such that at least a portion of the Ti^{3+} is reduced to Ti^{2+} in a second intermediate mixture, wherein the second intermediate mixture is an $AlCl_3$-based salt solution that includes the Ti^{2+}, wherein the Ti^{2+} is in the form of $TiCl_2$ complexed with $AlCl_3$; wherein heating the first intermediate mixture to the second reaction temperature is performed in an inert atmosphere having a pressure of 101 kPa (760 torr) to 506.6 kPa (3800 torr) and at a second reaction temperature of 180 °C to 250 °C; and
   further heating the second intermediate mixture to a third reaction temperature such that the Ti^{2+} forms the titanium alloy material via a disproportionation reaction; wherein reacting the Ti^{2+} via the disproportionation reaction to form the titanium alloy material is performed in an inert atmosphere having a pressure of 101 kPa (760 torr) to 506.6 kPa (3800 torr) and at the third reaction temperature of 300 °C to 900 °C.

2. The process of claim 1, wherein the input mixture comprises a plurality of particles, and wherein the plurality of particles comprise aluminum, $AlCl_3$ and,

optionally, one or more alloying element chloride, and further wherein the plurality of particles of the input mixture have a minimum particle dimension on average of about 0.5 μm to about 25 μm; optionally wherein the one or more alloying element chloride is present in the input mixture, and wherein the at least one alloying element chloride comprises VCl_3, $CrCl_2$, $CrCl_3$, $NbCl_5$, $FeCl_2$, $FeCl_3$, YCl_3, BCl_3, $MnCl_2$, $MoCl_3$, $MoCl_5$, $SnCl_2$, $ZrCl_4$, $NiCl_2$, CuCl, $CuCl_2$, WCl_4, WCl_6, $BeCl_2$, $ZnCl_2$, LiCl, $MgCl_2$, $ScCl_3$, $PbCl_2$, Ga_2Cl_4, $GaCl_3$, $ErCl_3$, $CeCl_3$, or mixtures thereof.

3. The process of claim 1, wherein the input mixture comprises reaction mixture to form Ti-6Al-4V (weight %); or Ti-48Al-2Cr-2Nb (atomic %).

4. The process of claim 1, wherein the aluminum is present the input mixture reduces the Ti^{4+} in the $TiCl_4$ to Ti^{3+}.

5. The process of claim 1, wherein $TiCl_4$ is added as a liquid or vapor mixed with other alloy chlorides.

6. The process of claim 1, wherein

(a) reducing the Ti^{4+} in the $TiCl_4$ to form Ti^{3+} is performed in a plow reactor, a ribbon blender, or another liquid/solid/vapor reactor; and/or
(b) heating the first intermediate mixture to a second reaction temperature is performed in at least one rotary kiln.

7. The process of claim 1, wherein the Ti^{3+} in the first intermediate mixture is in the form of $TiCl_3$ complexed with at least one metal chloride.

8. The process of claim 1, wherein the Ti^{3+} in the first intermediate mixture is in the form of $TiCl_3(AlCl_3)_x$ with x being greater than 0 to 10.

9. The process of claim 1, wherein the first intermediate mixture is maintained at the second reaction temperature until all of the Ti^{3+} in the first intermediate mixture is reduced to Ti^{2+}.

10. The process of claim 1, wherein reducing Ti^{3+} to Ti^{2+} and reacting the Ti^{2+} via a disproportionation reaction are performed in a single reactor or in a multi-zone reaction chamber.

11. The process of claim 1, further comprising:
flowing an inert gas through a multi-zone reaction chamber, wherein the inert gas flow is counter to the progression of the reaction products, and wherein the inert gas is introduced as a counter flow to carry gaseous titanium chloride complexes away from the titanium alloy material formed and back into the reaction zone for either or both reactions of Ti^{3+} to Ti^{2+} and/or Ti^{2+} to Ti alloy; optionally wherein any $TiCl_4$ produced during the reaction is reduced by an aluminum chloride or carried out of the reactor as a take-off by-product.

12. The process of claim 1, wherein any Ti^{3+} formed during the disproportionation reaction is internally recycled to be reduced to Ti^{2+} and further reacted in a disproportionation reaction.

13. The process of claim 1, wherein the titanium alloy material is a titanium alloy powder.

14. The process of claim 1, further comprising: high temperature processing the titanium alloy material at a processing temperature to purify the Ti alloy by removing residual chlorides and/or allowing diffusion to reduce composition gradients; optionally wherein the high temperature processing also continues disproportionation reactions to produce Ti alloy from any residual Ti^{2+}, and wherein the high temperature processing also continues distillation of any un-reacted metal sub-halides; and/or wherein the processing temperature is about 800 °C or higher.

15. The process of claim 1, further comprising:
adding alloying element halides into input mixture, during the reaction forming the first intermediate mixture, during the reaction forming the second intermediate mixture, during the disproportionation reaction, or during post processing.

Patentansprüche

1. Verfahren zum Produzieren eines Titanlegierungsmaterials, umfassend:

Zugeben von $TiCl_4$ zu einer Eingangsmischung bei einer ersten Reaktionstemperatur derart, dass mindestens ein Teil des Ti^{4+} in dem $TiCl_4$ zu Ti^{3+} reduziert wird, um ein erstes Reaktionsprodukt auszubilden, wobei die Eingangsmischung Aluminium und optional $AlCl_3$ und/oder optional ein oder mehrere Legierungselementhalogenide umfasst; wobei das Zugeben des $TiCl_4$ zu der Eingangsmischung in einer inerten Atmosphäre, die einen Druck von 101 kPa (760 Torr) bis 199,98 kPa (1500 Torr) aufweist, und bei einer ersten Reaktionstemperatur von 100 °C bis 165 °C durchgeführt wird;
nachdem eine Zugabe von $TiCl_4$ gestoppt wird, Erwärmen des ersten Reaktionsprodukts unter Trocknungsbedingungen, um eine Reduktion von Ti^{4+} abzuschließen oder um jegliches restliches $TiCl_4$ zu entfernen, um eine erste Zwischenmischung auszubilden, wobei die erste

Zwischenmischung eine Salzlösung auf Basis von $AlCl_3$ ist, die Ti^{3+} einschließt;
Erwärmen der ersten Zwischenmischung auf eine zweite Reaktionstemperatur derart, dass mindestens ein Teil des Ti^{3+} zu Ti^{2+} in einer zweiten Zwischenmischung reduziert wird, wobei die zweite Zwischenmischung eine Salzlösung auf Basis von $AlCl_3$ ist, die das Ti^{2+} einschließt, wobei das Ti^{2+} in Form von $TiCl_2$ vorliegt, das mit $AlCl_3$ komplexiert ist; wobei das Erwärmen der ersten Zwischenmischung auf die zweite Reaktionstemperatur in einer inerten Atmosphäre, die einen Druck von 101 kPa (760 Torr) bis 506,6 kPa (3800 Torr) aufweist, und bei einer zweiten Reaktionstemperatur von 180 °C bis 250 °C durchgeführt wird; und
weiteres Erwärmen der zweiten Zwischenmischung auf eine dritte Reaktionstemperatur derart, dass das Ti^{2+} das Titanlegierungsmaterial über eine Disproportionierungsreaktion ausbildet; wobei das Reagieren des Ti^{2+} über die Disproportionierungsreaktion, um das Titanlegierungsmaterial auszubilden, in einer inerten Atmosphäre, die einen Druck von 101 kPa (760 Torr) bis 506,6 kPa (3800 Torr) aufweist, und bei der dritten Reaktionstemperatur von 300 °C bis 900 °C durchgeführt wird.

2. Verfahren nach Anspruch 1, wobei die Eingangsmischung eine Vielzahl von Partikeln umfasst und wobei die Vielzahl von Partikeln Aluminium, $AlCl_3$ und optional ein oder mehrere Legierungselementchloride umfasst, und ferner wobei die Vielzahl von Partikeln der Eingangsmischung eine minimale Partikelabmessung von durchschnittlich etwa 0,5 μm bis etwa 25 μm aufweist; optional wobei das eine oder die mehreren Legierungselementchloride in der Eingangsmischung vorliegen und wobei das mindestens eine Legierungselementchlorid VCl_3, $CrCl_2$, $CrCl_3$, $NbCl_5$, $FeCl_2$, $FeCl_3$, YCl_3, BCl_3, $MnCl_2$, $MoCl_3$, $MoCl_5$, $SnCl_2$, $ZrCl_4$, $NiCl_2$, CuCl, $CuCl_2$, WCl_4, WCl_6, $BeCl_2$, $ZnCl_2$, LiCl, $MgCl_2$, $ScCl_3$, $PbCl_2$, Ga_2Cl_4, $GaCl_3$, $ErCl_3$, $CeCl_3$ oder Mischungen davon umfasst.

3. Verfahren nach Anspruch 1, wobei die Eingangsmischung eine Reaktionsmischung umfasst, um Ti-6Al-4V (in Gew.-%) oder Ti-48Al-2Cr-2Nb in (Atom-%) auszubilden.

4. Verfahren nach Anspruch 1, wobei das Aluminium vorhanden ist, die Eingangsmischung das Ti^{4+} in dem $TiCl_4$ zu Ti^{3+} reduziert.

5. Verfahren nach Anspruch 1, wobei $TiCl_4$ als Flüssigkeit oder Dampf zugegeben wird, die/der mit anderen Legierungschloriden gemischt ist.

6. Verfahren nach Anspruch 1, wobei

(a) das Reduzieren des Ti^{4+} in dem $TiCl_4$, um Ti^{3+} auszubilden, in einem Plow-Reaktor, einem Bandmischer oder einem anderen Flüssig-/Fest-/Dampf-Reaktor durchgeführt wird; und/oder
(b) das Erwärmen der ersten Zwischenmischung auf eine zweite Reaktionstemperatur in mindestens einem Drehrohrofen durchgeführt wird.

7. Verfahren nach Anspruch 1, wobei das Ti^{3+} in der ersten Zwischenmischung in der Form von $TiCl_3$ vorliegt, das mit mindestens einem Metallchlorid komplexiert ist.

8. Verfahren nach Anspruch 1, wobei das Ti^{3+} in der ersten Zwischenmischung in Form von $TiCl_3$ $(AlCl_3)\times$ vorliegt, wobei x größer als 0 bis 10 ist.

9. Verfahren nach Anspruch 1, wobei die erste Zwischenmischung bei der zweiten Reaktionstemperatur gehalten wird, bis das gesamte Ti^{3+} in der ersten Zwischenmischung zu Ti^{2+} reduziert ist.

10. Verfahren nach Anspruch 1, wobei das Reduzieren von Ti^{3+} zu Ti^{2+} und das Reagieren des Ti^{2+} über eine Disproportionierungsreaktion in einem einzelnen Reaktor oder in einer Mehrzonenreaktionskammer durchgeführt werden.

11. Verfahren nach Anspruch 1, ferner umfassend:
Strömen eines Inertgases durch eine Mehrzonenreaktionskammer, wobei der Inertgasstrom dem Fortschritt der Reaktionsprodukte entgegenwirken soll und wobei das Inertgas als ein Gegenstrom eingeführt wird, um gasförmige Titanchloridkomplexe weg von dem ausgebildeten Titanlegierungsmaterial und zurück in die Reaktionszone für eine oder beide Reaktionen von Ti^{3+} zu Ti^{2+} und/oder Ti^{2+} zu einer Ti-Legierung zu führen; wobei optional beliebiges $TiCl_4$, das während der Reaktion produziert wird, durch Aluminiumchlorid reduziert oder als ein Abzugsnebenprodukt aus dem Reaktor geführt wird.

12. Verfahren nach Anspruch 1, wobei beliebiges Ti^{3+}, das während der Disproportionierungsreaktion ausgebildet wird, intern recycelt wird, um zu Ti^{2+} reduziert zu werden und in einer Disproportionierungsreaktion weiter reagiert zu werden.

13. Verfahren nach Anspruch 1, wobei das Titanlegierungsmaterial ein Titanlegierungspulver ist.

14. Verfahren nach Anspruch 1, ferner umfassend:
Hochtemperaturverarbeiten des Titanlegierungsmaterials bei einer Verarbeitungstemperatur, um

die Ti-Legierung durch Entfernen von restlichen Chloriden und/oder Ermöglichen einer Diffusion zu reinigen, um Zusammensetzungsgradienten zu reduzieren; optional wobei das Hochtemperaturverarbeiten auch Disproportionierungsreaktionen fortsetzt, um aus beliebigem restlichem Ti^{2+} die Ti-Legierung zu produzieren, und wobei das Hochtemperaturverarbeiten auch eine Destillation beliebiger unreagierter Metallsubhalogenide fortsetzt, und/oder wobei die Verarbeitungstemperatur etwa 800 °C oder höher ist.

15. Verfahren nach Anspruch 1, ferner umfassend: Zugeben von Legierungselementhalogeniden in die Eingangsmischung während der Reaktion, die die erste Zwischenmischung ausbildet, während der Reaktion, die die zweite Zwischenmischung ausbildet, während der Disproportionierungsreaktion oder während der Reaktion eines Nachverarbeitens.

Revendications

1. Procédé de production d'un matériau en alliage de titane, comprenant :

l'ajout de $TiCl_4$ à un mélange d'entrée à une première température de réaction de telle sorte qu'au moins une partie du Ti^{4+} dans le $TiCl_4$ est réduite en Ti^{3+} pour former un premier produit de réaction, dans lequel le mélange d'entrée comprend de l'aluminium et facultativement $AlCl_3$ et/ou facultativement un ou plusieurs halogénures d'éléments d'alliage ; dans lequel l'ajout du $TiCl_4$ au mélange d'entrée est effectué dans une atmosphère inerte ayant une pression de 101 kPa (760 torr) à 199,98 kPa (1 500 torr) et à une première température de réaction de 100 °C à 165 °C ;
après l'arrêt de l'ajout de $TiCl_4$, le chauffage du premier produit de réaction dans des conditions de séchage pour terminer la réduction de Ti^{4+} ou pour éliminer tout $TiCl_4$ restant afin de former un premier mélange intermédiaire, dans lequel le premier mélange intermédiaire est une solution saline à base d'$AlCl_3$ qui comporte Ti^{3+} ;
le chauffage du premier mélange intermédiaire à une deuxième température de réaction de telle sorte qu'au moins une partie du Ti^{3+} est réduite en Ti^{2+} dans un second mélange intermédiaire, dans lequel le second mélange intermédiaire est une solution saline à base d'$AlCl_3$ qui comporte le Ti^{2+}, dans lequel le Ti^{2+} est sous la forme de $TiCl_2$ complexé avec $AlCl_3$; dans lequel le chauffage du premier mélange intermédiaire à une deuxième température de réaction est effectué dans une atmosphère inerte ayant une pression de 101 kPa (760 torr) à 506,6 kPa (3 800 torr) et à une deuxième température de réaction de 180 °C à 250 °C ; et
la poursuite du chauffage du second mélange intermédiaire à une troisième température de réaction de telle sorte que le Ti^{2+} forme le matériau en alliage de titane par le biais d'une réaction de dismutation ; dans lequel la réaction du Ti^{2+} par le biais de la réaction de dismutation pour former le matériau en alliage de titane est effectuée dans une atmosphère inerte ayant une pression de 101 kPa (760 torr) à 506,6 kPa (3 800 torr) et à la troisième température de réaction de 300 °C à 900 °C.

2. Procédé selon la revendication 1, dans lequel le mélange d'entrée comprend une pluralité de particules, et dans lequel la pluralité de particules comprend de l'aluminium, $AlCl_3$ et facultativement un ou plusieurs chlorures d'éléments d'alliage, et en outre dans lequel la pluralité de particules du mélange d'entrée a une dimension minimale de particules en moyenne d'environ 0,5 μm à environ 25 μm ; facultativement, dans lequel le ou les chlorures d'éléments d'alliage sont présents dans le mélange d'entrée, et dans lequel l'au moins un chlorure d'élément d'alliage comprend VCl_3, $CrCl_2$, $CrCl_3$, $NbCl_5$, $FeCl_2$, $FeCl_3$, YCl_3, BCl_3, $MnCl_2$, $MoCl_5$, $MoCl_5$, $SnCl_2$, $ZrCl_4$, $NiCl_2$, CuCl, $CuCl_2$, WCl_4, WCl_6, $BeCl_2$, $ZnCl_2$, LiCl, $MgCl_2$, $ScCl_3$, $PbCl_2$, Ga_2Cl_4, $GaCl_3$, $ErCl_3$, $CeCl_3$, ou des mélanges de ceux-ci.

3. Procédé selon la revendication 1, dans lequel le mélange d'entrée comprend le mélange de réaction pour former du Ti-6Al-4V (% en poids) ; ou Ti-48Al-2Cr-2Nb (% atomique).

4. Procédé selon la revendication 1, dans lequel l'aluminium est présent le mélange d'entrée réduit le Ti^{4+} dans le $TiCl_4$ en Ti^{3+}.

5. Procédé selon la revendication 1, dans lequel $TiCl_4$ est ajouté sous forme de liquide ou de vapeur mélangé à d'autres chlorures d'alliage.

6. Procédé selon la revendication 1, dans lequel

(a) la réduction du Ti^{4+} dans le $TiCl_4$ pour former Ti^{3+} est effectuée dans un réacteur à rabot, un mélangeur à ruban, ou un autre réacteur à liquide/solide/vapeur ; et/ou
(b) le chauffage du premier mélange intermédiaire à une deuxième température de réaction est effectué dans au moins un four rotatif.

7. Procédé selon la revendication 1, dans lequel le Ti^{3+} dans le premier mélange intermédiaire se présente sous la forme de $TiCl_3$ complexé avec au moins un

chlorure métallique.

8. Procédé selon la revendication 1, dans lequel le Ti^{3+} dans le premier mélange intermédiaire se présente sous la forme de $TiCl_3(AlCl_3)_x$, x allant de plus de 0 à 10.

9. Procédé selon la revendication 1, dans lequel le premier mélange intermédiaire est maintenu à la deuxième température de réaction jusqu'à ce que tout le Ti^{3+} dans le premier mélange intermédiaire soit réduit en Ti^{2+}.

10. Procédé selon la revendication 1, dans lequel la réduction de Ti^{3+} en Ti^{2+} et la réaction du Ti^{2+} par le biais d'une réaction de dismutation sont effectuées dans un seul réacteur ou dans une chambre de réaction multizone.

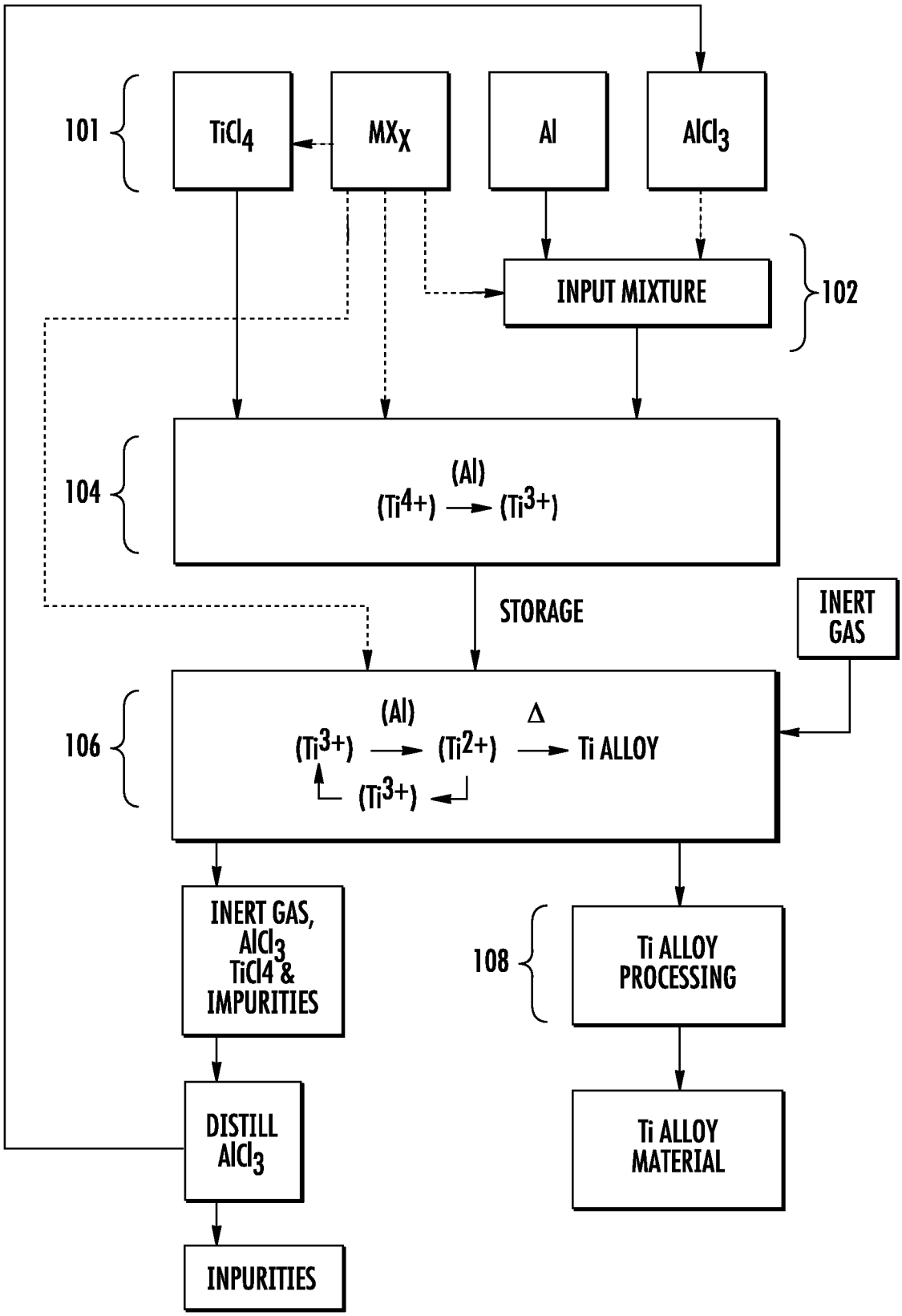
11. Procédé selon la revendication 1, comprenant en outre :
l'écoulement d'un gaz inerte à travers une chambre de réaction multizone, dans lequel l'écoulement de gaz inerte est contraire à la progression des produits de réaction, et dans lequel le gaz inerte est introduit en tant qu'écoulement contraire pour éloigner des complexes de chlorure de titane gazeux du matériau en alliage de titane formé, et renvoyé dans la zone de réaction pour l'une ou les deux réactions de Ti^{3+} en Ti^{2+} et/ou de Ti^{2+} en alliage de Ti ; facultativement dans lequel tout $TiCl_4$ produit pendant la réaction est réduit par un chlorure d'aluminium ou évacué du réacteur en tant que sous-produit retiré.

12. Procédé selon la revendication 1, dans lequel tout Ti^{3+} formé pendant la réaction de dismutation est recyclé en interne pour être réduit en Ti^{2+} et soumis à une nouvelle réaction de dismutation.

13. Procédé selon la revendication 1, dans lequel le matériau en alliage de titane est une poudre d'alliage de titane.

14. Procédé selon la revendication 1, comprenant en outre :
un traitement à haute température du matériau en alliage de titane à une température de traitement pour purifier l'alliage de Ti en éliminant des halogénures résiduels et/ou en permettant une diffusion afin de réduire les gradients de composition ; facultativement dans lequel le traitement à haute température poursuit également les réactions de dismutation pour produire un alliage de Ti à partir de tout Ti^{2+} résiduel, et dans lequel le traitement à haute température poursuit également la distillation de tout sous-halogénure métallique n'ayant pas réagi ; et/ou dans lequel la température de traitement est d'environ 800 °C ou plus.

15. Procédé selon la revendication 1, comprenant en outre :
l'ajout d'halogénures d'éléments d'alliage dans le mélange d'entrée, pendant la réaction formant le premier mélange intermédiaire, pendant la réaction formant le second mélange intermédiaire, pendant la réaction de dismutation, ou pendant un post-traitement.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Al
AlCl3
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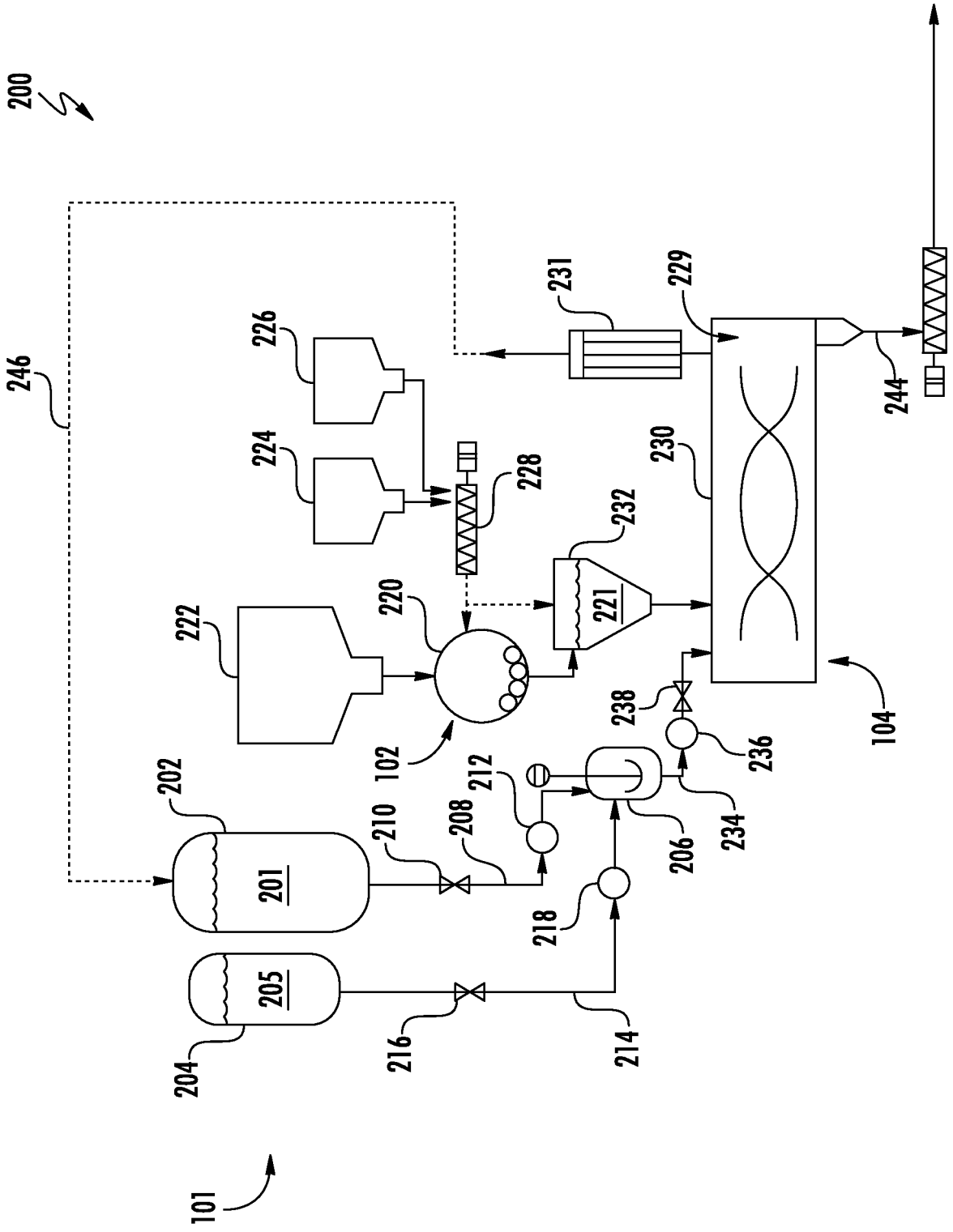
104
(Al)
(Ti4+) → (Ti3+)
STORAGE
INERT GAS
106
(Al)
Δ
(Ti3+) → (Ti2+) → Ti ALLOY
(Ti3+)
INERT GAS, AlCl3 TiCl4 & IMPURITIES
108
Ti ALLOY PROCESSING
DISTILL AlCl3
Ti ALLOY MATERIAL
INPURITIES

FIG. 1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101

FIG. 2

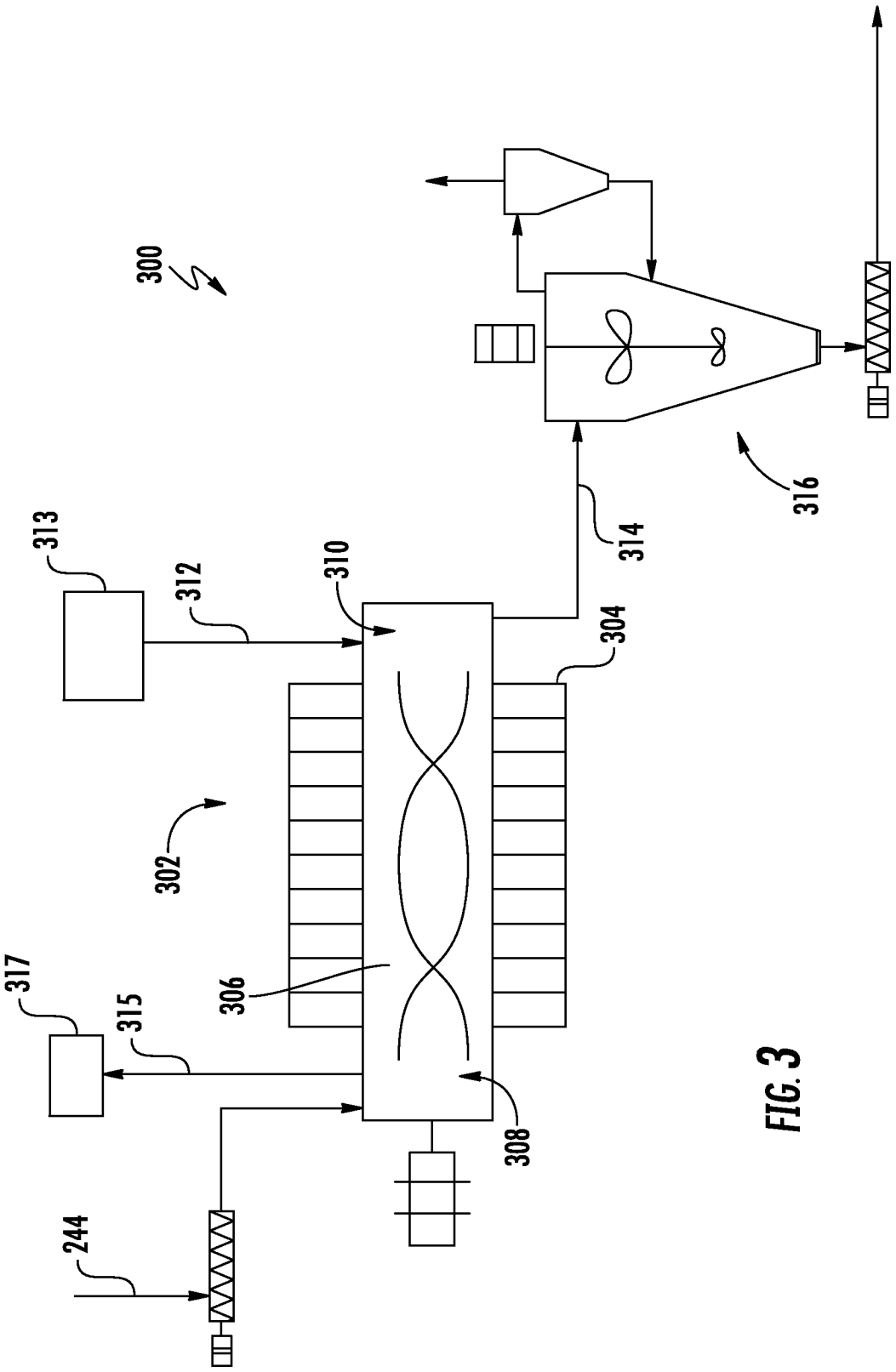
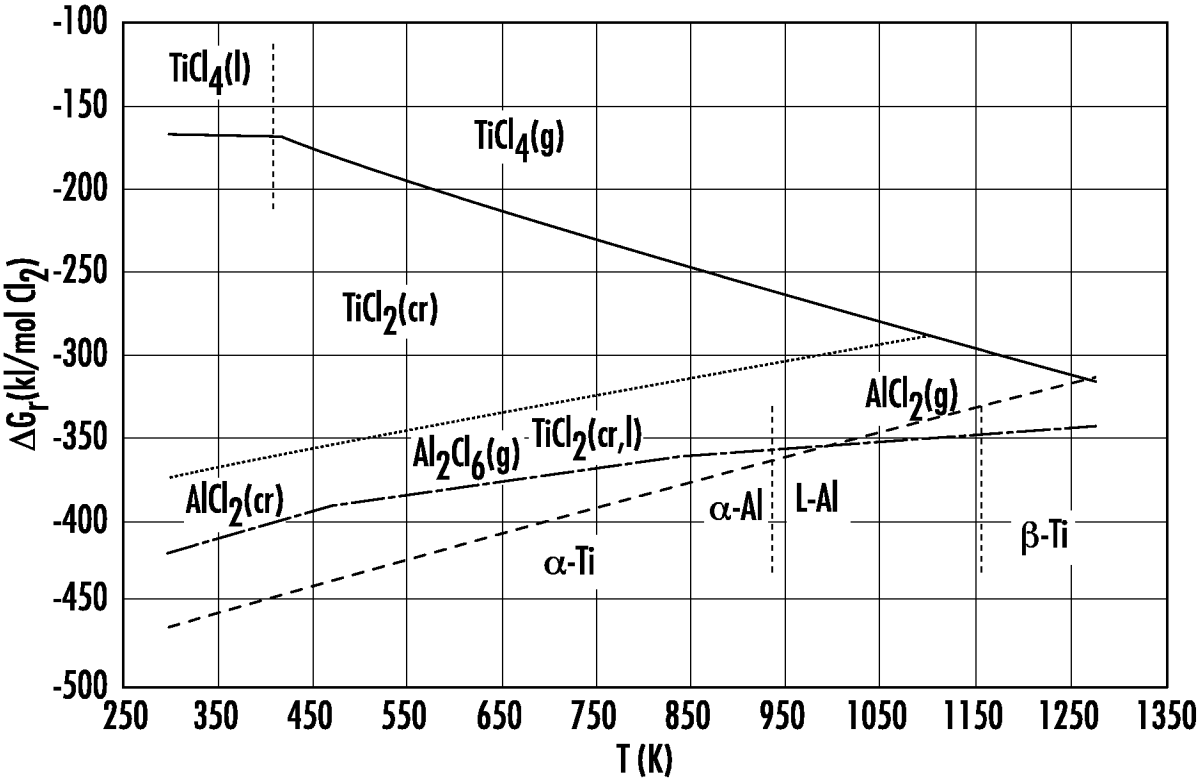


FIG. 3


-100
-150
-200
-250
-300
-350
-400
-450
-500
ΔGr(kJ/mol Cl2)
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350
450
550
650
750
850
950
1050
1150
1250
1350
T (K)
TiCl4(l)
TiCl4(g)
TiCl2(cr)
AlCl2(g)
Al2Cl6(g)
TiCl2(cr,l)
AlCl2(cr)
α-Al
L-Al
β-Ti
α-Ti

FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 62411205 **[0001]**
- WO 2007109847 A **[0004] [0005]**
- WO 2009129570 A **[0004] [0005]**
- WO 2011072338 A **[0005]**