

April 26, 1960

G. W. SLOMIN

2,934,480

TITANIUM COATING AND METHOD OF FORMING SAME

Filed Aug. 14, 1953

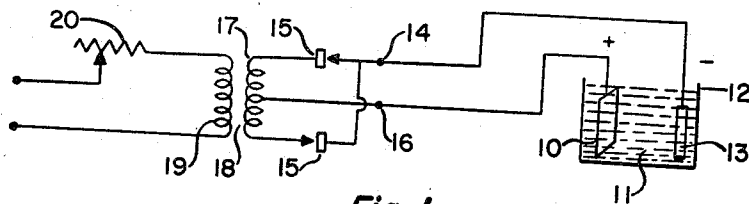


Fig. 1.

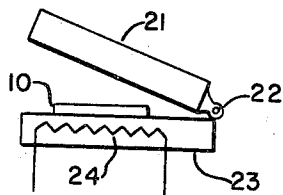


Fig. 2.

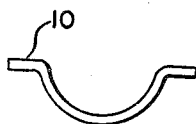


Fig. 4.

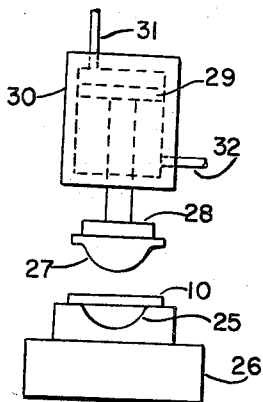


Fig. 3.

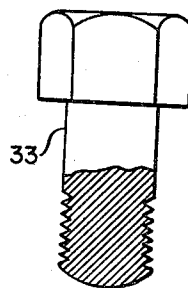


Fig. 5.

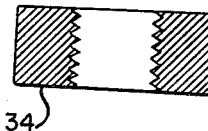


Fig. 6.

INVENTOR.
G.W. SLOMIN

BY

S. Tierney Jr.

1

2,934,480

TITANIUM COATING AND METHOD OF FORMING SAME

George W. Slomin, National City, Calif., assignor to Rohr Aircraft Corporation, Chula Vista, Calif., a corporation of California

Application August 14, 1953, Serial No. 374,217

3 Claims. (Cl. 204—37)

This invention relates to the coating of titanium and alloys of high titanium content and it is the main purpose of the invention to deposit on such metals electrolytically an oxide coating which has several desirable properties.

When forming titanium articles from flat sheet stock in dies or other forming tools the metal tends to stick to the die with resultant galling of the die and scoring or cracking of the article. It has been proposed to lubricate the die or sheet by applying oil or grease to reduce the friction but when the die or sheet must be heated to a temperature of 700° to 1,000° F. to effect the forming, the hot lubricant produced undesirable effects on the formed article. Among other effects it leaves a dark colored film on the surface of the article, which detracts considerably from its appearance and salability and moreover is very difficult to completely remove. It has been found that these difficulties may be overcome by forming an anodized coating on the sheet which acts as a lubricant to facilitate the forming and yet may be easily removed after the article is formed.

It is accordingly an object of this invention to provide such an anodized coating on titanium which clings strongly to the base metal when highly heated and acts as a lubricant while the metal is formed to a desired shape.

Another object is to provide such a coating which consists mainly of titanium oxides by immersing the article in an electrolyte and passing an electric current through the solution.

A further object is to provide means for controlling the voltage applied in such a manner as to produce a coating of definite known color and of predetermined composition, grain structure and quality so that uniformity in the coatings on a numbers of articles is assured.

Another object is to provide an alkaline electrolyte which not only coats the metal but also cleans it of foreign matter such as dust particles and oil film and also of compounds of the metal left on its surface by the process of manufacture.

A further object is to provide a coating which while non-porous is yet capable of adsorbing oil and other lubricants used to decrease the friction with a moving member in contact with the coated article.

A further object is to provide an oxide coating of the type described which may be easily removed from the article after it has been heated and formed.

When threaded bolts and nuts made of titanium or alloys of high titanium content are screwed together, after the lapse of time they seize or freeze together. A further object of the invention is to provide a coating on the fasteners which prevents such freezing and permits the ready unscrewing of the threaded parts.

Further objects will become apparent as the description of my improved coating process proceeds. For a better understanding of the invention reference is made to the accompanying drawing; in which:

Fig. 1 is a schematic diagram of an arrangement embodying the invention;

2

Fig. 2 is a diagrammatic view of a heater for heating articles coated according to the invention;

Fig. 3 is a diagrammatic view of a press for forming an article coated according to the invention;

Fig. 4 is an enlarged view of the formed article;

Fig. 5 is a view partly in section of a bolt and nut treated according to the invention and;

Fig. 6 is an enlarged view showing a portion of the thread of Figure 5.

Referring to Fig. 1, a sheet 10 of titanium or alloy having a high titanium content is immersed in an electrolyte 11 contained in a vessel 12 made of glass or other suitable material. A second electrode 13 of copper or other suitable material is immersed in the liquid and connected to the negative terminal 14 of a full wave rectifier 15, the positive terminal 16 of which is connected to sheet 10. Rectifier 15 is connected to the secondary winding 17 of a transformer 18 whose primary winding 19 is supplied with alternating current from a source (not shown) through a voltage control resistor 20. It will be understood that instead of rectified alternating current, the sheet 10 and electrode 13 may be supplied with direct current of controlled voltage by a direct current generator or other current source.

The preferred alkaline electrolyte is an aqueous solution of sodium or potassium hydroxide and sodium fluoride in water in the proportions 8 to 40 ounces of sodium or potassium hydroxide and 3 to 10 ounces sodium fluoride per gallon water. The electrolyte is preferably kept at a temperature of from 60° to 90° F. It has been found that an electrolyte of the composition stated has the property of thoroughly cleaning the metal before the electrodes are connected to current terminals 14—16, any dirt, oil film or other foreign matter which may have accumulated on the sheet during its manufacture or transportation being completely removed in a few moments.

When current is supplied to sheet 10 and electrode 13 at a voltage of 5 volts a light yellow coating is formed on the titanium. As the voltage is increased the color of the coating changes and also its composition, the coating being light brown at 10 volts, dark brown at 12 volts, violet at 18 volts, dark blue (ultramarine) at 20 volts, medium blue at 30 volts and lighter shades of blue at 35 and 40 volts. These several coating have been tested and those produced at from 35 to 40 volts have been found to have the desirable antifrictional properties above referred to. The coating produced by voltage within the range of 35 to 40 volts is considered the most desirable and is believed to be an oxide mixture consisting mainly of the sesquioxide (Ti_2O_3) and pentoxide (Ti_3O_5) of titanium. A coating of adequate thickness may be built up on the sheet within 5 minutes or less when it may be removed from the electrolyte, rinsed in hot water to remove the electrolyte and dried.

When dry the sheet may be formed to the desired shape by any known type of forming tool, preferably being previously heated to a temperature of 400° to 1,000° F. Such heating means may be a sandwich type electrical heater as illustrated in Figure 2 which comprises an upper metal plate 21 hinged at 22 to lower metal plate 23. Heating current is supplied to a resistor 24 embedded in but insulated from plate 23. To heat sheet 10 plate 21 is lowered against plate 23 and current supplied to heater 24. When both plates are hot, sheet 10 is placed on plate 23 and plate 21 then lowered into contact with the sheet. Heat is rapidly transferred by conduction to sheet 10 from both the plates 21 and 23 and after it becomes heated to the desired temperature, it is removed from the heater and immediately placed on female die 25 (see Fig. 3) which is supported on a fixed base 26. A complementary male die 27 is carried by the ram 28 of the press. The ram is

3

reciprocated by a piston 29 slidable within cylinder 30, compressed air being supplied above the piston through pipe 31 and after the forming the piston is raised by compressed air admitted through pipe 32. As the sheet is being bent into conformity with die 25, the oxide coating on it acts as a lubricant facilitating slippage along the dies and preventing metal to metal contact which would cause thinning of the sheet, and the formation of scratches therein. The oxide coating also prevents rapid wearing away of the dies which would occur with metal to metal contact with the titanium. After removal from the press the workpiece is immersed in a descaling aqueous solution of fluoboric and hydrofluoric acids to which a small percentage of 30% hydrogen peroxide solution has been added. This dissolves the scale and leaves the surface of the workpiece clean and of uniform color throughout. Upon rinsing and drying the workpiece is complete, as shown in Fig. 4. Two such parts may be used as the liner of a shaft bearing when treated with oil, grease, colloidal graphite, colloidal mica or other lubricant.

Referring to Figs. 5 and 6 a bolt 33 and mating nut 34 of titanium or alloy of high titanium content may be anodized in the manner above described and the oxide coating 35 left on the threads, the thickness of the coating being exaggerated for clarity. When the threads of titanium bolts, screws and other threaded fasteners are so treated, it is found that they may be left assembled under strain for long intervals of time without freezing together whereas untreated threads seize and are difficult to separate after a period of time.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment of the invention is therefore to be considered as in all respects illustrative and not restrictive, the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Having thus described my invention, what I claim as new and useful and desire to secure by Letters Patent is:

1. The steps preparatory to pressing a sheet of titanium against a curved die to conform the sheet to the die which comprise; dissolving sodium fluoride and a hydroxide of a metal of the group consisting of sodium and potassium in water to provide an alkaline aqueous anodizing solution consisting essentially of water, sodium fluoride and a hydroxide of a metal of the group consisting of sodium and potassium; immersing the sheet and a metal cathode

4

in said solution; applying an electric potential within the range of 35 to 40 volts between the sheet and cathode for a time long enough to form a light blue non-porous adherent coating which covers the entire sheet; removing the coated sheet from said solution; rinsing the coated sheet in water; and heating the coated sheet to a temperature above 400° F., said light blue coating remaining securely attached to the titanium as the sheet is heated.

2. The method of protecting a titanium fastener having a screw thread against freezing to a complementary thread which comprises: immersing the fastener in an aqueous solution consisting essentially of sodium fluoride and a hydroxide of a metal of the group consisting of sodium and potassium; and, while the fastener is immersed, passing electric current through the solution at a rate which deposits on the screw thread a coating composed substantially of the higher oxides of titanium.

3. The steps preparatory to forming a bearing surface on a sheet of titanium which comprise; immersing the sheet in an aqueous solution consisting essentially of sodium fluoride and a hydroxide of a metal of the group consisting of sodium and potassium; and, while the sheet is immersed, passing electric current through the solution at a rate which deposits on the sheet a light blue non-porous adherent film composed substantially of the higher oxides of titanium and adsorbent to minute particles of lubricant.

References Cited in the file of this patent

UNITED STATES PATENTS

2,036,740	Bengston	Apr. 7, 1936
2,202,773	Given	May 28, 1940
2,433,457	Jarrett	Dec. 30, 1947
2,469,015	Stareck et al.	May 3, 1949
2,615,840	Chapman	Oct. 28, 1952

FOREIGN PATENTS

455,077	Great Britain	Oct. 13, 1936
---------	---------------	---------------

OTHER REFERENCES

- Davies et al.: "Journal of Metals," May 1952, pages 534-536.
 "The Iron and Coal Trades Review," August 10, 1951, pages 295 thru 299, article by Harvey.
 "Handbook on Titanium Metal," 6th edition, October 15, 1952, published by Titanium Metals Corporation of America, pages 79, 80, 81 and 91.
 "Chemical Abstracts," volume 39 (1945), page 874.
 Abstract of Belgian Patent 446,888.