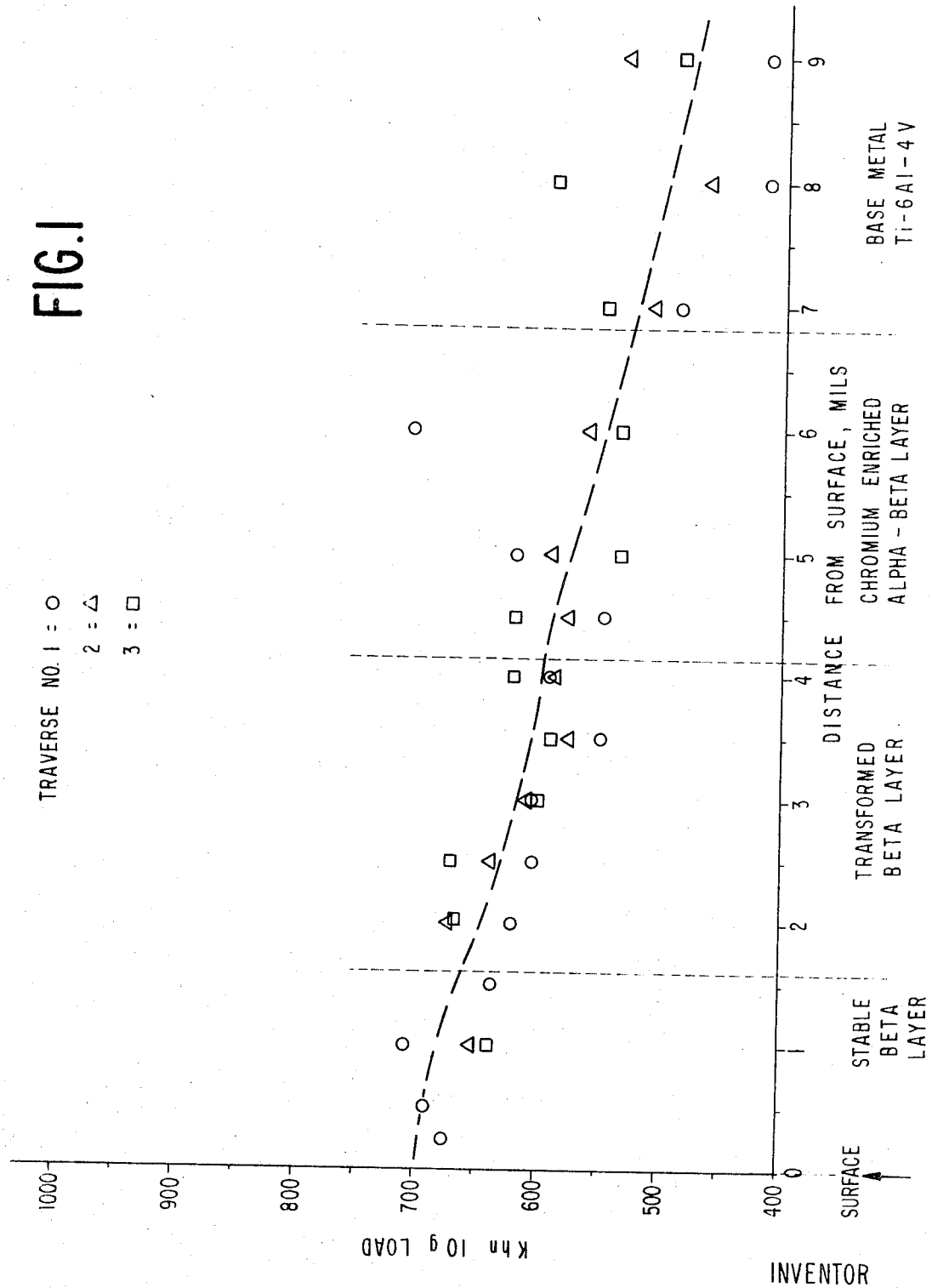
Feb. 2, 1971 H. R. OGDEN 3,560,274

WEAR-RESISTANT TITANIUM AND TITANIUM ALLOYS AND METHOD FOR PRODUCING SAME

Original Filed July 29, 1966

3 Sheets-Sheet 1

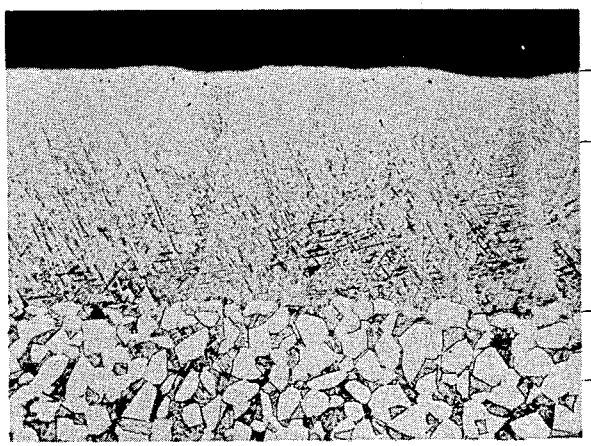
FIG. 1



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WEAR-RESISTANT TITANIUM AND TITANIUM ALLOYS AND METHOD FOR PRODUCING SAME
Original Filed July 29, 1966 3 Sheets-Sheet 2



500 X

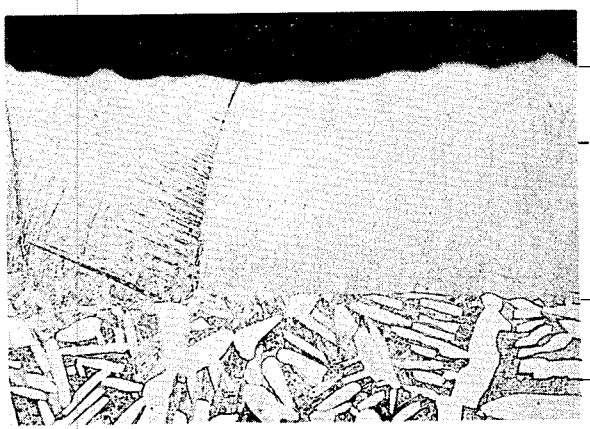
0.05 - MIL Cr PLATE

DIFFUSION ANNEALED FOR 15 Hrs. AT 1700°F, AND AIR COOLED.

(BLACK IN PHOTO IS MOUNTING MATERIAL)	ESTIMATED CHROMIUM CONTENT, %	SCALE OF PHOTO, MILS SURFACE	HARDNESS PENETRATION DATA (Khn vs. DISTANCE FROM SURFACE) DISTANCE FROM SURFACE, MILS	KNOOP HARDNESS, 10g LOAD ONE TRAVERSE
			0.25	386
			0.50	394
DIFFUSED CHROMIUM-STABILIZED STABLE BETA LAYER.	30	1	1.0	591
	11		1.5	
DIFFUSED CHROMIUM-STABILIZED TRANSFORMED BETA LAYER.		2	2.0	656
			2.5	
		3	3.0	549
			3.5	
	4		4.0	503
CHROMIUM ENRICHED (BY DIFFUSION) ALPHA-BETA LAYER		4	4.5	
			5.0	478
		5	5.5	
BASE METAL (ESSENTIALLY Ti-6 Al-4V ALLOY)	0		6.0	447
		6	6.5	
			7.0	394
			7.5	
		7	8.0	437
			9.0	428
		8	10.0	457
			11.0	410
		9	12.0	364
			13.0	410
		10	14.0	357
			17.0	418
			20.0	447
		11	40.0	523
			60.0	394

FIG. 2

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WEAR-RESISTANT TITANIUM AND TITANIUM ALLOYS AND METHOD FOR PRODUCING SAME
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500 X

0.05 - MIL Cr PLATE

DIFFUSION ANNEALED FOR 16 Hrs. AT 1700° F, AND AIR COOLED.

(BLACK IN PHOTO IS MOUNTING MATERIAL)	ESTIMATED CHROMIUM CONTENT, %	SCALE OF PHOTO, MILS SURFACE	HARDNESS PENETRATION DATA (KNOOP vs. DISTANCE FROM SURFACE) DISTANCE FROM SURFACE, MILS	KNOOP HARDNESS, 10g LOAD ONE TRAVERSE
			0.25	467
			0.5	410
DIFFUSED CHROMIUM-STABILIZED STABLE BETA LAYER.	30	1	1.0	378
			1.5	447
DIFFUSED CHROMIUM-STABILIZED TRANSFORMED BETA LAYER.	11	2	2.0	535
			2.5	622
		3	3.0	535
			3.5	467
CHROMIUM ENRICHED (BY DIFFUSION) ALPHA - BETA LAYER	4	4	4.0	656
			4.5	511
			5.0	563
BASE METAL (ESSENTIALLY Ti - 6Al - 4V ALLOY)	0	5	6.0	489
		6	7.0	410
			8.0	489
		7	9.0	437
			10.0	357
		8	12.0	673
			14.0	691
		9	16.0	437
			18.0	457
		10	20.0	410
		11		

FIG.3

United States Patent Office 3,560,274 Patented Feb. 2, 1971

3,560,274

WEAR-RESISTANT TITANIUM AND TITANIUM ALLOYS AND METHOD FOR PRODUCING SAME

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Continuation of application Ser. No. 568,903, July 29, 1966. This application Oct. 10, 1969, Ser. No. 866,151
Int. Cl. C23b 5/06, 5/52; B32b 15/00
U.S. Cl. 148—31.5 14 Claims

ABSTRACT OF THE DISCLOSURE

Producing a titanium or titanium alloy base metal article having a hard surface region of high adherence comprising plating the surface of the base metal with a layer consisting essentially of chromium to a maximum thickness of 0.5 mil and diffusion annealing the plated article to substantially completely diffuse the chromium into the base, thereby forming a chromium-stabilized surface layer of beta titanium-chromium alloy on said base metal.

An article of titanium or titanium alloy base metal having a hard surface comprising a body of said base metal and a diffused zone on the surface of the base metal consisting of essentially of a chromium-stabilized, beta titanium-chromium alloy.

This application is a continuation of application Ser. No. 568,903, filed July 29, 1966, now abandoned.

The present invention is concerned with titanium and titanium alloy articles having hard, wear-resistant surfaces. The invention is also concerned with methods for producing such articles.

It is well recognized that titanium and titanium alloys possess properties of strength and light weight which make them highly desirable for a variety of uses. For example, such metals have wide application in the space and aircraft industries and more recently are finding utility in components for high speed business machines.

Despite the basic advantages of titanium and its alloys for many purposes, their resistance to wear is notoriously inadequate for applications involving friction contact. In an attempt to overcome this problem, the metal and its alloys have been provided with various coatings of other metals to alleviate the condition of wear and galling.

However, prior attempts to coat titanium and titanium alloys have generally been unsatisfactory for a number of reasons. In some cases, the resulting coating or surface layer did not provide hardness on the order sought. In other instances, the coating was not sufficiently adherent to the base metal, especially where the metal was subsequently subjected to solution heat treating and aging to improve yield strength or other properties.

Accordingly, an object of the present invention is to provide titanium and titanium alloy articles having high surface hardness and improved wear resistance. A collateral object is to provide titanium and titanium alloy articles which have the desired properties and which remain substantially unimpaired by solution heat treatment and aging of the base metal.

A further object of the present invention is to provide a method for producing titanium and titanium alloy articles having high surface hardness and improved resistance to wear, even where the articles are subjected to subsequent solution heat treatment and aging.

An additional object of the invention is to provide titanium and titanium alloy articles having surface layers or zones which have improved wear resistance and remain highly adherent to the base metal regardless of subsequent impact, wear and thermal treatments.

The foregoing objects and many other highly desirable advantages are achieved in accordance with the present invention which comprises, in general, plating a titanium or titanium alloy base metal with a layer of chromium and then substantially completely diffusion annealing the chromium layer into the base metal to develop a hard, chromium-stabilized, beta titanium layer on the surface of the base metal.

Preferably, the initial chromium layer is sufficiently thin so that upon subsequent diffusion annealing, the chromium is substantially completely diffused into the titanium or titanium alloy workpiece. The diffused surface layer is then a chromium rich alloy of titanium-chromium, plus whatever other elements may be alloyed in the substrate. The surface layer of titanium-chromium thus formed contains from about 10% to 30% chromium and retains the beta structure on quenching from the beta field, as may occur during subsequent heat treatment. The chromium concentration gradually decreases from the surface inwardly of the body. This layer can be subsequently age-hardened, as in an additional aging heat treatment. A second layer of chromium-stabilized transformed beta titanium alloy underlies the surface layer and contains from about 10% to 4% of chromium, the chromium content being decreasingly graduated inwardly. A third layer of alpha plus unstable beta titanium alloy is formed under the unstable beta layer and contains from 4% to 0% chromium.

The exact conditions of plating and diffusion annealing may be varied somewhat and this will have an effect on the nature of the layers formed. Likewise, variations in the titanium base metal composition will result in different, but comparable results. In general, the titanium base metal is plated with a layer of chromium having a thickness such that it may be substantially completely diffused into the base metal by thermal treatment of practical duration and intensity. Thus, the chromium plating should have a maximum thickness of about 0.5 mil and preferably 0.3 mil or less. The thermal diffusion should be conducted for a period of up to about 24 hours at a maximum temperatures of about 1900° F. The annealing temperature generally will not be less than about 1600° F.

The invention is described below with reference to the accompanying drawings wherein:

FIG. 1 is a graph, the vertical axis of which is graduated for Knoop hardness, 10 g. load and the horizontal axis for distance from the surface of the base metal in mils. The data plotted are derived from tests of a sample prepared in accordance with the invention.

FIG. 2 is a photomicrograph of a cross-section at the surface of a titanium alloy base metal treated in accordance with the invention. The legends adjacent to the photomicrograph identifies the layers formed in the product. The tables to the right of the legends set forth estimated chromium content of the layers and hardness data at given distances from the surface of the base metal.

FIG. 3 includes a similar photomicrograph, legends and tables to those set forth in FIG. 1, but for a base metal sample treated under different conditions.

The present invention will be more fully appreciated when considered in the light of the following detailed example which is concerned with preferred hard, wear-resistant titanium articles and their method of manufacture.

The present invention is applicable to titanium metal and titanium based alloys. A titanium-base alloy is generally considered to be one containing at least about 50% by weight titanium. For example, the invention may be applied to a titanium –6Al–4V alloy.

The titanium and titanium alloys of interest have potential value in the fabrication of components for high speed business machines. For example, Ti–6Al–4V alloys

are light-weight and can be heat treated to high strength levels on the order of 160–170 K.s.i. (K.s.i.=1000 p.s.i.). However, the wear resistance of titanium and its alloys is generally unsatisfactory for friction contact applications. In order to improve surface hardness in accordance with the present invention, samples of a Ti–6Al–4V alloy were treated.

The samples were in the form of rods having a diameter of approximately 0.25 inch. Ti–6Al–4V alloy samples of the following composition were employed:

MATERIAL

Alloy constituent:	Percent by wt.
Aluminum	6.3
Vanadium	4.1
Iron	0.14
Carbon	0.027
Oxygen	0.196
Nitrogen	0.016
Hydrogen	0.006
Titanium	balance

The sample rods may also be machined into the form of type bars or other printing elements or components of high speed business machines in which surface hardness and wear resistance of the materials are critical.

Preliminary preparation

(1) The titanium alloy rods were chemically polished in a HF—HNO_3 solution to remove disturbed metal from the ground surface. A very slight reduction in the diameter of the samples results from the chemical polishing.

(2) The rods were then alkaline degreased and rinsed in commercial alkaline cleaner and tap water.

(3) The rods were repolished in the following solution at 85° F. for twenty minutes:

NH_4FHF—100 g./l.
H_2SiF_6(31%)—200 ml./l.
HNO_3(70%)—400 ml./l.
H_2O (distilled)—Balance

After polishing, the samples were rinsed in tap water.

(4) The rods were activated in the following solution at 120° F. with an anode current density of 20 amp per square foot and a titanium cathode. Initially, an activation period of 40 minutes was employed, but this was found to produce a rough surface. Later, a shorter period of about 2 minutes was adopted and found to be satisfactory for a separate group of samples.

	Ml./l.
Glacial acetic acid	875
Hydrofluoric acid (48%)	125

After activating, the samples were rinsed in tap water.

Chromium plating

The titanium alloy rods were electroplated using the chromium plating solution and conditions set forth below:

Chromic acid (CrO_3)—250 g./l.
Sulfuric acid (H_2SO_4)—2.5 g./l.
Distilled water—Balance
Temperature—130° F.
Current density—300 amp/sq. ft.
Anodes—93% Pb–7% Sn
Plating rate—1 mil per 100 min.

Electroplating is the chromium deposition method of choice, but other techniques producing a firmly adherent plate of the desired thickness are acceptable. Thus, vapor plating or other comparable procedure may be followed.

Diffusion annealing

After the chromium plating was completed, the samples were enclosed in argon-filled Vycor capsules and individual rod samples were diffusion annealed according to the following different schedules:

(a) Four hours at 1550° F., followed by air cooling
(b) Four hours at 1600° F., followed by air cooling
(c) Fifteen hours at 1700° F., followed by air cooling
(d) Sixteen hours at 1700° F., followed by air cooling
(e) Sixteen hours at 1750° F., followed by water quenching

The articles may be diffusion annealed by placing them in sealed capsules containing a substantially inert atmosphere and heating for the desired period. For example, the article may be placed in an Argon-filled Vycor capsule. Annealing temperatures on the order of from about 1600° to 1900° F., are preferred.

Additional samples A, B, C and D were prepared, generally in accordance with the preceding description. Chromium plate layers of 0.05 and 0.10 mil were applied. The thermal treatments of the samples after diffusion annealing also were varied.

Samples A and B, plated with a chromium thickness of 0.05 and 0.10 mil respectively, were diffusion annealed

TABLE I.—HARDNESS PENETRATION DATA

[Ti-6Al-4V Samples,[1] Cr plated, diffusion annealed and solution treated plug aged.]

	Sample A			Sample B			Sample C			Sample D		
	0.05-mil Cr, Traverse Number			0.10-mil Cr, Traverse Number			0.05-mil Cr, Traverse Number			0.10-mil Cr, Traverse Number		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
Distance from surface, mils	Diffusion annealed 16 hrs.[2]						Diffusion annealed and solution heat treated [3]					
0.25	673			638			511			577		
0.5	691			577			591			535		
1.0	709	656	638	577	638	729	563	489	577	489	535	549
1.5	638			523			523			523		
2.0	622	673	673	591	622	577	523	638	577	523	656	511
2.5	606	638	673	622	591	622	563	489	549	656	591	563
3.0	606	606	606	577	622	622	729	549	549	591	638	535
3.5	549	577	591	523	563	549	656	622	656	656	563	563
4.0	591	591	622	535	549	591	656	549	591	673	691	563
4.5	549	577	622	638	638	577	563	563	577	577	591	622
5.0	622	591	535	770	673	489	523	622	577	591	638	563
6.0	709	563	535	563	691	549	428	478	606	447	673	577
7.0	489	511	549	503	638	622	549	523	606	428	563	511
8.0	418	467	591	523	523	467	523	591	467	418	591	511
9.0	418	535	489	523	489	622	535	478	563	523	503	535
10.0	503	511	549	503	447	489	591	535	467	418	606	503
12.0	457	447	591	503	535	622	489	591	549	447	591	535
14.0	535	523	563	523	535	563	563	549	503	478	638	511
16.0	437	523	511	577	535	523	467	563	577	378	591	511
18.0	489			523		535	549			437		
20.0	549	535	549	549	523	549	489	535	549	523	535	437

[1] Activation treatment prior to Cr plating was for 40 minutes.
[2] 1,700° F., air-cooled. Solution heat-treated ½ hour, 1,750° F., waterquenched. Aged for 6 hours, at 1,000° F., air-cooled.
[3] In one treatment of 16 hours, at 1,750° F., waterquenched and aged for 6 hours at 1,000° F., air-cooled.

for 16 hrs. at 1700° F., air cooled, solution heat treated for ½ hr. at 1750° F., water quenched, and aged for 6 hrs. at 1000° F., followed by air cooling.

Samples C and D, plated with 0.05 and 0.10 mil of chromium respectively were diffusion annealed and solution heat treated in one treatment for 16 hrs. at 1750° F., water quenched and aged for 6 hrs. at 1000° F., followed by air cooling.

Hardness data for three traverses of each sample are set forth in Table I.

The hardness data for Sample A are presented graphically in FIG. 1. The vertical axis of the graph is graduated, for KHM, 10 g. load, and the horizontal for distance from the surface of the sample, in mils.

It will be seen that hardness near the surface is on the order of 700 KHN and decreases gradually to about KHN, about 9 mils from the surface. This shows a high hardness in the surface region influenced by the diffusion annealed chromium, gradually decreasing hardness in the intermediate layers, and substantially lower hardness of the base metal itself. The legends below the horizontal axis of the graph identify the metal structures formed in the sample at the depths indicated.

Generally, the articles of the invention will have a Knoop hardness, in at least a portion of the diffused, chromium-stabilized, beta zone, above 500 and usually on the order of from 600 to 700, measured under a 10 g. load.

The traverse numbers refer to successive sections taken through the same sample rod in the course of testing hardness, after treatment.

FIG. 2 is a photomicrograph of a sample prepared by chromium plating to a thickness of about 0.05 mil and diffusion annealing for 15 hrs. at 1700° F. The sample was then air cooled. Activation prior to chromium plating was for 2 minutes. The base metal is Ti–6Al–4V.

As will be seen from the identifying legends accompanying the photomicropgraph, the surface layer is a chromium-stabilized stable beta layer having an estimated chromium content ranging from about 30% at the surface to about 11% at a distance of 1.0 mil from the surface.

The next layer formed by the treatment is a chromium-stabilized transformed beta layer having an estimated chromium content ranging from about 11% at a distance 1.0 mil from the surface to about 4% at a distance between 3.0 and 4.0 mils from the surface.

The next layer is a chromium enriched alpha-beta layer having an estimated chromium content ranging from about 4% at a distance of between 3.0 and 4.0 mils from the surface and 0% at a distance approaching 5.0 mils from the surface.

A scale of the sample dimension in mils keyed to the photomicrograph is provided adjacent to the tabulated hardness and depth data. Note that high hardness was found in the surface layers extending over the zone from about 1.0 mil to 5.0 mils from the surface.

FIG. 3 is a photomicrograph and related data for another titanium article prepared in accordance with the invention. A Ti–6Al–4V alloy rod, activated for 40 minutes as described above, was plated with a 0.05 mil thickness of chromium. The sample was diffusion annealed for 16 hrs. at 1700° C., and air cooled. Legends and data identifying the layers, estimated chromium content and hardness of the sample are presented adjacent to the photomicrograph, as in FIG. 2.

The data indicates high hardness in the surface layers formed by diffusion annealing of the chromium plate and subsequent heat treatment.

What is claimed is:

1. A method for producing an article of titanium or titanium alloy base metal having a hard surface region of high adherence to the base metal comprising:

(a) electroplating at least a portion of the surface of said base metal with a layer consisting essentially of chromium, said layer having a maximum thickness of 0.5 mil; and

(b) diffusion annealing the resulting plated article in a substantially inert atmosphere at a temperature of 1600–1900° F. for up to about 24 hours to substantially completely diffuse said chromium into said base metal and to form a high hardness, wear-resistant, chromium-stabilized surface layer of beta titanium-chromium alloy on said base metal.

2. The method of claim 1 wherein said base metal is a titanium alloy comprising by weight about 6% aluminum, 4% vanadium, and the balance substantially all titanium.

3. The method of claim 1 further comprising solution heat treating and aging said article after diffusion annealing to improve the strength thereof.

4. The method of claim 1 wherein said electroplating is conducted to a maximum thickness of 0.3 mil.

5. The method of claim 1 which comprises, prior to electroplating, chemically polishing said titanium alloy base meal, degreasing said base metal, repolishing said base metal, and then electrolytically activating said base metal to produce a roughened surface thereon.

6. An article of titanium or titanium alloy base metal having a hard surface comprising:

(a) a body of said base metal; and

(b) a diffused zone on the surface of said base metal consisting essentially of an outer surface layer of a chromium-stabilized, beta titanium-chromium alloy containing 30–10% chromium, and

a second layer of chromium-stabilized transformed beta titanium alloy thereunder containing 10–4% chromium, and

a third layer of alpha plus unstable beta titanium alloy formed thereunder containing from 4% to 0% chromium.

7. The process of claim 6 wherein said chromium content of each of said zones gradually decreases inwardly.

8. The article of claim 6, wherein the diffused zone has a depth of up to about 10 mils.

9. The article of claim 6, wherein said diffused zone comprises a portion having a Knoop hardness on the order of from 600 to 700, measured under a 10 g. load.

10. The article of claim 6, wherein said titanium base metal is a titanium alloy comprising by weight about 6% aluminum, 4% vanadium and the balance substantially all titanium.

11. The article of claim 6, wherein said outer surface layer extends to a depth of about 1.0 mil in from the surface, wherein said second layer terminates at a distance between 3.0 and 4.0 mils from the surface, and wherein said third layer terminates at a distance approaching 5.0 mils from the surface.

12. The method of claim 1 wherein said high hardness, wear-resistant, chromium-stabilized surface layer of beta titanium-chromium alloy contains 30–10% chromium, and, there is present thereunder in the following order,

a second layer of chromium-stabilized transformed beta titanium alloy containing 10–4% chromium, and

a third layer of alpha plus unstabled beta titanium alloy formed thereunder wherein the chromium content decreases from 4% to 0%.

13. The process of claim 1 wherein said chromium is electroplated on said base metal in a layer having a maximum thickness of from 0.3 mil to 0.5 mil.

14. The process of claim 1 wherein said diffusion annealing results in a diffused zone having a Knoop hardness on the order of from 600 to 700, measured under a 10 g. period load.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

29—198; 148—32, 127, 133; 204—37, 41, 51