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2,837,426

CYCLIC PROCESS FOR THE MANUFACTURE OF TITANIUM-ALUMINUM ALLOYS AND REGENERATION OF INTERMEDIATES THEREOF

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This invention relates to a cyclic process for the manufacture of titanium-aluminum alloys and the regeneration of the intermediates of said process. More particularly, it relates to a process for the manufacture of titanium-aluminum alloys containing from 0.1% to 95% of titanium, and for the processing of the by-products of said process to regenerate the intermediate chemical compounds required for the manufacture of said alloys.

Manchot and Richter (Annalen 357, 140-144 (1907)) reacted potassium fluotitanate with metallic aluminum in quantity far in stoichiometric excess of that required by the equation:



at advanced temperatures, and obtained a titanium-aluminum alloy containing 9.4% of titanium. In my co-pending application Serial No. 382,206, filed September 24, 1953, now Patent No. 2,785,971, granted March 19, 1957, I have shown that alloys containing from 53% to 95% of titanium (the remainder being aluminum) may be obtained by the reaction, at advanced temperatures, of alkali metal fluotitanates with aluminum in quantities within a closely specified range. I now find that alloys of titanium and aluminum containing from 0.1% to 95% of titanium can be obtained by the reaction, at advanced temperatures, of alkali metal fluotitanates with metallic aluminum, employing per gram-mole of alkali metal fluotitanate (i. e. per 207.9 grams of Na_2TiF_6 , or per 175.8 grams of Li_2TiF_6 , or per 240.1 grams of K_2TiF_6), from 38.5 grams to 47.9 kilograms of metallic aluminum, and that this reaction may be adapted to a cyclic regeneration of the reagents thereof.

This very broad range of titanium contents in the alloys obtained requires somewhat different modes of operating, depending on the melting point of the alloy to be prepared. The following chart represents the approximate melting point of the series of alloys preferable by the process of this invention:

Percent Ti:	Approximate melting point, ° C.
0.1 to 1	660 to 700
5	860
10	1020
20	1150
30	1280
37.3 (TiAl ₃)	1350
40	1370
50	1425
60	1440
70	1510
80	1600
90	1725
95	1730

Binary alloys containing up to 37.28% of titanium consist of crystals of titanium aluminide (TiAl₃) dispersed in excess aluminum. The binary alloy containing 37.28% of titanium corresponds to TiAl₃ in composition. Binary

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alloys containing 37.28% to 53% of titanium consist of crystals of titanium aluminide dispersed in excess titanium metal. Binary alloys containing more than 53% of titanium comprise simple solutions of the aluminum in the titanium and do not form intermetallic compounds. Formation of alloys containing up to 75% of titanium proceeds at a rapid rate. As a rule, the more aluminum that is used (within the limits above described), the more rapid and complete is the reaction between the alkali metal fluotitanate and the aluminum, and the formation of the titanium-aluminum alloy. As the amount of aluminum is decreased, the reaction with the alkali metal fluotitanate becomes slower, and there is a greater tendency for incomplete reduction of the alkali metal fluotitanate with formation of divalent and trivalent titanium compounds. By prolonged heating, however, alloys containing up to 95% titanium may however be obtained by this method.

The temperatures at which this reaction may be effected may vary quite widely. It is desirable to have at least one of the reagents (i. e. the aluminum) in a molten state, and preferably both the aluminum and the alkali metal fluotitanates should be in a molten state. Thus, the lower limit of temperature for this reaction is set by the melting point of aluminum, i. e. 660° C. Both reagents are molten in the range of 90°-1100° C. The upper limit of temperature for this reaction is set by the boiling point of aluminum (1800° C.) and the melting point of the alloy being prepared. It is desirable, at the conclusion of the reaction, to be able to separate a molten regulus of titanium-aluminum alloy from the concomitant "slag" consisting of molten alkali metal aluminum fluoride and aluminum fluoride. Thus, the temperature range for this reaction may be given as 660° C. to 1800° C., with a preferred range between 900° C. and 1550° C., depending on the composition of the alloy being prepared. In the case of the higher melting alloys, it may be found preferable to allow the reaction mixture of titanium-aluminum alloy and slag to cool and solidify and thereafter to separate the crystallized slag (consisting of alkali metal fluoaluminate and aluminum fluoride) from the alloy by leaching or dissolving the former in water and separating the resultant solution from the insoluble alloy (e. g. by filtering or centrifuging).

A preferred method for effecting this step of the invention is to mix the calculated quantity of molten aluminum and alkali metal fluotitanate in a refractory-lined crucible in an induction furnace, and then to heat the mixture with agitation, if necessary, until the reaction is complete and a final temperature between 900° C. and 1550° C. is attained at which the salt mixture (i. e. the slag) is molten and the binary alloy may or may not be molten. If both components of the reaction mixture are molten, they may be separated by decantation in the usual manner. If the slag is molten and the alloy is solid, they may be separated by decantation or filtration (e. g. by screening through a metal mesh filter), in the usual manner.

Another preferred method of effecting this step is to permit the reaction mixture of slag and alloy to cool and solidify, and thereafter to separate these components by comminution and screening or (as above described, by leaching the water-soluble slag from the insoluble alloy by treatment with water. Graphite-lined crucibles are, as a rule, suitable for effecting the reaction of this invention since they are not attacked by the reagents at the indicated reaction temperatures.

Although some of the alkali metal fluotitanates are known to form crystalline hydrates at lower temperatures, they are, of course, employed as anhydrous salts at the temperature ranges involved in the process of this in-

vention. Since the aluminum is always employed in the molten state, it need not be comminuted prior to addition to the reaction mixture, but may be added to the crucible as bar or pig aluminum or in the molten state.

The titanium-aluminum alloys thus prepared have a wide range of utility in industrial metallurgy. They are employed to refine grain structure, remove gas occlusions, increase tensile strengths, increase resistance to leaking of castings, improve mechanical properties, decrease the electrical conductivity, increase impact resistance, increase resistance to acids, saline and other aggressive solutions, increase corrosion resistance, improve castings and lower the casting temperatures of various metals and alloys (Journ. Inst. Metals 1930, 531; Chem. Zentr. 1937I, 2002; 1944I, 242; Alluminio 16, 5 (1947); U. S. Patents 2,252,241 and 2,376,681; Metallurtschaft 21, 683 (1942); Chimie & Industrie 26, 338 (1932); Aluminum 17, 79 (1934); 16, 635 (1937); 20, 452 (1938); 26, 2 (1944); British Patent 473,916; Zeit. anorg. Chem. 150, 26 (1926); Comptes rendus 220, 690 (1945); Journ. Metals 3 Trans. 1143 (1951).

Thus, weldable titanium alloys containing 5% aluminum and 2.5% tin show good ductility with yield strengths of about 110,000 p. s. i. Other titanium alloys containing 6% aluminum and 4% vanadium show excellent high-temperature properties with reported yield strengths of 190,000 p. s. i. and 14% elongation at room temperature. Titanium alloys containing 35%–40% of aluminum demonstrate superior elevated-temperature properties.

Similarly, alloys containing 95% of aluminum and 5% of titanium, preparable by the process of this invention, show excellent corrosion resistance. The development of such titanium-aluminum alloys is discussed by Gonser (Industrial and Engineering Chemistry 42, 222–226 (1950) and by Hansen and Kessler (Society of Automotive Engineers, January 12–16, 1953), and by Larsen, Swazy, Busch and Freyer in the United States Office of Naval Research, Rept. Titanium Symposium, 105–124 (1949).

A very important industrial outlet for the titanium-aluminum alloys of this invention is as a partial or total replacement of the manganese alloys employed for sulfur control in the manufacture of steel (Roach and Stewart, Iron Age, June 4 and June 11, 1953; Goldschmidt and Weil, U. S. Patents 1,075,782 (1913) and 1,136,670 (1915).

Another highly important industrial outlet for the titanium-aluminum alloys of this invention is as intermediates in the manufacture of pure metallic titanium. In my co-pending patent application Serial No. 382,206, filed September 24, 1953, I describe a process whereby alloys of titanium and aluminum containing more than 53% of titanium (and therefore free of the intermetallic compound $TiAl_3$) are leached with aqueous alkali solutions whereby the aluminum is separated from the alloy and metallic titanium remains behind.

Pure metallic titanium may also be obtained from such alloys of titanium and aluminum containing more than 53% titanium (devoid of the intermetallic compound $TiAl_3$) by distilling off the aluminum (preferably under reduced pressure). A preferred procedure involves the removal of the aluminum from the alloy by heating in the presence of an aluminum halide (e. g. AlF_3 , $AlCl_3$, $AlBr_3$), whereby the subhalide is formed (e. g. AlF , $AlCl$, $AlBr$) and distilled from the alloy under reduced pressure. This technique is described by Cuellerson and Pascaud (Comptes rendus a l'Academie des Sciences 233, 745–747 (1951), *ibid*, 235, 1220–1221 (1952) and by Ramamurthy (Journ. Scien. Industr. Research (India) 11B, 545–546 (1952), and is a modification of the well-known "subhalide" process for the recovery of aluminum from alloys and for the refining of aluminum from scrap and secondary metal. The alloy or aluminum-containing scrap is heated to 1000°–1200° C. and the aluminum

trihalide (usually $AlCl_3$) is added, whereby the aluminum monohalide ($AlCl$) distills over. The distilling vapor is passed through a condenser at 500°–600° C. whereby the aluminum monohalide dismutates to the aluminum trihalide and metallic aluminum. The aluminum trihalide is in the vapor state ($AlCl_3$ sublimes at 192° C.) and may be recirculated through the alloy or aluminum-containing scrap, whereas the aluminum formed in the dismutation is recovered in a compact form and in a state of high purity. Thus, by the circulation of the sublimed $AlCl_3$ through the alloy, the process can be operated on a continuous or semicontinuous basis. (Zintl, Krings, Bauning, Morawietz and Gasting, Zeit. anorg. allgem. Chemie 245, 8 (1940), German Patent 742,330 (1939); Wellmore, U. S. Patent 2,184,705 (1939); Klemm and Voss, Zeit. anorg. allgem. Chemie 251, 233 (1943); Gross, Mining Magazine 81, #2,126 (1929), German Patent 830,113 (1949); Weiss, Erzmetall 8, 214 (1950); Ardel Werke, Swiss Patent 255,157 (1946) and British Patent 631,585 (1947); Aluminum Industrie, Swiss Patent 261,162 (1947) and German Patent 812,118 (1950); Vereingten Aluminiumwerke, German Patents 816,017, 843,598 and 846,016; Gross, Campbell, Kent and Levi, Discussions Faraday 1948, #4, 206–215; Weiss, Zeit. Erzbergbau u. Metallhutenw. 3, 241–4 (1950).

By the application of this "subhalide" process to the removal of the aluminum from titanium-aluminum alloys containing 53% to 95% of titanium, it is possible to obtain a pure sponge titanium assaying less than 0.06% of nitrogen, less than 0.10% of oxygen, less than 0.25% of aluminum, less than 0.15% of chloride; with Brinnell hardness between 160 and 250.

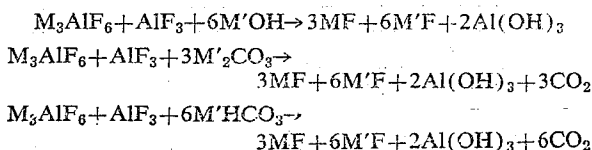
In effecting the process of this invention, the choice of the reagents is often of considerable importance. In the preparation of the high-titanium alloys required as intermediates in the manufacture of pure metallic titanium (the specifications for which are quite stringent), it is usually desirable to employ a pure virgin aluminum as a reagent. In the preparation of many other alloys, such as those intended for use in the manufacture of steel as a partial or a total replacement for manganese, it is entirely feasible and practical to employ the cheaper scrap or secondary aluminum, the contaminants or alloyed elements contained therein not being deleterious to the use of the ultimately obtained titanium alloy in steel manufacture.

The by-product mixture of molten salts obtained with these titanium-aluminum alloys consists of substantially equimolecular proportions of alkali metal fluoaluminate (M_3AlF_6) and aluminum fluoride. Since the starting material—the alkali metal fluotitanate—is not a common article of commerce, it is a further purpose of this invention to provide a simple process for the conversion of this by-product mixture of M_3AlF_6 and AlF_3 to the original starting material, i. e. the alkali metal fluotitanate M_2TiF_6 .

I have found that this regeneration of the alkali metal fluotitanates may be effected by the following sequence of steps:

Step A

The slag, comprising a substantially equimolecular mixture of alkali metal fluoaluminate and aluminum fluoride, separated from the titanium-aluminum alloy as above described is dissolved in water and is then reacted with a quantity of a member of the group consisting of the hydroxides, carbonates and bicarbonates of the alkali metals and ammonium at least sufficient to precipitate all of the aluminum ion as aluminum hydroxide. The reaction involved is:



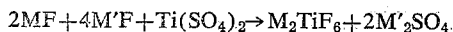
where M' is a member of the group consisting of ammonium and alkali metal ions, and M is an alkali metal ion. The reaction is effected at any desired temperature, but proceeds most rapidly at temperatures near the boiling point of the reaction mixture, i. e. from 70° C. to 100° C. The preferred reagent on the basis of cost and effectiveness is sodium carbonate (soda ash). If ammonia or an alkali metal hydroxide is employed, it is desirable to avoid the use of a stoichiometric excess of the reagent which may dissolve some of the precipitated aluminum hydroxide. If an excess of one of these reagents is employed and some aluminum hydroxide is redissolved, the treatment of the reaction mixture with a carbon dioxide-containing gas will reprecipitate the dissolved Al(OH)₃.

At the conclusion of this step, the preprecipitated aluminum hydroxide is filtered from the solution of alkali metal fluoride (which may contain NH₄F if ammonia was used as a precipitant). The filtercake of aluminum hydroxide is washed with water and the combined filtrate and washings are used in the next step of the process.

The aluminum hydroxide thus recovered may be calcined by the processes well known in the art (e. g. at 1000°–1200° C.) to recover a good grade of alpha-alumina suitable for use in the electrolytic manufacture of aluminum metal.

Step B

The combined filtrate and washings from the preceding step, comprising a solution of ammonium fluoride and/or alkali metal fluorides, is now reacted with titanic sulfate, in acidic medium, where the following reaction occurs:



The alkali metal fluotitanate precipitates from the solution. The formation of the co-product of alkali metal sulfate or ammonium sulfate further serves to "salt out" or insolubilize the alkali metal fluotitanate.

The reaction of the fluoride salt solution with the titanic sulfate may be effected at any temperature between 10° C. and the boiling point of the reaction mixture. I prefer to effect the reaction at a temperature between 70° C. and 105° C. and thereafter to cool and (if necessary) concentrate the reaction mixture to precipitate the alkali metal fluotitanate and separate it from the concomitant by-product of ammonium sulfate and/or alkali metal sulfate.

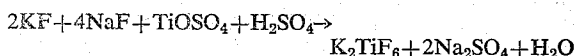
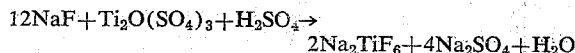
Sodium fluotitanate is soluble in water at 20° C. to the extent of 60–70 grams per liter, potassium fluotitanate to the extent of 11–13 grams per liter, and these solubilities are further diminished by the "salting-out" effect of the alkali metal sulfate produced as co-products of the reaction of this invention.

It is essential that the reaction of this invention be effected in an acidic medium. In an alkaline medium, alkali metal fluotitanates will hydrolyze with the precipitation of hydrated titanium dioxide. It is therefore essential that sufficient free sulfuric acid be present in the reaction medium to yield an acidic reaction.

Titanic sulfate, or titanium disulfate—Ti(SO₄)₂—can be obtained by the action of hot sulfuric acid or oleum on titanium dioxide (Von Bichowsky, U. S. Patent 1,915,393; Weizmann and Blumenfeld, British Patent 209,480; Titan Co., British Patent 471,397; French Patent 813,785; Kirkham and Spence, British Patent 263,886; Boguslavskaya and Ottamanovskaya, Journ. Gen. Chem. (USSR) 10, 673 (1940) and exists as the anhydrous salt and in the form of a number of hydrates.

I find further that the basic titanium sulfates, such as titanium oxytrisulfate (Ti₂O(SO₄)₃) and titanyl sulfate (TiOSO₄) or the hydrates thereof, may be used in the process of this invention, providing that the reaction medium contains sufficient sulfuric acid to provide a total of at least two sulfate ions for each titanium ion in the

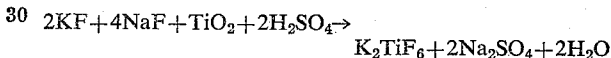
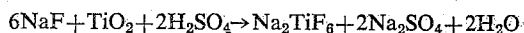
reaction mixture and in addition to render the mixture acidic in reaction, e. g.



These basic titanium sulfates may be prepared by the hydrolysis of titanic sulfate or by the controlled reaction of titanium dioxide with sulfuric acid (Chem. Zentralblatt 1924II, 2289; 1927I, 2234, 1930I, 1672; Rosenheim and Schutte, Zeitschr. anorg. Chemie 26, 239, 50 (1901); German Patent 123,860; British Patent 290,491; U. S. Patent 1,980,812; U. S. Patent 1,559,113; British Patent 364,613; German Patent 599,502).

I also find that a mixture of titanium dioxide and sulfuric acid may be used in the process of this invention, providing that at least two moles of H₂SO₄ are used per mole of TiO₂ and sufficient sulfuric acid in excess is employed to give an acidic reaction in the medium.

Thus, a solution of ammonium and/or alkali metal fluorides may be digested with TiO₂ and H₂SO₄ in an acidic medium, preferably at 70° C. to 105° C., to give the corresponding alkali metal fluotitanate, according to the reaction, e. g.:



The titanium dioxide used in this modification may be in the form of anatase, brookite, rutile, as amorphous metallurgical grade titanium dioxide, as a concentrate derived by chemical beneficiation (e. g. the high titania slag derived in the Sorel, Quebec, operation of the Quebec Iron & Titanium Corporation as a co-product in the electrothermal smelting of ilmenite) or as the low-iron titania concentrate obtained by the chemical process described in my co-pending application Serial No. 358,161, filed May 28, 1953. An excellent and highly reactive form of titanium dioxide for use in this modification of the process is the hydrated titanium dioxide (titanic acid or metatitanic acid) derived by the hydrolysis of titanium salts (such as Ti₂(SO₄)₃ or TiCl₄) and now manufactured in large tonnages as intermediates in the preparation of pigment grade titanium dioxide.

A preferred embodiment of the process of this invention involves the use of the crude technical solution of titanic sulfate, which may contain considerable amounts of iron sulfates, obtained in the Washburn process for the manufacture of titanium dioxide (U. S. Patent 1,889,027 (1933); British Patent 288,569 (1927); French Patent 652,357 (1928); Canadian Patent 299,992 (1930). Ilmenite (or a high-titania iron-oxide containing ore or slag) is ground, digested with concentrated sulfuric acid, diluted with water, treated with a reducing agent to convert ferric sulfate to the ferrous state clarified by the addition of antimony sulfide and a proteinaceous material which serve to carry down all suspended matter, cooled to separate and crystallize out a large portion of the ferrous sulfate in the solution, and thereafter filtered to separate the filtrate of titanic sulfate.

The solution at this stage will contain 420 to 450 gms. Ti(SO₄)₂, 80 to 85 gms. FeSO₄ and 65 to 70 gms. free H₂SO₄ per liter. This solution may be further evaporated in lead-lined evaporators to approximately 600 gms. Ti(SO₄)₂, 160 gms. FeSO₄ and 70 gms. free H₂SO₄ per liter. Either of these technical solutions may be used as a source of titanic sulfate in the process of this invention. As long as the reaction mixture is maintained in the acidic state, the iron salts show no tendency to precipitate, and the alkali metal fluotitanates are precipitated in a state of high purity. The ferrous sulfate re-

mains dissolved in the filtrate and in no ways interferes with the recovery of the alkali metal fluotitanate.

Thus, it becomes feasible by this process to make alkali metal fluotitanates employing the cheapest technical form of titanium salt solution now industrially available, i. e. the crude FeSO_4 -containing titanic sulfate solution of the Washburn process. This solution is often concentrated further, cooled and filtered to remove more FeSO_4 , and finally allowed to form a solid cake containing the equivalent of about 20% TiO_2 , 50% H_2SO_4 and 30% water and ferrous sulfate, proportions corresponding approximately to $\text{Ti}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ in composition. This cake is also ideally suitable for use in the process of this invention. All present processes for the manufacture of titanium metal require the use of a highly purified titanium salt as a starting material, as does the sodium reduction of alkali metal fluotitanate process described and claimed in my co-pending application Serial No. 438,873, filed June 23, 1954. It is therefore highly important to stress that such high purity alkali metal fluotitanates may be obtained by the process of this invention although we use as raw material the crude FeSO_4 -containing titanic sulfate solution obtained in the widely practiced Washburn process.

The following examples are given to define and to illustrate the present invention but in no way to limit it to reagents, proportions or conditions described therein. Obvious modifications will occur to any person skilled in the art.

Example I

A graphite-lined crucible is charged with 172 kgs. of molten aluminum metal and 623 kgs. of anhydrous sodium fluotitanate is added in small portions. The reaction mixture is placed in an induction furnace and is heated with agitation, until the reaction is complete and the reaction mixture has attained a temperature of about 1400°C . The molten reaction mixture is maintained near this temperature for about 15 minutes and is then cooled and allowed to solidify. The solidified mass is broken mechanically into lumps and is then leached with 17,000 liters of hot water. The hot solution is filtered from the insoluble alloy, which is washed free of soluble matter with a further 2000 liters of hot water. The filtrate and washing are combined. The alloy thus recovered is dried. There is thus obtained 200 kgs. of an alloy containing 70% of titanium and 30% of aluminum.

To the hot filtrate obtained above, there is now added 636 kgs. of soda ash and the reaction mixture is heated and agitated at 90° – 100°C . until no further carbon dioxide is evolved and the precipitation of aluminum hydroxide is complete. The precipitate is filtered off and is washed with small amounts of boiling water until free of soluble matter. The filtrate and washings are combined. The filtercake of aluminum hydroxide, on being calcined at 1000° – 1200°C . by the well known techniques of the prior art, is converted to 200 kgs. of a good grade of alpha-alumina.

The combined filtrate and washings (containing NaF) are now treated with a slurry of titanic sulfate obtained by the digestion of 240 kgs. of titanium dioxide in 675 kgs. of 66° Bé. sulfuric acid. The reaction mixture is heated with agitation for 30 minutes at 90° – 100°C ., and is then concentrated to a volume of 4000 liters, preferably under reduced pressure. (In the cyclic operation of this process, it is desirable to add 38 kgs. of sodium fluoride (5% per cycle) to the filtrate and washings prior to reaction with titanic sulfate to compensate for mechanical losses). The reaction mixture is now cooled, and the precipitated sodium fluotitanate is filtered off, and dried by a short heating (e. g. in a rotary kiln at 150° – 200°C .). There is thus recovered (in the cyclic operation of this process) the 623 kgs. of anhydrous sodium fluotitanate required in the first step of the process.

On concentrating and crystallizing the filtrate from the Na_2TiF_6 precipitate, preferably at a temperature above 35°C ., there is recovered a salable by-product of 840 kgs. of saltcake.

Example II

A crucible is charged with 252 kgs. of molten aluminum metal and 721 kgs. of anhydrous potassium fluotitanate is added in small portions. The reaction mixture is placed in an induction furnace and is heated, with agitation, until the reaction is complete and the reaction mixture has attained a temperature of about 1300°C . The molten reaction mixture is maintained near this temperature for about 20 minutes and is then cooled and allowed to solidify. The solidified mass is broken mechanically into lumps and is then leached with 15,000 liters of hot water. The hot solution is filtered from the insoluble alloy, which is then washed free of soluble matter with a further 3,000 liters of hot water. The filtrate and washings are combined. The alloy thus recovered is dried. There is thus obtained 290 kgs. of an alloy containing 50% titanium and 50% aluminum.

To the hot filtrate obtained above, there is now added with good agitation 730 kgs. of 28% aqua ammonia and the reaction mixture is heated and agitated at 90° – 100°C ., while passing through a stream of a carbon dioxide-containing gas (e. g. filtered flue gas) until the precipitation of aluminum hydroxide is complete. The precipitate is filtered off and is washed with small amounts of boiling water until free of soluble matter. The filtrate and washings are combined. The filtercake of aluminum hydroxide, on being calcined at 1000° – 1200°C ., is converted to 190 kgs. of a good grade of alpha-alumina.

The combined filtrate and washings (containing KF and NH_4F) are now heated with a quantity of the titanic sulfate filtercake from the Washburn process (containing about 20% TiO_2 , 50% H_2SO_4 , 30% water and minor amounts of FeSO_4) containing the equivalent of 240 kgs. of titanium dioxide. The reaction mixture is heated with agitation for 30 minutes at 90° – 100°C ., and is then concentrated to a volume of 4500 liters, preferably under reduced pressure. (In the cyclic operation of this process, it is desirable to add 85 kgs. of $\text{KF} \cdot 2\text{H}_2\text{O}$ (5% per cycle) to the filtrate and washings prior to reaction with titanic sulfate to compensate for mechanical losses.) The reaction mixture is now cooled, and the precipitated potassium fluotitanate hydrate is filtered off and dehydrated by calcining at 200° – 300°C . in a rotary kiln. There is thus recovered (in the cyclic operation of this process) the 721 kgs. of anhydrous potassium fluotitanate required in the first step of the process.

On neutralizing the filtrate with aqua ammonia, concentrating and crystallizing, there may be recovered a salable by-product of 795 kgs. of ammonium sulfate.

Having described my invention, what I claim and desire to protect by Letters Patent is:

1. A cyclic process for the manufacture of titanium-aluminum alloys containing 0.1% to 95% of titanium, and the regeneration of the intermediates of said process which comprises in combination the steps of initially reacting an alkali metal fluotitanate with metallic aluminum in stoichiometric excess at temperatures between 660°C . and 1800°C . to obtain the said titanium-aluminum alloy and a by-product salt mixture of alkali metal fluoaluminate and aluminum fluoride, thereafter separating said alloy from said salt mixture, reacting said salt mixture of alkali metal fluoaluminate and aluminum fluoride, in an aqueous medium, with at least one member of the group consisting of ammonium hydroxides, ammonium carbonates, ammonium bicarbonates, alkali metal hydroxides, alkali metal carbonates, and alkali metal bicarbonates in quantity sufficient to precipitate all of the aluminum ions in the salt mixture as aluminum hydroxide, separating said precipitate of aluminum hy-

dioxide from the resulting solution containing at least one member of the group consisting of ammonium fluoride and alkali metal fluorides, reacting said solution with a titanium containing product comprising at least one member of the group consisting of titanic sulfate, basic titanium sulfate, and titanium dioxide, the reaction mixture containing at least two equivalents of sulfate ion for each equivalent of titanium ion, separating the resultant alkali metal fluotitanate from the reaction mixture, and recycling said separated alkali metal fluotitanate to the above said initial reaction of alkali metal fluotitanate and metallic aluminum.

2. The process of claim 1 where from 38.5 grams to 47.9 kilograms of metallic aluminum is reacted with each gram-mole of alkali metal fluotitanate.

3. The process of claim 1 where the alkali metal fluotitanate is sodium fluotitanate.

4. The process of claim 1 where the alkali metal fluotitanate is potassium fluotitanate.

5. The process of claim 1 where the reaction mixture of the alkali metal fluotitanate and metallic aluminum is brought to a terminal temperature within the range of 900° C. to 1550° C.

6. The process of claim 1 wherein the titanium-containing product employed is titanic sulfate of composition $Ti(SO_4)_2$.

7. The process of claim 1 wherein the titanium-containing product employed is titanium dioxide in the presence of at least sufficient sulfuric acid to provide an acidic reaction medium containing at least two moles of sulfate ion per mole of titanium ion.

8. The process of claim 1 wherein the titanium-containing product employed is titanic sulfate containing iron sulfate and free sulfuric acid.

9. The process of claim 1 wherein the titanium-containing product employed is in the form of a solution containing 400 to 700 grams per liter of $Ti(SO_4)_2$ together with iron sulfate and free sulfuric acid.

10. The process of claim 1 wherein the titanium-containing product employed is a hydrated titanium dioxide obtained by the hydrolysis and filtration of a member of the group consisting of titanic sulfate and titanium tetrachloride.

11. The process wherein the titanium-aluminum alloys prepared as described in claim 1 containing more than 53% of titanium are comminuted and leached with an alkali metal hydroxide solution to dissolve the aluminum contained therein and separate the titanium metal content thereof.

12. The process wherein the titanium-aluminum alloys prepared as described in claim 1 containing more than 53% of titanium are distilled to volatilize the aluminum contained therein and separate the titanium metal content thereof.

13. The process wherein the titanium-aluminum alloys prepared as described in claim 1 containing more than 53% of titanium are distilled in the presence of an aluminum trihalide to volatilize the aluminum contained therein as the aluminum monohalide and separate the titanium metal content thereof.

14. The process wherein the titanium-aluminum alloys prepared as described in claim 1 containing more than 53% of titanium are distilled in the presence of aluminum trichloride to volatilize the aluminum contained therein as aluminum monochloride and separate the titanium metal content thereof.

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U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,837,426

Jonas Kamlet

June 3, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 26, for "90°-1100° C." read -- 900°-1100°C. --; column 3, line 16, for "Patents 2,252,241" read -- Patents 2,252,421 --; line 18, for "16," read -- 19, --; column 4, line 17, for "(1929)" read -- (1949) --.

Signed and sealed this 5th day of August 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,837,426

Jonas Kamlet

June 3, 1958

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 26, for "90°-1100° C." read -- 900°-1100°C. --; column 3, line 16, for "Patents 2,252,241" read -- Patents 2,252,421 --; line 18, for "16," read -- 19, --; column 4, line 17, for "(1929)" read -- (1949) --.

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