

[54] **SURFACE-HARDENED TITANIUM AND TITANIUM ALLOYS AND METHOD OF PROCESSING SAME**

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[22] Filed: **Mar. 22, 1971**

[21] Appl. No.: **126,634**

[52] **U.S. Cl.**..... **148/20.3**, 29/198, 148/31.5, 148/32.5, 148/133

[51] **Int. Cl.**..... **C23c 11/14**, C22c 15/00

[58] **Field of Search**..... 148/13.1, 15.5, 16.6, 148/20.3, 31.5, 32.5, 133; 75/175.5; 29/198; 204/37, 38

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[57] **ABSTRACT**

Surface-hardened pure titanium or titanium-base alloys having a coating of a substitution type metal, which metal is characterized by a larger diffusion constant than titanium, is more readily nitrided than titanium, has a higher density than the base metal, is rich in stable beta phase, and which has a Vickers hardness of above 400. This hardened titanium or titanium-base alloy is produced by a method of hardening the surface of pure titanium or a titanium-base alloy which includes the steps of coating a substitution type metal of the above-mentioned type and heating the coated metal in a nitrogen-containing atmosphere.

6 Claims, 9 Drawing Figures

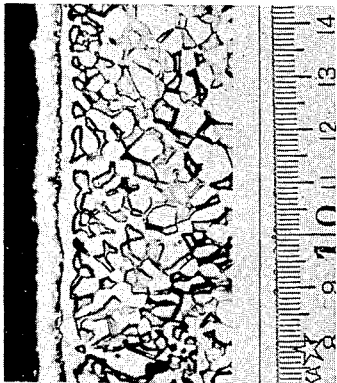


FIG. 1



FIG. 2A

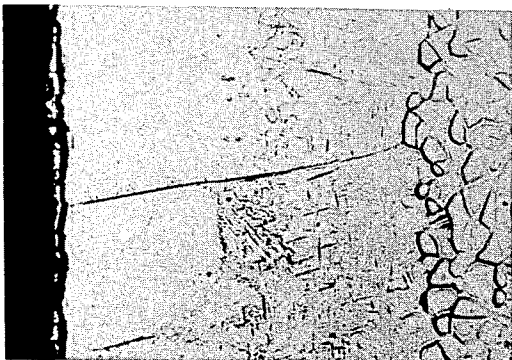


FIG. 2B

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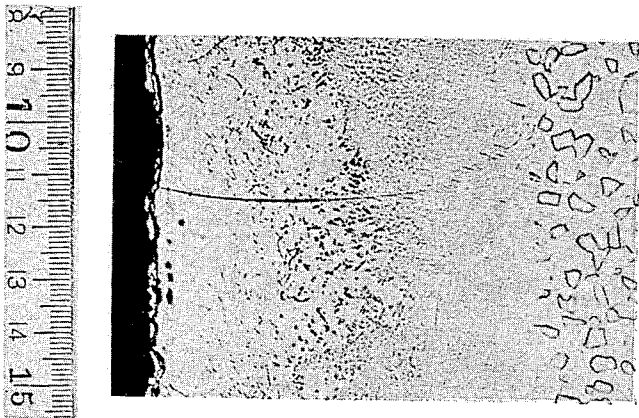


FIG. 4



FIG. 6

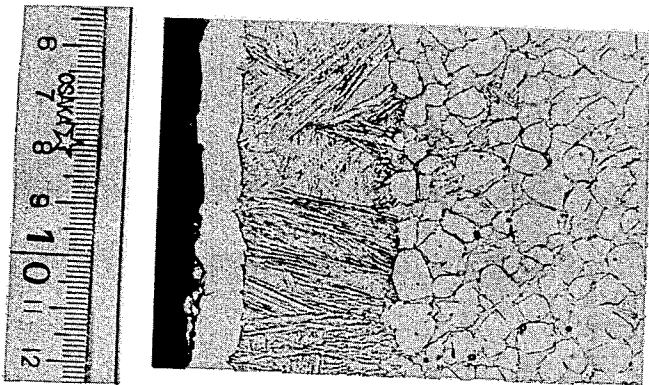


FIG. 8

FIG. 3

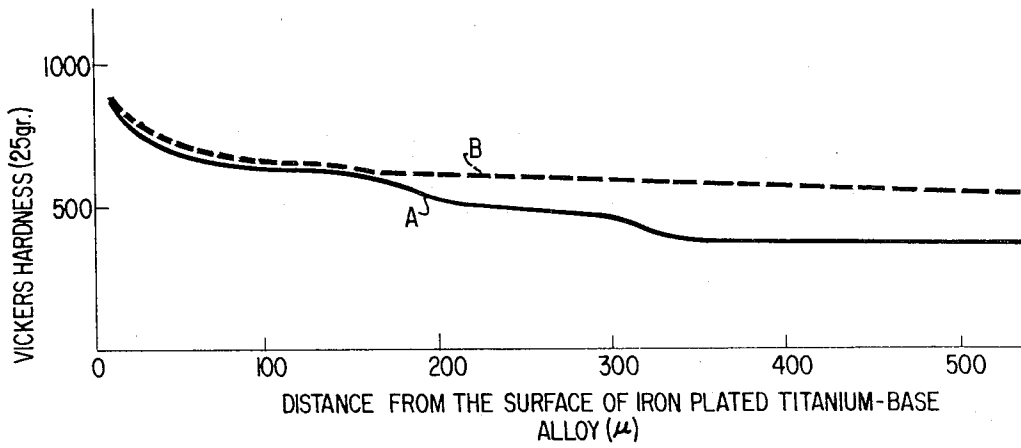
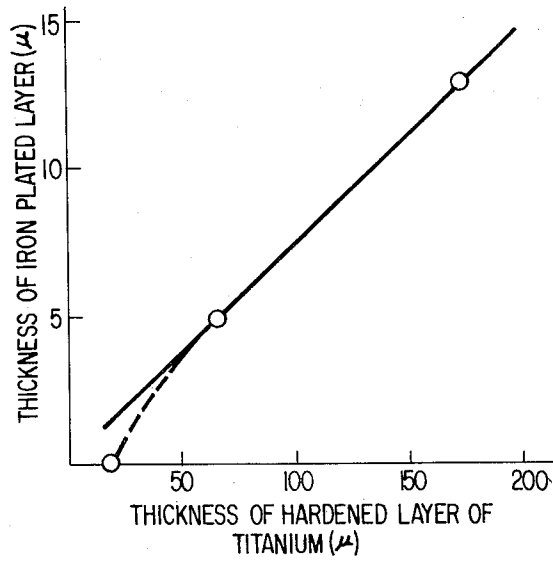


FIG. 5

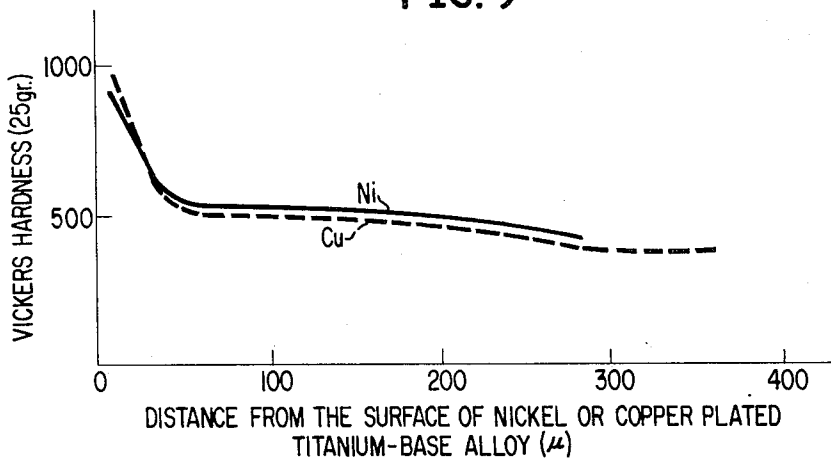


FIG. 7

SURFACE-HARDENED TITANIUM AND TITANIUM ALLOYS AND METHOD OF PROCESSING SAME

BACKGROUND OF THE INVENTION

1. Field of Invention

This invention relates to surface-hardened pure titanium or titanium-base alloys and to a method of processing same. More particularly, this invention relates to surface-hardened pure titanium or titanium-base alloys having a relatively harder and thicker surface, and to a method of hardening said surface.

2. Description Of The Prior Art

Since titanium and titanium-base alloys have superior corrosion resistance, relatively low specific weight, and high tensile strength, they are used in strengthening members of aircraft and spacecraft and as materials in the rotary portions of a jet engine. Since they also have proper refractoriness, they have also been used as materials in various devices and equipment in the chemical industry. Thus, titanium and titanium-base alloys are broadly used in various fields.

However, titanium and titanium-base alloys have, as their chief disadvantage, a very seizable property, and accordingly are characterized by a low wear resistance, thereby rendering them unsuitable for those applications which require high wear resistance.

In order to overcome these disadvantages of titanium and titanium-base alloys, it is common to surface-harden the metal or to plate the metal with a different metal to obtain increased wear resistance.

Commonly used surface-hardening methods include nitriding treatment, oxidation treatment, surface-hardening treatment for depositing titanium in an inert gas including small amounts of nitrogen and oxygen, and carbonization treatment. As methods of coating a different metal, there are chrome or nickel plating treatments and high hardness special alloy welding treatments.

These methods are adapted for practical use for their respective utilities, but each of these methods has corresponding disadvantages in addition to their advantages. For instance, when the surface is nitrided, the thickness of the nitrided layer is usually approximately 40 microns, in the case of pure titanium (heated at a temperature of 850°C. for 100 hours), plus or minus approximately 20 microns, depending upon the type (heated at a temperature of 850°C. for 100 hours). Since these heat treatments are conducted at a high temperature for long periods of time, the treated metal tends to be deformed. If the deformation is corrected, such as by polishing, the hardened layer will be disadvantageously removed.

In the oxidation treatment, the oxidized layer, obtained in a molten glass bath, is even thicker than the nitrided layer, but the interstitial type elements for hardening of titanium, such as oxygen and nitrogen, abruptly reduce its hardening capacity if the temperature becomes 250°-300°C., with the resultant disadvantage that the effectiveness of this surface-hardening treatment is extremely decreased. Even a surface-hardening treatment similar to the aforementioned oxidizing treatment has disadvantages, in that blow-holes may form during surface-hardening, and machining is required to form the final shape after surface-hardening.

Though the carbonization treatment increases the hardness of the surface by the formation of carbonized titanium, the hardened layer disadvantageously becomes porous and fragile.

Though chrome and nickel plating methods are effective, it is not always easy to obtain sufficient exfoliation strength in the plated layer, and hydrogen absorption by the plating occurs to cause so-called hydrogen fragility and an extreme reduction of the fatigue strength of the base metal.

Thus, none of the aforesaid methods improve the wear resistance of titanium and titanium-base alloys in a completely satisfactory manner.

SUMMARY OF THE INVENTION

Accordingly, one object of this invention is to eliminate the aforementioned disadvantages of the conventionally surface-hardened titanium, and titanium-base alloys and methods of processing same by providing novel and improved surface-hardened pure titanium and titanium-base alloys and a method of producing the same.

Another object of the present invention is to provide surface-hardened pure titanium and titanium-base alloys which have hardened layers of both sufficient surface hardness and thickness.

It is another object of the present invention to provide a method of hardening the surface of pure titanium and titanium-base alloys.

Another object of the present invention is to provide a method of hardening the surface of pure titanium and titanium-base alloys which comprises the steps of coating a substitutional metal thereon and heating the coated metal in an atmosphere including nitrogen.

According to a further object of the present invention, there is also provided a method of hardening the surface of pure titanium and titanium-base alloys which comprises the step, in addition to the above steps, of aging the surface.

According to one aspect of the present invention, the foregoing and other objects are attained by a process for preparing surface-hardened pure titanium and titanium-base alloys which comprises coating with a substitutional metal having a larger diffusion constant than titanium, which can be more readily nitrided than titanium, which has a higher density than the base metal, which is rich in the stable beta phase, and which has a Vickers hardness of above 400.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention will be readily obtained as the same becomes better understood by reference to the following detailed description when taken in conjunction with the accompanying drawings, wherein:

FIG. 1 is a microscopic photograph of the surface layer obtained by nitriding a titanium-base alloy (5% Al - 2% Cr - 1% Fe - balance Ti) at a temperature of 850°C. for 100 hours in a nitrogen atmosphere;

FIGS. 2A and 2B are microscopic photographs of the surface layer of iron plates in thickness of 5 and 13 microns, respectively, on the surface of the titanium-base alloy and nitrided at a temperature of 850°C. for 50 hours in a nitrogen atmosphere;

FIG. 3 is a graph showing the relationship between the thickness of the iron plated layer and that of the hardened layer of titanium;

FIG. 4 is a microscopic photograph of the surface layer on the titanium-base alloy shown in FIG. 2B, age treated at a temperature of 500°C. for 6 hours in a vacuum atmosphere;

FIG. 5 is a graphical representation of the relationship between the Vickers hardness and the distance from the surface of iron plated titanium-base alloys shown in FIGS. 2B and 4;

FIG. 6 is a microscopic photograph of the surface of the aforementioned titanium-base alloy, plated with a nickel layer having a thickness of 10 microns, and nitrided at a temperature of 850°C. for 50 hours in a nitrogen atmosphere;

FIG. 7 is a graph showing the relationship between the Vickers hardness and the distance from the surface of the nickel or copper plated titanium-base alloys shown in FIGS. 6 and 8; and,

FIG. 8 is a microscopic photograph of the surface of the aforesaid titanium-base alloy, copper plated to a thickness of 10 microns, and nitrided at a temperature of 850°C. for 50 hours in a nitrogen atmosphere.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In this method, metal diffusion and nitriding are accomplished simultaneously. It follows that the substitutional metal is first coated onto the base, and then it is heated in an atmosphere of pure nitrogen gas or in a nitrogen-containing atmosphere, such as in a gas derived by cracking ammonia.

The pure titanium may be commercially pure metal, and the titanium-base alloy may be any of the Ti-Al-V types such as Ti-6Al-4V; Ti-Al-Sn types such as Ti-5Al-2.5Sn; Ti-Al-Cr-Fe types such as Ti-5Al-2Cr-1Fe; Ti-Al-Mo-V types such as Ti-4Al-3Mo-1V; Ti-Al-V-Sn types such as Ti-6Al-6V-2Sn; Ti-13V-11Cr-3Al, Ti-12Mo-6Zr-4.5Sn, Ti-2.25Al-11Sn-5Zr-Mo-0.1Si, and other commercial titanium alloys.

The substitutional metal may be, for example, iron, nickel, copper, aluminum, manganese, chromium, molybdenum, silicon, or cobalt. The most preferred metal is one which can prevent the hardness at high temperature from decreasing due to diffusion into the titanium, and which can thicken the hardened layer. For this purpose, the ideal metal is one which has as large a diffusion constant as possible, relative to titanium, a large strengthening capacity, and is easily nitridable. In considering the diffusion constant, strengthening capacity and nitriding capacity, iron is the most preferred substitutional metal.

The coating can be applied by any convenient method such as plating, deposition, welding, discharge coating and painting. It is only required that the coating be applied without undue concern over other existing problems such as separation of the coated layer.

The coated titanium or titanium-base alloy is then heated in a pure nitrogen atmosphere. Then, the coated metal is nitrided. It is then heated at a raised temperature with the result that the coated metal starts to diffuse into the titanium or titanium-base alloy in the nitrogen atmosphere. Thus, in addition to the coated metal on the titanium or titanium-base alloy, nitrogen is also diffused into the titanium or titanium-base alloy so that the hardened layer becomes a ternary alloy metal of titanium-coated metal-nitrogen. Thus, the hardness of the surface layer becomes sufficiently high by the nitriding, and yet, since the coated metal is dif-

fused into the base, the thickness of the surface-hardened layer is greater, above approximately 150 microns, than the layer hardened only by nitrogen. Since the substitutional metal is diffused, its strengthening capacity is not reduced even at relatively high temperatures.

The nitriding conditions of the metal in a nitrogen atmosphere will vary depending upon the type of alloy used, but temperatures of 750°-1050°C. for periods of 10-100 hours are preferable. The particular conditions will depend upon the particular shape and size of the treating material, and accordingly may not always be within these stated ranges.

If the coated metal is a beta stabilizing element, it will diffuse to form an alloy with the titanium or titanium alloy of the base metal, and the beta phase portion will increase with the result that it sometimes becomes a beta single phase. However, if such a metastable beta phase is aged at temperatures of about 400°-600°C., a fine alpha phase will be precipitated to increase the hardness. Thus, the hardness of the surface-hardened layer may be further increased while simultaneously enlarging the effective thickness of the hardened layer.

Having now generally described the invention, a further understanding can be obtained by reference to certain specific Examples which are provided herein for purposes of illustration only and are not intended to be limiting unless otherwise specified.

EXAMPLE 1:

Titanium-base alloy, iron plated and nitrided

It is known that in comparing pure titanium with titanium-base alloys, pure titanium is nitrided more readily and accordingly the nitrided layer is thicker. Therefore, this Example has used a titanium-base alloy, which is more difficultly nitrided.

Iron was electrically plated by conventional methods to a thickness of 5 to 13 microns on the surface of a titanium-base alloy (5% Al - 2% Cr - 1% Fe - balance Ti). The thusly iron-plated titanium-base alloy was at once placed in a heating furnace of nitrogen atmosphere to be nitrided.

Nitriding conditions:

Temperature:	850 ± 15°C.
Heating period:	50 hours
Atmospheric pressure:	+50 - 80 mmHg

The thus-obtained surface-hardened titanium-base alloy is shown in FIGS. 2A and 2B. In comparison, a surface-hardened titanium-base alloy which was not plated but heated for 100 hours under conditions otherwise the same as above, is shown in FIG. 1.

As clearly seen from the microscopic photographs shown in FIGS. 1 and 2, the thickness of the surface-hardened layer obtained by the conventional method shown in FIG. 1 is approximately 20 microns, while that obtained according to the method of this invention shown in FIGS. 2A and 2B was approximately 65 microns for iron plated to a thickness of 5 microns, and was approximately 175 microns for iron plated to a thickness of 13 microns. Thus, the effect of the method of this invention is clear.

The relationship between the thickness of the iron plated layer and that of the surface-hardened layer is proportional, as shown in FIG. 3, so that the thicker the plated layer is, the greater becomes the thickness of the hardened layer. Thus, the thickness of the sur-

face-hardened layer may freely be selected by adjusting the thickness of the plated layer. However, in order to prevent the surface-hardened layer from being removed by polishing, it is considered necessary to have a surface-hardened plate in a thickness of at least approximately 100 microns, and accordingly it is required to plate in a thickness of above approximately 8 microns prior to nitriding.

Next, the titanium-base alloy was iron plated to a thickness of 13 microns thereon and was then nitrided. Thereafter, it was aged in vacuo at a temperature of 500°C. for 6 hours. The result of this treatment of the titanium-base alloy is shown in FIGS. 4 and 5. It is clearly seen from this that aging provides a fine structure in the hardened layer in comparison with that which is not aged. As shown in FIG. 5, comparing the hardened layer and the hardness of the titanium-base alloy with that which is not aged, as illustrated by curve A, the Vickers hardness became above 500 even in the interior 500 microns from the surface, as seen by curve B. Thus, according to this treatment, the surface was superiorly hardened, and the effect of this invention may be further improved by the aging treatment.

EXAMPLE 2

Titanium-base alloy, nickel plated.

Nickel was plated to a thickness of 10 microns on the surface of a titanium-base alloy (5% Al-2%Cr-1%Fe-balance Ti), and the titanium-base alloy was then nitrided under the same conditions as in Example 1. The results of this treatment of the alloy are shown in FIGS. 6 and 7.

As seen in FIG. 6, the nitrided layer is approximately 25 microns at the outermost portion of the surface of the hardened titanium-base alloy. Next to the nitrided layer there exists a nickel diffused layer in a thickness of approximately 100 microns, which has succeeded to increase the thickness of the hardened layer in the same manner as in Example 1. As to the relationship between the hardness and the thickness of the hardened layer of the titanium-base alloy, the thickness of the layer hardened above Vickers hardness of 500 reached approximately 200 microns. Thus, sufficient hardness of the surface-hardened titanium-base alloy may be provided. Since nickel is an abrupt eutectoid alloy element for titanium, the same effect as achieved in Example 1 may be provided by relatively shorter aging treatment.

EXAMPLE 3

Titanium-base alloy, copper plated.

Copper was plated to a thickness of 10 microns on the surface of a titanium-base alloy (5%Al - 2%Cr - 1% Fe - balance Ti), and the titanium-base alloy was then nitrided under the same conditions as in Example 1. The results of the treatment of the alloy are shown in FIGS. 7 and 8.

The nitrided layer is approximately 25 microns at the outermost portion of the surface of the hardened titanium-base alloy, and next to the nitrided layer there exists a copper diffused layer having a thickness of approximately 75 microns. Thus, a hardened layer which is thicker than that obtained by conventional methods is obtained. As seen in FIG. 7, the hardened layer on the surface of the titanium-base alloy is almost the same as that in the case of nickel, but the thickness of the surface-hardened layer is slightly thinner, such as

approximately 100 microns, and therefore it is considered to be necessary to form a copper plated layer thicker than about 10 microns. Aging treatment may provide the same effect as in Example 2.

It should be understood from the foregoing description that since the method of the present invention simultaneously diffuses and nitrides the substitutional type metal entered into the titanium, the thickness of the surface-hardened layer becomes above 100 microns and is harder than heretofore attainable, with the result that it is no longer a severe drawback when portions of the hardened surface are to be removed by polishing. Yet, since the method provides a layer diffused with a substitutional metal, it will not suffer a weakened strengthening capacity at high temperatures, with the result that problems of separation of the plated layer from the surface-hardened layer, such as are encountered with the conventional plating method, do not exist.

It should also be understood that the thickness of the surface-hardened layer of the titanium-base alloy may be freely adjusted in response to desired requirements.

It will be appreciated that, while the foregoing disclosure relates only to preferred embodiments of the invention for preparing surface-hardened titanium or titanium-base alloys, numerous modifications or alterations will be apparent to those skilled in the art without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed as new and desired to be secured by letters patent of the United States is:

1. A surface hardened pure titanium or titanium base alloy, which is formed by coating a substitutional metal selected from the group consisting of Fe, Ni, and Cu, onto a titanium or titanium base alloy metal in sufficient thickness to provide a surface hardened layer of at least 100 microns and heat treating said metal in a nitrogen atmosphere at a temperature of 750° - 1,050°C. for periods of 10 - 100 hours whereby the coated metal is nitrided and is diffused into the base metal and simultaneously nitrogen is diffused into the base metal, whereby a hardened layer which is richer in stable beta phase than the base metal and which has a Vicker's hardness of about 400 is obtained.

2. A surface-hardened titanium-base alloy as set forth in claim 1, wherein said alloy is of the Ti-Al-V type Ti-Al-Sn type, Ti-Al-Cr-Fe type, Ti-Al-Mo-V type, Ti-Al-V-Sn type, Ti-V-Cr-Al type, Ti-Mo-Zr-Sn type, or the Ti-Al-Sn-Zr-Mo-Si type.

3. A method of hardening the surface of pure titanium or a titanium base alloy metal, which comprises coating onto said base metal a substitutional metal, selected from the group consisting of Fe, Ni, Cu, in sufficient thickness to provide a surface hardened layer of at least 100 microns heating said coated metal in a nitrogen atmosphere at a temperature of 750° - 1,050°C. for a period of 10 - 100 hours, whereby the coated metal is nitrided and is diffused into the base metal and simultaneously nitrogen is diffused into the base metal whereby a hardened layer which is richer in stable beta phase than the base metal and which has a Vicker's hardness of above 400 is obtained.

4. A method as set forth in claim 3, wherein said coating step is plating, depositing, welding, discharge coating, or painting.

5. A method as set forth in claim 3, further comprising the step of aging.

6. A method as set forth in claim 3, wherein said aging step is conducted at a temperature of 400° - 600°C.

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