

1

2,285,682

PROCESS AND COMPOSITION FOR COATING TITANIUM SURFACES

Leo Missel, North Hollywood, and James O. Powell, Glendale, Calif., assignors to Menasco Manufacturing Company, Burbank, Calif., a corporation of California

No Drawing. Application August 31, 1953
Serial No. 377,706

10 Claims. (Cl. 204—38)

This invention relates to the metal coating art and has particular reference to a process and composition for coating the surfaces of titanium and titanium alloys to permit subsequent treatment, such as electroplating, of the same.

The primary object of this invention is to provide a novel process and composition for coating surfaces of titanium and titanium alloys with a film of metal.

Titanium and titanium alloys are finding increasing uses and applications, particularly in the aircraft industry, due primarily to the excellent strength-weight ratios of the metal and its alloys. However, these materials exhibit tendencies toward galling, seizing and excessive wear when utilized in applications requiring motion between components such as in bearings, sliding assemblies and the like. Attempts have been made to produce a metallic bearing surface on members formed of titanium and its alloys, but such attempts have heretofore been unsuccessful.

One of the principal objects of this invention is, therefore, to provide a process for the treatment of titanium and its alloys to permit the application thereto of a hard coating having satisfactory bearing characteristics.

Another object of this invention is to provide a process for the treatment of surfaces of titanium and titanium alloys to permit the electroplating thereon of metallic films having characteristics of adhesion, hardness, electrical conductivity, solderability, etc., comparable to films produced on common metals by conventional methods.

Another object of this invention is to provide a process for chromium plating the surfaces of titanium and titanium alloys.

Other objects and advantages of this invention, it is believed, will be readily apparent from the following detailed description of preferred embodiments thereof.

Briefly, this invention includes the discovery that the surfaces of articles of titanium and titanium alloys may be provided with a metallic film by chemical deposition of the film brought about by immersion of the article in an aqueous solution of a mixture of hydrofluoric acid, a salt of the metal to be deposited, and a chromium compound, which metallic film permits subsequent electrolytic plating of the articles. It has been further discovered that good results can also be obtained by immersion of the article in an aqueous solution of a mixture of hydrofluoric acid and a copper salt.

The following are specific examples of processes and compositions embodying the present invention, but it is to be understood that it is not intended to limit the invention to the specific steps set forth therein:

Example 1

Aircraft landing gear parts forged of a titanium alloy including 5% chromium and 3% aluminum were cleaned by a conventional degreasing agent, rinsed and then immersed in an acid etch bath consisting of 3 parts nitric acid and 1 part hydrofluoric acid. The temperature of

2

the bath was 75° F. and the time of immersion was 30 seconds. The purpose of this step is to remove the gross oxide layers typical of those found on forged titanium and titanium alloys. While best results are obtained with the described acid mixture, other acids such as sulfuric, hydrochloric, hydrofluoric acid alone and mixtures of sulfuric and hydrofluoric may be and have been used.

The next step was to water rinse the parts from the acid etch bath, and they were then dipped into a chemical deposition bath for a period of 60 seconds, the temperature of the bath being maintained at 212° F. The bath comprised an aqueous solution of the following ingredients in the proportions indicated:

Example 1a

	Grams/liter
Hydrofluoric acid (anhydrous HF)-----	50
Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)-----	5
Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$)-----	100

The parts were removed from the bath and water rinsed. The parts were then chromium plated in a conventional hard chrome electroplating bath at 3 amperes per square inch for 4 hours, the bath temperature being maintained at 130° F. The plating solution consisted of 33.0 oz./gal. of chromic acid and 0.33 oz./gal. of sulfate ion.

The thickness of the chrome plating obtained by the above process was 0.0045 inch. The adherence of the plating under steel ball indentation tests and under specially designed bearing load tests was excellent and qualified the parts for use in heavy duty aircraft landing gear.

The chemical reactions and/or physical phenomena involved in the deposition of the metallic coating prior to electroplating are not entirely understood. It would appear, however, that the hydrofluoric acid in the deposition bath set forth in Example 1a plays an important part in the removal of the oxide film during the deposition step. The hydrofluoric acid may be formed in situ by the addition of a water soluble salt of hydrofluoric acid and another acid, such as, for example, sulfuric, hydrochloric, citric, phosphoric, etc.

The inclusion of the dichromate in the deposition composition of Example 1a is also an important feature of the invention. It has been found that the dichromate makes possible a chromium plate which meets the rigid requirements for heavily-loaded bearing surfaces. It is believed that this is due in part to a competitive reaction with the zinc salt wherein tightly bound zinc remains adhered to the titanium, and the more loosely bound zinc is redissolved, permitting tightly bound zinc to be deposited in the less adherent areas. Although somewhat less satisfactory, other chromium compounds such as, for example: chromic acid; alkali metal salts of a chromium acid such as sodium chromates, potassium and ammonium chromates and dichromates and the hydrates of these compounds; and other water-soluble salts of a chromium acid may be substituted for the sodium dichromate.

Heavy metal salts other than zinc sulfate have been successfully used in the chemical deposition bath of Example 1a. Copper sulfate has been found to be particularly efficacious as a substitute for the zinc sulfate. Similarly, other soluble salts of heavy metals such as, for example, copper chloride, copper acetate, silver sulfate, cadmium chloride and nickel perchlorate may be used.

The production of maximum adherence of chromium plating appears to be favored by a relatively high content of sodium dichromate, varying between approximately 10% to 30% by weight of the solution, a relatively low zinc sulfate content, varying from approximately 0.5% to 2.0%, and hydrofluoric acid concentration from approximately 2.5% to 5%. However, even with relatively

3

large variations in concentrations, hard chrome plating with a marked degree of adhesion is produced. Concentrations of hydrofluoric acid substantially above 15% by weight are to be avoided since such solutions exhibit a violent reaction and result in a spongy metal deposit. From a standpoint of commercial practicability, the relative proportions of the deposition bath solution of Example 1a may be varied as follows:

Hydrofluoric acid-----	0.01-15.0% (by weight as anhydrous HF).
Chromic acid or soluble salt thereof-----	0.1% by weight to saturation point.
Heavy metal salt-----	0.01% by weight to saturation point.
Water-----	Balance.

The temperature of the deposition bath of Example 1a may be varied from about 60° F. to the boiling point of the solution. The immersion time is not critical, but for best results should be not substantially less than 60 seconds, and can be as long as 3 minutes or more.

Example 2

Titanium alloy parts were cleaned and acid etched in the same manner as set forth in Example 1. They were then immersed for a period of 30 seconds in a deposition bath maintained at a temperature of 212° F. The bath consisted of an aqueous solution of the following ingredients in the proportions indicated:

Example 2a

Hydrofluoric acid (anhydrous)-----	Grams/liter
Copper sulfate-----	10
	225

After rinsing, the parts were plated in a conventional hard chrome plating solution at 3 amperes per square inch for four hours, producing a plating of excellent appearance and having a thickness of 0.0055 inch. The adhesion of the chrome plate produced by the process of this example 2 is not sufficiently high to permit use of the parts where high bearing loads are experienced. However, the adhesion is excellent for relatively low bearing loads, and for decorative plate and other less critical uses, it is more than adequate.

Other copper salts such as, for example, copper chloride, copper acetate, copper bromide, etc., may be substituted for the copper sulfate.

Best results are obtained by relatively high concentrations of copper sulfate and relatively low hydrofluoric acid concentrations. The immersion time is not critical but should not be substantially more than 3 minutes or less than about 5 seconds. The proportion of the ingredients of Example 2a may be varied as follows:

Hydrofluoric acid-----	0.1 to 10% by weight as anhydrous HF.
Copper salt-----	0.5% by weight to saturation point.
Water-----	Balance.

Here again, the temperature may be varied from about 60° F. to the boiling point of the solution.

It will be readily understood by those skilled in the art that the process and composition of this invention are not limited to the chromium plating operation. For example, parts treated as described may be given a copper plating from a conventional acid copper bath, or may be plated with any other conventional metal.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. A composition for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, consisting essentially of an

4

aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.1% by weight to the saturation point of an alkali metal salt of a chromium acid, and from about 0.01% by weight to the saturation point of a soluble salt of a heavy metal selected from the group consisting of copper, zinc, silver, cadmium and nickel.

2. A composition for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, consisting essentially of an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.1% by weight to the saturation point of a compound selected from the group consisting of chromic acid and water soluble salts of a chromium acid, and from about 0.01% by weight to the saturation point of a soluble salt of a heavy metal selected from the group consisting of copper, zinc, silver, cadmium and nickel.

3. A composition for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, consisting essentially of an aqueous solution of from about 0.01% to about 15% of hydrofluoric acid, from about 0.1% by weight to the saturation point of sodium dichromate, and from about 0.01% by weight to the saturation point of zinc sulfate.

4. A process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, including the step of immersing said articles in a bath consisting essentially of an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.01% by weight to the saturation point of a soluble salt of a heavy metal selected from the group consisting of copper, zinc, silver, cadmium and nickel, and from about 0.1% by weight to the saturation point of a compound selected from the group consisting of chromic acid and water soluble salts of a chromium acid, to deposit the heavy metal on the surfaces of said articles.

5. A process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, including the steps of immersing said articles in a bath consisting essentially of an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.01% by weight to the saturation point of a soluble salt of a heavy metal selected from the group consisting of copper, zinc, silver, cadmium and nickel, from about 0.1% by weight to the saturation point of a compound selected from the group consisting of chromic acid and water soluble salts of a chromium acid, and maintaining the temperature of said bath between about 60° F. and the boiling point of said solution, to deposit the heavy metal on the surfaces of said articles.

6. A process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, including the step of immersing said articles in a bath consisting essentially of an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.1% by weight to the saturation point of sodium dichromate, from about 0.01% by weight to the saturation point of zinc sulfate to deposit zinc on the surfaces of said articles.

7. In a process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, the steps of cleaning the articles to be coated, immersing the articles in an acid etch bath, removing said articles and rinsing the same, immersing the articles in an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.1% by weight to the saturation point of sodium dichromate, and from about 0.01% by weight to the saturation point of zinc sulfate for a period of about 60 seconds at a temperature corresponding approximately to the boiling point of said solution to deposit zinc on the surfaces of said articles, removing said articles and rins-

5

ing the same, and electroplating said articles in a plating solution.

8. In a process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, the steps of cleaning the articles to be coated, immersing the articles in an acid etch bath, removing said articles and rinsing the same, immersing the articles in an aqueous solution of from about 0.01% to about 15% by weight of hydrofluoric acid, from about 0.1% by weight to the saturation point of a compound selected from the group consisting of chromic acid and water soluble salts of a chromium acid, and from about 0.01% by weight to the saturation point of a soluble salt of a heavy metal selected from the group consisting of copper, zinc, silver, cadmium and nickel for a period of about 60 seconds at a temperature corresponding approximately to the boiling point of said solution, to deposit said heavy metal upon the surfaces of said articles, removing said articles and rinsing the same, and electroplating said articles in a plating solution.

9. A composition for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, consisting essentially of an aqueous solution of about 50 g./l. of hydrofluoric acid,

6

about 100 g./l. of sodium dichromate and about 5 g./l. of zinc sulfate.

10. A process for coating the surfaces of articles of titanium base alloys containing about 5% chromium and about 3% aluminum, including the step of immersing said articles in a bath consisting essentially of an aqueous solution of about 50 g./l. of hydrofluoric acid, about 100 g./l. of sodium dichromate, and about 5 g./l. of zinc sulfate to deposit zinc on the surfaces of said articles.

References Cited in the file of this patent

UNITED STATES PATENTS

2,580,773 Heiman ----- Jan. 1, 1952

FOREIGN PATENTS

378,872 Great Britain ----- Aug. 17, 1932

OTHER REFERENCES

Handbook on Titanium Metal; 7th edition, Titanium Metals Corporation of America, New York, August 1, 1953, p. 92.