United States Patent Office 2,864,732
Patented Dec. 16, 1958

2,864,732

METHOD OF COATING TITANIUM ARTICLES AND PRODUCT THEREOF

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No Drawing. Application October 5, 1953
Serial No. 384,341

15 Claims. (Cl. 148—6.15)

This invention relates to surface preparation of titanium, and titanium-containing metals. More particularly, this invention relates to chemically active baths for treating said surfaces, and to processes utilizing said baths, and articles of titanium, and titanium-containing metals treated thereby.

It is well known that the fabrication and use of titanium, and titanium-containing metals, present certain severe and inherent difficulties. Of particular difficulty are the poor antigalling and antiseizing properties of such metals when they are subjected to reciprocal, rotary, or shaping forces and pressures, especially when their surfaces are in loaded contact with another metal surface.

It is known that heating titanium, and titanium-containing metals, in air tends to reduce the galling and seizing properties inherent in such metals when brought into contact with another metal surface in the presence of a lubricating film and subjected to light-reciprocating, low-rotary, and limited-shaping forces and pressures. The reduction in galling and seizing properties is due to the formation of a thin oxide film on the surface of the base metal. This oxide film functions to separate the metal surfaces and retain the lubricant, thereby reducing the tendency to gall and seize when subjected to light-reciprocating forces, low rotary speeds and forces, and limited-shaping forces and pressures. However, the separation of the metal surfaces continues only so long as the relatively thin oxide film is not destroyed by the abrasion of foreign particles, rough surfaces, or by merely wearing away.

Thus, even though a lubricating film is placed between a heat-treated titanium surface and another metal surface, the lubricant does not eliminate galling and seizing problems.

It is, therefore, an object of this invention to provide prepared surfaces of titanium, and titanium-containing metals, that will exhibit superior antigalling and antiseizing properties when subject to reciprocal, rotary, or shaping forces and pressures, when in loaded contact with other metal surfaces.

Further, it is an object of this invention to provide a variety of chemically active baths for the surface treatment of titanium, and titanium-containing metals.

Still further, it is an object of this invention to provide processes utilizing chemically active baths, and articles of titanium and titanium-containing metals treated thereby.

Further objects and advantages of the present invention will be apparent in view of the following detailed disclosure and description thereof.

The present invention relates to the formation of surface coatings on articles of titanium, and titanium-containing metals, with an aqueous chemically active bath solution comprising a halide, at least one salt selected from the group consisting of phosphates, borates, oxalates, citrates, and tartrates of alkali and alkaline earth metals, and a halogen acid.

The present invention also relates to a process wherein the metal articles are treated with the aforesaid aqueous bath solution by immersion, dipping, spraying, or other suitable means; the aqueous bath solution being stirred, agitated, heated, or cooled, as required. The process also includes, if required, the step of furnacing the treated metal articles in a gaseous atmosphere at a temperature of from 600° F. to 1000° F. for a period of from one to five hours. Lastly, the process includes the steps of subjecting the treated metal to shaping forces and pressures, such as are required to draw wire or form tubing.

The titanium, and titanium-containing metals, hereinafter referred to simply as "titanium metal" are defined as pure unalloyed titanium or titanium-base alloys. Examples of suitable alloying elements include: manganese, aluminum, molybdenum, vanadium, tin, iron, nitrogen, oxygen, copper, and chromium. Other refractory metals, such as zirconium and its alloys, could be treated by the practice of this invention.

The halide of the aqueous, chemically active bath composition may be defined as a binary compound of fluorine, chlorine, bromine, or iodine, with an element or radical. In the practice of this invention, it has been found that halides of the alkaline metals and alkaline earth metals are satisfactory. Potassium fluoride, potassium chloride, and sodium fluoride have been found to be particularly adapted for use in the subject bath.

The salt used in the aqueous, chemically active bath composition has been previously described as being selected from the group consisting of phosphates, borates, oxalates, citrates, and tartrates of alkali and alkaline earth metals. In the practice of this invention, it has been found that, when one or more of the acid hydrogens of the acid have been replaced by an alkali or alkaline earth metal, satisfactory results are obtained. Tribasic sodium phosphate, dibasic sodium phosphate, potassium dihydrogen phosphate, sodium tetraborate, and sodium metaborate have been found to be particularly well adapted for use in the subject bath.

The halogen acid may be hydrofluoric acid, hydrochloric acid, bromic acid, or iodic acid. Hydrofluoric and hydrochloric acids have been found to be particularly well adapted for use in the subject bath. The halogen acid need not be the same as the halogen of the halide.

Further, each of the above three groups of bath ingredients could be used singly or in combination with others of the same group.

In the use of the aqueous, chemically active bath, the temperature range may satisfactorily be from about 15° C. up to 100° C. However, if a temperature lower than 25° C. is used, the immersion time becomes unduly long and quality of the coating may be lessened. The pH of the bath should not be greater than 6.8.

The coatings formed on the titanium metal by treatment in the bath have a filmlike gray appearance. The coating is soluble in HCl, HNO_3, HF, concentrated NaOH, and boiling H_2O. The coating demonstrates high adsorption affinities for nonviscous fluids, such as lubricating oils, inks, dyes, and paints.

The surface of the titanium metal should be clean and free of any scale or oxide prior to immersion in the

bath. If the titanium metal has a grease film covering the surface, it has been found that the use of a hot sodium metasilicate degreasing bath prior to treating in the stripping bath will remove such a grease film and facilitate the action of the stripping bath. An HF—HNO_3 bath will satisfactorily remove scale or oxide subsequent to degreasing. The compositions of the above degreasing and stripping baths are set forth only for the purpose of aiding one skilled in the art to practice the subject invention, and are not intended to limit the process claims hereinafter set forth to the use of specific degreasing and stripping baths as herein illustrated. Any such baths that will prepare a clean surface, free of oxide and scale, will be satisfactory in the practice of this invention.

After the treatment of the surfaces of titanium metal to form a coating thereon, it has been found that the properties of said surface with regard to wear resistance and adsorption of lubricants and oils will be improved if the treated titanium metal is heated in an air circulating furnace at 600° F. to 1000° F. for a period of from one to five hours. Experimental evidence indicates that the outer surface layer of the treated titanium metal is not altered by the heat treatment, but that a layer of anatase (TiO_2) is built up at the interface between the base metal and the surface coating layer. There is no oxygen penetration into the grain boundaries of the base metal, thus indicating that the formation of the anatase takes place at the base-metal surface-coating interface. The treatment coating permits the rapid formation of the desirable anatase layer, the formation of which is limited and ineffective when bare, untreated titanium metal is heated in air. Further, the anatase thus formed does not weaken or alter the grain structure of the metal because there is no penetration into the grain boundaries of the base titanium metal. A gaseous furnace atmosphere other than air, which would supply oxygen for the formation of the anatase, could also be used in the practice of this invention.

The following examples of the practice of this invention are set forth only for the purpose of illustrating said invention and are not to be construed as limiting or restricting it thereto.

In the examples set forth below, reference will be made to the following titanium and titanium-containing metals. RC 55 is pure titanium metal. RC 130A contains 7% manganese, the balance being titanium. RC 130B contains 4% manganese, 4% aluminum, with the balance being titanium. Ti 75A contains 0.1% iron, 0.02% nitrogen and traces of oxygen, the balance being titanium. Ti 150A contains 1.3% iron, 0.02% nitrogen, 0.25% oxygen, 0.2% carbon, and 2.7% chromium, the balance being titanium.

Example I

A 1-liter fluoride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
50 g./l. $Na_3PO_4 \cdot 12H_2O$ and
11.5 ml./l. HF solution (HF of a concentration 50.3% by weight was used in all of the bath solutions set forth by way of example)

The solution was placed in a stainless steel container, fitted with a condenser and heating means. The pH was 5.2 when measured colorimetrically. The solution was heated to a temperature of 85° C. Test specimens of RC 55, 130B, and Ti 75A were immersed, one at a time, for 10-minute intervals in the solution. A light, silvery gray, adherent coating was formed on the surfaces of each test specimen thus immersed. An analysis of the coating indicated the following percent by weight composition; Ti 16.6, Na 8.5, K 24.7, F 38.8 and PO_4 3.1%, the balance being indeterminable by standard analytical procedures.

Example II

A 1-liter fluoride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
35 g./l. $Na_3PO_4 \cdot 12H_2O$ and
15 ml./l. HF solution

The solution was placed in a stainless steel container open at the top. The pH was 3.0 when determined by indicator paper. No cover for the container, or condenser, was required because this bath was intended to operate at room temperature (25–32° C.). Test specimens of RC 55, 130A, 130B, and Ti 75A were immersed, one at a time, for 35-minute intervals. Gray, adherent coatings were formed on the surfaces of each test specimen thus immersed.

Example III

A 1-liter fluoride-phosphate bath solution was prepared having the following ratio of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
50 g./l. $Na_3PO_4 \cdot 12H_2O$ and
28 ml./l. HF solution

The solution was placed in a polyethylene container, which was closed at the top. A 20 ml. sample of the bath was taken and added to 100 ml. of distilled water. This portion was titrated with 1 N NaOH solution using a phenolphthalein indicator. 11.8 to 12.0 ml. of NaOH were neutralized, indicating a pH of less than 1. With the bath solution at 85° F., test specimens of RC 55, 130A, 130B, Ti 75A, and 150A were immersed, one at a time, for 1¼ minutes to form a silvery gray, adherent coating on the surface. When the bath was operated at 75° F., an immersion period of 1¾ minutes was sufficient to produce a similar coating.

Example IV

A 2-liter fluoride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

84 g./l. $KF \cdot 2H_2O$
160 g./l. $Na_3PO_4 \cdot 12H_2O$ and
30 ml./l. HF solution

This solution was placed in a stainless steel container fitted with a cover, condenser, stirring and heating means. The pH was 6.3 as determined by a Beckman indicator. The bath was heated to 95° C. and test specimens of RC 55, 130B, and Ti 75A were immersed, one at a time, for 30 minutes. A gassing of the solution was noted when the test specimens were first immersed. A slate-gray, adherent coating was formed on the surfaces of the test specimens.

Example V

A 1-liter fluoride-borate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

18 g./l. $KF \cdot 2H_2O$
40 g./l. $Na_2B_4O_7 \cdot 10H_2O$ and
16 ml./l. HF solution

This solution was placed in a stainless steel container equipped with a cover, condenser, stirring and heating means. The pH was determined colorimetrically to be 6.4. Upon a 20-minute immersion of test specimens of RC 55, 130A, 130B, Ti 75A, and Ti 150A at a temperature of 85° C., a dark gray, slippery, adherent coating was formed on the surfaces of each test specimen thus immersed. An analysis of the coating indicated the following per cent by weight composition; Ti 29.9, Na 7.4,

K 24.2, F 35.9 and B_4O_7 0.5, the balance being indeterminable by standard analytical procedures.

Example VI

A 1-liter fluoride-borate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

30 g./l. $KF \cdot 2H_2O$
50 g./l. $Na_2B_4O_7 \cdot 10H_2O$ and
22 ml./l. HF solution

This solution was placed in a stainless steel container equipped with a cover, condenser, stirring and heating means. The pH was determined colorimetrically to be 6.4. With the bath solution at 85° C., test specimens of Ti 75A and 130B were immersed, one at a time, for 18 minutes, to form a silvery gray, adherent coating on the surfaces of each test specimen thus immersed.

Example VII

A 1-liter fluoride-oxalate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

6 g./l. $KF \cdot 2H_2O$
20 g./l. $Na_2C_2O_4$ and
3 ml./l. HF solution

The bath solution was placed in a stainless steel container. The pH was 4.2 as determined by a Beckman indicator. Test specimens of RC 55, 130A, 130B, and Ti 75A were immersed, one at a time, for 30-minute intervals at a temperature of 31° C. Coatings were formed, which were gray, fairly thin, but durable and adherent. A dark color developed in the solution adjacent to the test specimens upon immersion, and the bath turned a dark amber color as the duration of the immersion continued. A special test conducted with five Ti 75A test specimens indicated that the coating reaction reaches an equilibrium point after 30 minutes and then proceeds in the opposite direction, after this time, removing the coating. The five test specimens were immersed simultaneously and removed at 15-minute intervals. The most satisfactory coating was formed after a 30-minute immersion. Coatings formed by longer immersion became dark gray and increasingly nonadherent until, after a 75-minute immersion, the coating was completely nonadherent and easily rubbed off. The temperature of the bath for this test was maintained at 31° C.

Example VIII

This example was intended to show the effect of an increase in temperature on the time required to satisfactorily coat the surface of test specimens. A 1-liter fluoride-oxalate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
30 g./l. $Na_2C_2O_4$ and
1 ml./l. HF solution

This solution was placed in a stainless steel container, fitted with a condenser, stirring and heating means. The pH was 4.1 as determined by a Beckman indicator. Test specimens of RC 55, 130A, 130B, and Ti 75A and 150A were immersed, one at a time, for 30 minutes at room temperature (15° C.) to produce light gray, durable, and adherent coatings. The temperature was raised to 60° C. and a 20-minute immersion was sufficient to produce satisfactory coatings. By this time, the color of the bath was dark amber. When the temperature was further raised to 90° C., an immersion time of 15 minutes was sufficient to produce satisfactory coatings, although the coatings were of a darker gray than those formed by immersion in the bath at lower temperatures.

Example IX

A 1-liter fluoride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
50 g./l. KH_2PO_4

and sufficient HF solution, so as to give a pH of less than one when measured by titration of the free acid content. The solution was placed in a stainless steel container open at the top. Test specimens of RC 130B and Ti 75A were immersed, one at a time, for 5-minute intervals at a temperature of 30° C. A dark gray, adherent coating was formed on the surfaces of each test specimen thus immersed.

Example X

A 1-liter chloride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. KCl
50 g./l. $Na_3PO_4 \cdot 12H_2O$

and sufficient HF solution so that the pH of the solution was 4.0 when determined by titration of the free acid content. The solution was placed in a stainless steel container with a closed top, condenser, and heating means. Test specimens of RC 55, 130A, 130B, Ti 75A and 150A were immersed, one at a time, for 10-minute intervals at a temperature of 85° C. Thick, greenish-gray coatings, adherent and durable, were formed on the surfaces of each test specimen thus immersed.

Example XI

To the chloride-phosphate bath solution, as described in Example X, was added sufficient HF solution so that the pH was indicated to be less than one. A 5-minute immersion at room temperature produced a coating similar to that formed on the surfaces of the test specimens in Example X, except that larger crystal formations, slightly less adherent than those coatings formed in Example X, were formed on the surfaces of each test specimen thus immersed.

Example XII

A 1-liter fluoride-phosphate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

5 g./l. $KF \cdot 2H_2O$
10 g./l. $CaHPO_4 \cdot 2H_2O$

and sufficient HF solution so as to give a pH of 1.0 as determined by titration of the free acid content. This solution was placed in a stainless steel container equipped with a cover and heating means. The test specimens of RC 55, 130A and 130B, Ti 75A and 150A were immersed, one at a time, at room temperature for 5-minute intervals. A dark gray, slippery filmlike, yet fairly adherent coating was formed on the surfaces of each test specimen thus immersed.

Example XIII

A 1-liter fluoride-tartrate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
50 g./l. $KNaC_4H_4O_6 \cdot 4H_2O$

and sufficient HF solution so as to give a pH of 5.0 when determined by colorimetric means. This solution was placed in a stainless steel container equipped with a cover and heating means. Test specimens of RC 55, 130A and 130B, Ti 75A and 150A were immersed, one at a time, for 10-minute intervals at a temperature of 85° C. Light gray, adherent and durable coatings were formed on the surfaces of each test specimen thus immersed.

Example XIV

To the bath solution, as described in Example XIII, was added sufficient additional HF solution so as to lower the pH to 4.0. The temperature was maintained at 85° C. and the test specimens were immersed, one at a time, for 10-minute intervals. Thin, yet durable and adherent, mottled, dark gray coatings were formed on the surfaces of each test specimen thus immersed.

Example XV

To the fluoride-tartrate bath solution, as described in Example XIV, was added sufficient additional HF solution so as to lower the pH to less than one. The bath solution was cooled to room temperature and the test specimens were immersed, one at a time, for 1-minute intervals. A thick, dark gray, durable and adherent coating was formed on the surfaces of each test specimen thus immersed.

Example XVI

A 1-liter fluoride-citrate bath solution was prepared having the following composition of ingredients per liter of aqueous solution:

20 g./l. $KF \cdot 2H_2O$
50 g./l. $Na_3C_6H_5O_7 \cdot 11H_2O$

and sufficient HF solution so as to give a pH of 5.0 when measured by a Beckman indicator. The solution was placed in a stainless steel container equipped with a cover and heating means. The temperature was raised to 85° C. and test specimens of RC 55, 130A, 130B, Ti 75A and 150A were immersed, one at a time, for 10-minute intervals. Medium gray, adherent, durable coatings were formed on the surfaces of each test specimen thus immersed.

Example XVII

To the fluoride-citrate bath solution, as described in Example XVI, was added sufficient additional HF solution so as to lower the pH to less than one. The bath solution was cooled to room temperature and the test specimens were immersed, one at a time, for 2-minute intervals. A thin, brownish gray, durable, and adherent coating was formed on the surfaces of each test specimen thus immersed.

Example XVIII

Test specimens of RC 55, 130A, 130B, and Ti 75A and 150A, treated to form coatings as per Examples I through XVII, were introduced into a tube furnace and heated to temperatures in the range of from 600° F. to 1000° F. for a period of from one to five hours. During the heating, there was a constant circulation of outside air through the furnace. This "furnacing" or heat treatment caused the formation of anatase (TiO_2) at the interface of the base metal and the surface coating.

The coatings thus formed on the surface of titanium metals may be evaluated by different types of tests. Two of these are:

Reciprocating wear against steel or titanium wear plates under high loads, and

Wire drawing under simulated commercial conditions. These evaluation tests show the effectiveness of the coating in preventing galling and seizing of the treated metal. The end points of these evaluation tests are clearly evident by galling and seizing of the titanium metals when a breakdown of the surface coating occurs.

Data obtained from tests for improved reciprocating wear properties are set forth below in Tables 1 and 2. The tests were conducted with an apparatus in which two test specimens (½-inch diameter by ¼-inch thick) were mounted on a carriage which reciprocated on machined wear plates, set in an oil-retainer recess which was filled with SAE 20 oil. The carriage was weight-loaded from underneath, thus bringing the test specimens directly against the wear plates under the full-weight load.

Actual pressure of the test specimens against the wear plate varied, depending upon the weight load and the contact area. The apparatus was run at 23 reciprocating strokes per minute until the prepared surfaces broke down, causing the test specimens to gall on the wear plates, automatically shutting off the apparatus.

The test specimens for which data are set forth in Table 1 were run against 1045 steel wear plates, hardened to 50 Rockwell C. No. 1 was machined Ti 75A; No. 2 was machined Ti 75A, treated to form a coating as per Example I, but not furnaced; No. 3 was machined Ti 75A, furnaced as per Example XVIII; No. 4 was machined Ti 75A, lapped to optical flatness and furnaced as per Example XVIII; No. 5 was machined Ti 75A, treated to form a coating as per Example I, and furnaced as per Example XVIII; No. 6 was machined Ti 75A, treated to form a coating as per Example V and furnaced as per Example XVIII.

TABLE I

Test Specimen Number	Number of Strokes (and time) before Galling and Seizing Occurred	Load (p. s. i.)
1	2 (0.1 min.)	400
2	15 (0.7 min.)	400
3	17 (0.7 min.)	1,000
4	4,500 (3.3 hrs.)	1,000
5	1,156,998 (837 hrs.)	2,500
6	1,077,317 (780 hrs.)	2,500

The test specimens for which data are set forth in Table 2 were run against Ti 75A wear plates, prepared as indicated. No. 1 was machined Ti 75A run against Ti 75A wear plates; No. 2 was machined Ti 75A treated to form a coating as per Example I run against Ti 75A wear plates; No. 3 was machined Ti 75A treated to form a coating as per Example I run against Ti 75A wear plates also treated as per Example I; No. 4 was machined Ti 75A treated to form a coating as per Example I and furnaced as per Example XVIII, run against Ti 75A wear plates; No. 5 was machined Ti 75A treated to form a coating as per Example I and furnaced as per Example XVIII, run against Ti 75A wear plates, also treated to form a coating as per Example I and furnaced as per Example XVIII.

TABLE 2

Test Specimen Number	Number of Strokes (and time) before Galling and Seizing Occurred	Load (p. s. i.)
1	4 (0.2 min.)	600
2	8 (0.4 min.)	550
3	17 (0.7 min.)	550
4	354 (15.4 min.)	550
5	142,090 (103 hrs.)	1,250

The surfaces of titanium metal coated and furnaced by the practice of this invention clearly exhibit superior new and novel properties over uncoated, but furnaced surfaces of titanium metal when subjected to the above-described evaluation tests.

The improved properties of coated and furnaced titanium metal surfaces over uncoated, but furnaced titanium metal surfaces may be explained as follows:

The improved reciprocating wear properties are due to the fact that the wear-resistant coating also adsorbs and retains the lubricant on its surface, thereby providing a lubricating phase at the points of contact and thus effectively reduces the friction between the surfaces of the metals. The friction being reduced, there is less friction heat generated and, thus, galling conditions are alleviated or prevented almost completely.

Another evaluation test was wire drawing through a series of dies, with a planned reduction in diameter of 85%. The wire sections were drawn using Molykote-G as a die lubricant and were not annealed between passes.

No. 1 was bare Ti 75A wire; No. 2 was Ti 75A wire treated to form a coating as per Example I; No. 3 was Ti 75A wire treated to form a coating as per Example III; No. 4 was Ti 75A wire treated to form a coating as per Example V; No. 5 was Ti 75A wire treated to form a coating as per Example I and furnaced as per Example XVIII.

TABLE 3

Test Specimen Number	Initial Diameter, Inches	Final Diameter, Inches	Percent Total Reduction	Total Number Passes Through Dies
1	0.125			0
2	0.124	0.048	85	8
3	0.144	0.057	84	11
4	0.125	0.076	63	8
5	0.125	0.048	85	9

In the case of wire drawing, the coating on the surfaces serves two functions: it acts as a carrier for solid-phase lubricants, such as Molykote-G, as the blank moves into the die, and it functions as a lubricant itself under the high temperatures and pressures of the die by melting and forming a fluid layer between the blank and the die. This fluid layer acts not only to separate the surfaces but distributes evenly over the surface of the blank the hydraulic pressure exerted by the die face.

This invention represents, so far as is known, the first instance of the surface preparation of titanium metals by forming on the metal surface a coating by treatment with an aqueous chemically active bath solution containing a halide, at least one salt selected from the group consisting of phosphates, borates, oxalates, citrates, and tartrates of alkali and alkaline earth metals and a halogen acid. Further, the processes utilizing said bath wherein the treated titanium metal surfaces are furnaced at 600° F. to 1000° F. for from one to five hours, or subjected to shaping forces and pressures, are believed to be new and novel in the art.

Articles composed of, or fabricated from titanium metal, the surfaces of which have been prepared by the practice of this invention, will be useful in any application where titanium, or titanium-containing metal, articles are to be put in loaded contact with another titanium or metal surface. The prepared surfaces will be particularly useful in applications where it is necessary that there be a lubricant phase present to lower the coefficient of friction between surfaces in loaded contact with each other.

While the particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that various changes and modifications may be made without departing from the invention in its broader aspects, and, therefore, the appended claims are intended to cover all such changes and modifications as fall within the true spirit and scope of this invention.

What is claimed is:

1. A composite article comprising a basis material selected from the group containing titanium and titanium-base alloys, and a coating on the surface of said basis material, said coating consisting essentially of a major proportion of chemically combined titanium, at least one metal selected from the group consisting of the alkali metals and the alkaline earth metals, and at least one halide, and a minor proportion of a non-metallic radical selected from the group consisting of phosphate, borate, oxalate, citrate, and tartrate.

2. A composite article comprising a basis material selected from the group consisting of titanium and titanium-base alloys, and a coating on the surface of said basis material, said coating consisting essentially of a major proportion of chemically combined titanium, at least one alkali metal, and fluoride, and a minor proportion of a non-metallic radical selected from the group consisting of phosphate, borate, oxalate, citrate, and tartrate.

3. The article of claim 2 wherein the non-metallic radical is phosphate.

4. The article of claim 2 wherein the non-metallic radical is borate.

5. In combination with the composite article of claim 1, a layer of anatase at the interface of said basis material and said coating.

6. In combination with the composite article of claim 2, a layer of anatase at the interface of said basis material and said coating.

7. A process for coating the surfaces of titanium, and titanium-base alloys to form thereon a coating consisting essentially of a major proportion of chemically combined titanium, at least one metal selected from the group consisting of alkali and alkaline earth metals, and at least one halide, and a minor proportion of a nonmetallic radical selected from the group consisting of phosphate, borate, oxalate, citrate, and tartrate, said process comprising: contacting said surfaces with an aqueous bath solution consisting essentially of a halide, at least one salt selected from the group consisting of phosphate, borates, oxalates, citrates, and tartrates of alkali and alkaline earth metals, and a halogen acid, the pH of said aqueous bath solution being not greater than 6.8; and removing said surfaces from contact with said aqueous bath solution.

8. The process of claim 7 characterized in that said aqueous bath solution consists essentially of potassium fluoride, tribasic sodium phosphate, and hydrofluoric acid, and the temperature of said aqueous bath solution is maintained in the range of from 25° C. to 100° C.

9. The process of claim 7 characterized in that said aqueous bath solution consists essentially of potassium fluoride, dibasic sodium phosphate, and hydrofluoric acid; and the temperature of said aqueous bath solution is maintained in the range of from 25° C. to 100° C.

10. The process of claim 7 characterized in that said aqueous bath solution consists essentially of potassium fluoride, potassium dihydrogen phosphate, and hydrofluoric acid; the pH of said aqueous bath solution being not greater than 6.0; and the temperature of said aqueous bath solution is maintained in the range of from 25° C. to 100° C.

11. The process of claim 7 characterized in that said aqueous bath solution consists essentially of potassium fluoride, sodium tetraborate, and hydrofluoric acid; the pH of said aqueous bath solution being not greater than 6.6; and the temperature of said aqueous bath solution is maintained in the range of from 25° C. to 100° C.

12. The process of claim 7 characterized in that said aqueous bath solution consists essentially of potassium fluoride, sodium metaborate, and hydrofluoric acid; and the temperature of said aqueous bath solution is maintained in the range of from 25° C. to 100° C.

13. The process of claim 7 including subsequently subjecting the coated surface to shaping forces and pressures.

14. The process of claim 7 including subsequently heating the coated surface to a temperature of from 600° F. to 1000° F. in a gaseous oxidizing atmosphere for from one to five hours.

15. The process of claim 14 including subsequently subjecting the heated, coated surface to shaping forces and pressures.

References Cited in the file of this patent

UNITED STATES PATENTS

1,549,410	Gravell	Aug. 11, 1925
1,723,067	Pacz	Aug. 6, 1929
2,105,015	Singer	Jan. 11, 1938

(Other references on following page)

11

UNITED STATES PATENTS

2,148,331	Weisberg et al.	Feb. 21, 1939
2,213,263	Thompson et al.	Sept. 3, 1940
2,230,319	Canzler	Feb. 4, 1941
2,276,353	Thompson	Mar. 17, 1942
2,487,137	Hoover et al.	Nov. 8, 1949
2,500,673	Gibson et al.	Mar. 14, 1950
2,665,231	Amundsen et al.	Jan. 5, 1954
2,711,364	Beach	June 21, 1955

12

FOREIGN PATENTS

534,471	Great Britain	Mar. 7, 1941
661,385	Great Britain	Nov. 21, 1951

OTHER REFERENCES

"American Machinist," June 11, 1951, pages 145–153, page 152 relied on.

Schuster et al.: Abstract of Appl. Serial No. 37,498, published November 20, 1951, 652 O. G. 891.