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[54] **METHOD AND BATH FOR TREATING TITANIUM**

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[58] **Field of Search** 156/18, 6, 19; 252/79.3

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[57] **ABSTRACT**

Method of treating titanium and titanium alloys, especially hot-worked products such as bar, rod, wire and various flat-rolled forms so as to remove seams, fissures and the like, as well as a desired amount of surface metal. The products are immersed in a bath comprising some 5 percent to 15 percent by volume hydrofluoric acid, with remainder phosphoric acid and water, maintained at such temperature and for such time as to remove a desired quantity of metal and yield a dull, satin-like finish free of pitting and ready for further processing. Where desired, the products may be subjected to a preliminary treatment in a molten salt bath, such as sodium hydroxide, and washed in water, this to best condition the products for metal removal.

9 Claims, No Drawings

METHOD AND BATH FOR TREATING TITANIUM

In point of introduction, while our invention particularly relates to the removal of seams, fissures and the like from titanium and titanium alloy mill products to give a surface suited to further treatment and processing of the products, it more broadly relates to the removal of metal generally from the surface of titanium and its alloys. This we refer to as "chem milling".

Among the objects of the invention is the provision of an economical and reliable method for chemically removing metal from the surface of titanium and various titanium alloys in the form of bar and billet, sheet, strip and plate, wire, tubes, special extruded shapes and the like, to eliminate seams, fissures, or other surface discontinuities or to so modify the surface of the titanium and titanium alloys as to permit correction by subsequent mechanical processing, all with minimum contamination from hydrogen generated as a result of the chemical action.

Other objects of our invention in part will appear from the description which follows and in part will be more particularly pointed to as the description proceeds.

Our invention, then, may be considered to consist in the combination of ingredients forming the bath employed, in the several operational steps resorted to and in the relation of each of the same to one or more of the others, all as more especially described herein. The scope of the invention is set out in the claims at the end of this specification.

BACKGROUND OF THE INVENTION

As an aid to a more ready understanding of certain features of our invention, it may be well to note that unalloyed titanium, as well as alloyed titanium, is now rather widely used, particularly in those applications where a savings in weight justifies the higher cost as compared with other metals. Actually, the unalloyed titanium is available in various grades with mechanical properties ranging from a tensile strength of some 35,500 psi and elongation of about 25 percent on up to strengths on the order of 80,000 psi tensile, with elongations on the order of 15 percent. The unalloyed titanium is fusion-weldable and is available in the forms of weld rod and weld wire for welding various titanium alloys.

As to the titanium alloys, tensile strength on the order of some 130,000 psi with yield of 120,000 psi and elongation of 10 percent characterizes a typical alpha-beta alloy analyzing about 6 percent aluminum, about 4 percent vanadium with remainder titanium. The alloy is characterized by good corrosion resistance along with strength as noted. A further alpha-beta titanium alloy of somewhat greater strength contains about 6 percent aluminum, 6 percent vanadium, 2 percent tin, with remainder titanium. This alloy enjoys good welding and fabricating characteristics.

A titanium alloy which is especially suited for cold-heading applications contains about 11.5 percent molybdenum, 6 percent zirconium, 4.5 percent tin, with remainder titanium. This is the Beta III alloy and is available in the form of bar and billet, sheet, strip and other flat-rolled products, as well as wire. It is readily weldable.

While the unalloyed titanium, as well as the various titanium alloys, enjoy a combination of weldability, formability, corrosion-resistance and heat-resistance, along with a high ratio of strength to weight, making them suited to a wide variety of applications in the arts and industry, they nevertheless are inclined to oxidize at hot-working temperatures. And unfortunately, they are extremely sensitive to hydrogen embrittlement in processing and in heat treatment.

Various methods have been developed for removing the scale or other oxidation product resulting from heating at working temperatures. And so, too, certain efforts have been made to correct the more subtle imperfections deriving from mechanical working, particularly forging, rolling, drawing, piercing and extruding. With these working operations, hairlines, surface cracks, fissures and the like commonly appear as a result of processing variables or imperfections in the equipment employed. Mechanical methods for ridding the surface of imperfections, such as griding and polishing, are time-consuming. And the results are spotty. Although a number of acid baths have been devised for removing metal, this to minimize the minute hairlines, surface cracks, fissures and the like, for example, those employing a combination of two or more of sulphuric acid, nitric acid, chromic acid, hydrofluoric acid, and hydrochloric acid, the results obtained with these acids leave much to be desired. The bath is either too costly, too difficult to maintain or much too unpredictable in result. Perhaps of even greater consequence, many of the prior baths are inclined to result in an excessive hydrogen pickup and others, notably those employing a chloride in solution, leave a chloride film on the treated metal. Although the film may be removed by appropriate wash, there nevertheless is the risk of increasing the probability of stress-corrosion cracking.

It is one of the objects of our invention, then, to provide an inexpensive, reliable and practical method for removing blemishes such as hairlines, surface cracks and fissures from the titanium and alloyed titanium forged, drawn and flat-rolled products, such as billet, bar, rod, plate, sheet, strip and special shapes, all with minimum contamination by hydrogen and without either pitting or polishing the metal, to fit the same for further processing, e.g., cold-rolling, cold-drawing, cold-forming and the like.

SUMMARY OF THE INVENTION

We find that the common converted forms of titanium and titanium-alloyed products such as billets, bar, rod, wire, plate, sheet, strip, tubing and extrusions, as well as forgings, ordinarily are characterized by minute surface discontinuities, such as hairlines, seams, cracks and microfissures. These discontinuities, unfortunately, adversely affect further processing, that is, in the production of cold-drawn wire, cold-rolled plate, sheet and strip, as well as cold-worked tubing and extrusions. The surface imperfections sometimes originate from minute mechanical defects in the surface of the conversion equipment. They also derive from the combination of hydrogen contamination and working stresses encountered in the processing from ingot to billet, bar, rod, wire and the further conversion to plate, sheet or strip.

In general, we find that the surface imperfections extend beneath the surface a distance of some 2 to 10 mils, that is, some 0.002 inches to some 0.010 inches. And that, with the removal of surface metal in accordance with the teachings of our invention, these imperfections are either eliminated or so minimized, as by rounding off the edges or flattening out the depres-

sions, that with further processing, e.g., cold-rolling, cold-drawing or the like, a uniform surface free of physical blemish is effectively achieved.

In the method of our invention, the surface metal is removed by employing a bath essentially consisting of hydrofluoric and phosphoric acids in aqueous solution. There is an absence of chlorides. While the amount of phosphoric acid may vary over a fairly broad range of concentration, the amount of hydrofluoric acid employed is most critical. Phosphoric acid is used in the amount of about 5 percent to about 25 percent by volume of concentrated acid (85 percent by weight), this ordinarily amounting to some 5 percent to 15 percent by volume. The amount of concentrated (48 percent by weight) hydrofluoric acid employed, however, is limited to some 5 percent to 15 percent by volume, especially some 7 percent to 15 percent or even 10 percent to 15 percent. In all instances, the remainder of the bath is principally water.

In our bath, we find as noted above, that the amount of hydrofluoric acid employed is most critical, for with a hydrofluoric acid content less than 5 percent by volume, hydrogen absorption becomes excessive. Actually, for an assured freedom from hydrogen contamination, the concentration of the bath should be at least 7 percent by volume hydrofluoric acid. For best assurance, the hydrofluoric acid should be present in the amount of about 10 percent by volume.

In the practice of our method, we find that there is an exothermic reaction between bath and metal which takes place, with the result that the bath temperature is inclined to creep up. And although for efficient practice we maintain the bath at a temperature of at least 115° F., it is most undesirable that the temperature exceed 145° F., because the action becomes too violent and hydrogen is objectionably absorbed by the steel.

In general, the time of treatment in the bath ranges from some five minutes to some 25 minutes, this, of course, depending upon hydrofluoric acid concentration and bath temperature, as well as the amount of metal to be removed.

Upon withdrawing the products from the bath, the metal is washed with water under pressure and set aside to dry. Seams and fissures are seen to have been opened up and dished out. We find the surface to be of dull, satin-like quality. There is no pitting. And there is no polish.

When desired, as where significant oxide film is present as a result of prior mill treatment, we first subject the titanium products to a preliminary or conditioning treatment in a molten salt bath. Molten sodium hydroxide with addition of oxidizing salts is conveniently used, following which the products are washed in water in readiness for further treatment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

While in broad aspect, the method of treating titanium and titanium alloys in accordance with our invention contemplates immersion in a bath comprising hydrofluoric acid in the amount of about 5 percent to 15 percent by volume, phosphoric acid in the amount of about 5 percent to about 25 percent by volume, with remainder substantially all water, as set out above, a best combination of results is had with particular amounts of the hydrofluoric and phosphoric acids. And although the temperature of the bath may vary somewhat, that is, between about some 115° F. up to some 145° F., we feel that best results in matters of metal removal consistent with a minimum of hydrogen absorption is had where the bath is maintained at a temperature of some 120° to 140° F. The time of treatment generally depends upon the hydrofluoric acid concentration and upon bath temperature. Within the broad ranges indicated of the bath composition and temperature, time of treatment usually ranges from some two minutes to 20 minutes.

A preferred method in accordance with the teachings of our invention employs a bath comprising about 10 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid with remainder water. The bath is maintained at a temperature of about 120° F. to about 140° F., although satisfactory results are had where the temperature is as low as 115° F. A temperature exceeding 145° F., however, is not acceptable because the speed of the reaction between metal and bath becomes difficult to control and because of excessive hydrogen absorption. With the bath maintained at the temperatures indicated, however, metal is removed from the surface at the rate of about one-half mil per minute. Hydrogen absorption amounts to about 1 part per million for each mil removed from the surface of the metal. Treatment for about 20 minutes results in the removal of about 10 mils from the surface. This assures a freedom from hair cracks, microfissures and the like. A surface of dull satin finish, free of pitting and free of polish, is achieved. And the amount of hydrogen taken up in the 20-minute treatment comes to about 10 parts per million, an acceptable figure.

A further preferred method and bath comprises about 7 percent to 10 percent by volume hydrofluoric acid and about 5 percent to 15 percent by volume phosphoric acid. The remainder of the composition, of course, is water. With such a bath maintained at a temperature of some 115° to 145° F., more particularly 120° to 140° F., a desired quantity of metal is removed in a matter of 15 or 20 minutes' time. Here, again, the rate of removal is on the order of one-half mil per minute. Edges of seams and fissures are rounded off. A dull satin finish is had with freedom from pitting and freedom from polish. The surface is readily conditioned to accept a suitable lubricant, soap, lead or the like, for further treatment, that is, cold-drawing, extruding or the like.

A further preferred method and bath comprises about 10 percent to 15 percent by volume hydrofluoric acid and about 5 percent to about 15 percent phosphoric acid or, more broadly, about 5 percent to 25 percent by volume phosphoric acid, with remainder water. With the bath temperature maintained at some 120° to 140° F., metal is removed from the surface at the rate of about one-half mil per minute. Because of the high concentration of hydrofluoric acid, hydrogen absorption is at a minimum. There is achieved in a matter of minutes a surface of dull satin finish suited to the application of lubricant and further processing.

Where there is contemplated, as in commercial production, the treatment of a series of titanium or titanium alloy coils of rod, wire or the like, there is a depletion of the hydrofluoric acid content of the bath. In order then to maintain effective metal removal, and also to preclude excessive hydrogen absorption, we spike the bath with further additions of hydrofluoric acid. More particularly, when we find that the rate of

metal removal falls to one-fourth mils per minute, that is, a removal of only 5 mils from the surface in a matter of 20 minutes' time (10 mils from the diameter), we add a further quantity of hydrofluoric acid in the amount of about 10 percent or even about 2 percent to 15 percent by volume. The bath then is again effective for rapid metal removal with minimum hydrogen absorption.

As illustrative of the practice of our invention, particularly with regard to the criticality of the composition of the bath employed, and that of the operating temperatures of the bath and the effectiveness of the treatment with passage of time or, rather, with increasing amounts of titanium in solution, we prepared a series of baths of differing phosphoric acid contents. And immersing samples of the titanium alloy of 6 percent aluminum, 4 percent vanadium and remainder titanium, for periods of 10 minutes each with bath temperature maintained between 130° and 140° F., we found that with a bath of 5 percent by volume hydrofluoric acid and 5 percent by volume phosphoric acid, there was removed 2.8 grams of metal; with the 5 percent hydrofluoric acid bath containing 10 percent by volume phosphoric acid there was removed 3.5 grams; and with 15 percent by volume phosphoric acid added to the 5 percent hydrofluoric acid bath, there was removed 3.1 grams.

We also prepared a series of baths of constant phosphoric acid content, namely about 5 percent by volume phosphoric acid and differing amounts of hydrofluoric acid, and for samples of wire 0.266 inch diameter, immersed for 10 minutes with bath temperature maintained at some 130° to 140° F., 0.3 grams of metal were removed where there was employed the solution with 2 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid; 1.1 grams where the solution contained 5 percent by volume hydrofluoric acid; 4.0 grams where the bath contained 10 percent by volume hydrofluoric acid; and 11.5 grams where the bath contained 15 percent by volume hydrofluoric acid. The 15–10 hydrofluoric acid-phosphoric acid bath gave an excessive rate of metal removal with rapid heat development and an actual boiling of the bath.

As further illustrative of the practice of our invention, samples of the titanium-6 percent aluminum-4 percent vanadium alloy in form of 0.206 inch diameter wire we treated in a bath consisting of about 10 percent by volume phosphoric acid and with hydrofluoric acid in the amounts of one-half percent, 3 percent, 5 percent, 7 percent and 10 percent by volume. The bath was maintained at a temperature of about 120° F. Samples also were treated with the bath temperature maintained at 140° F. The time of the treatment was 1 hour. Measurement was made of metal removal, that is the metal taken from the diameter of the samples, as well as the loss in weight. Measurement also was made of the hydrogen absorption encountered. The test results are given below in Table I.

TABLE I

The Effect of HF Concentration and Temperature on Chem Milling of Ti-6Al-4V in 10 percent H_3PO_4 Solutions

Temperature 120° F.

H_3PO_4 +	Diameter Loss Inches	Hydrogen Absorption*	Total Wt. Titanium Dissolved
	(Average 5 Samples 0.206 Start)	(ppm Average 5 Samples)	This Test Grams
½% HF	0.001	318	.3990
3% HF	0.015	50	3.6980
5% HF	0.022	51	5.8076
7% HF	0.034	34	8.4720
10% HF	0.051	34	11.5454
	Temperature 140° F.		
½% HF	0.002	275	.4277
3% HF	0.019	47	4.9731
5% HF	0.029	42	7.4840
7% HF	0.041	35	10.8461
10% HF	0.059	35	15.8714

* Determined by subtracting 26 ppm, the average starting hydrogen value, from the final hydrogen value

Study of the data presented in Table I above rather clearly reveals that the baths with the lower hydrofluoric acid content not only are comparatively ineffective in the matter of metal removal, but reveal a great gain in hydrogen content. For example, with the bath of one-half percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid, the metal removal is insignificant but the amount of hydrogen absorbed by the samples comes to some 318 parts per million. With the 3 percent by volume hydrofluoric acid bath, there is a loss in diameter of 0.015 inches and the amount of metal removal comes to 3.6980 grams. Hydrogen absorption falls to 50 ppm. With the 5 percent hydrofluoric acid bath, there is a loss of 0.022 inches in diameter and the amount of metal removal comes to 5.8076 grams with hydrogen absorption 51 ppm. And although the metal removal increases for the bath containing 7 percent hydrofluoric acid and even further for the bath containing 10 percent hydrofluoric acid, namely, a loss of 0.034 inches and 0.051 inches in diameter, respectively, and 8.4720 and 11.5454 grans respectively, the amount of hydrogen absorption reaches the constant figure of about 34 ppm.

With the higher bath temperature of 140° F., the rate of metal attack is increased significantly, although the amount of hydrogen absorption is virtually the same. The samples treated in the 7 percent hydrofluoric acid and 10 percent hydrofluoric acid baths reveal in hydrogen absorption of some 34 or 35 ppm, whether it is the 7 percent bath or the 10 percent bath and whether the bath temperature is maintained at 120° F. or at 140° F. With the higher rate of attack, it is the 10 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid bath and the bath temperature of 140° F. that is preferred, this by reason of achieving a best combination of maximum metal removal and minimum hydrogen absorption.

With continuous treatment of titanium or titanium alloy, the metal removed from the surface of the products, of course, is taken up by the bath. We find this slows the further rate of attack, that is, decreases the effectiveness of the bath. For comparison purposes, therefore, a series of wire samples having a diameter of 0.206 inches were treated in a solution of 10 percent by volume phosphoric acid with differing amounts of hydrofluoric acid, this again ranging from one-half percent by volume to 10 percent by volume, as before, for one hour at 140° F. with results as reported below in Table II.

TABLE II

The Effect of 10% Dissolved Titanium and HF Concentration on the Chem Milling of Ti-6Al-4V in a 10% H_3PO_4 Solution—1 hour at 140°F.

10% H_3PO_4 + 0.206 Start)	Diameter Loss Inches (Average 5 Samples	Hydrogen Absorption* (ppm Average 5 Samples)	Total Wt. Titanium Dissolved This Test Grams
½% HF	0.001	156	0.2989
3% HF	0.005	265	1.4569
5% HF	0.009	168	2.4199
7% HF	0.015	82	4.2123
10% HF	0.024	92	7.0523

* Determined by subtracting 26 ppm, the average starting hydrogen value, from the final hydrogen value

Comparison of the results presented in Table II and those set out in Table I above immediately reveals that with the presence of 10 percent titanium dissolved in the solution, the effectiveness in matters of metal removal is almost halved, while the hydrogen absorption is almost tripled. Particularly is this true in the more effective baths with 5 percent, 7 percent or even 10 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid. For the bath containing 7 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid, the bath free of any dissolved titanium effects the removal of 8.4720 grams with one hour treatment of sample at 140°F., as against 4.2123 grams for the bath containing the 10 percent of dissolved titanium. And the amount of hydrogen absorption by the sample in the fresh bath comes to 34 ppm, as against some 82 ppm where it is the bath containing the 10 percent dissolved titanium which is employed.

We find that the effectiveness of the bath largely is restored with the addition of further amounts of hydrofluoric acid. These further additions not only assure adequate metal removal, but also assure a control over the hydrogen absorption. In Table III below, we present the effect of continuous additions of hydrofluoric acid (and dissolved titanium) on the rate of metal removal and the amount of hydrogen absorption, this for a series of wire samples of 0.206 inch diameter, each subjected to 1 hour in the solution maintained at 140° F.

Review of the results presented in Table III clearly establishes that effective metal removal is had by spiking each succeeding bath with some 10 percent to 13 percent by volume hydrofluoric acid. The initial bath of 10 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid removes 0.056 inches off the diameter of the samples involved while removing a total of 14.6678 grams and giving an hydrogen absorption of 31 ppm. This same bath, with 14.6678 grams of titanium dissolved in it, when spiked with 12 percent by volume hydrofluoric acid, attacks further samples to the extent of 0.071 inches off the diameter and metal is removed in the amount of 16.6886 grams. The hydrogen absorption here comes to 25 ppm. With further spiking of the bath, the effctiveness is retained, as evidenced by the solution Number 5, with an addition of hydrofluoric acid in the amount of 10 percent by volume having a rate of metal removal namely 0.056 inches off the diameter, just as with the initial solution, and hydrogen absorption in the amount of 32 ppm, as compared to 31 ppm for the treatment of metal in the initial bath.

In processing a series of coils of the 6Al–4V–Ti alloy, this in the form of wire of three-eighths inch diameter, there was employed a bath initially containing 10 percent by volume hydrofluoric acid and 10 percent by volume phosphoric acid. The remainder of the composition was water. The bath was brought to a temperature of 120° F. by the introduction of live steam. The coils of wire, mounted on a yoke holding two at a time, were immersed in the bath for a period of about 6 minutes then withdrawn and measured for metal loss across the diameter of the wire. The loss averaged 6 mils off the diameter.

Following measurement, the wires of each coil were moved about on the yoke, so as to expose surfaces previously in contact with each other, and the coils then further immersed in the bath for an additional period of time. After another 4 minutes in the bath, the coils were withdrawn and a check made of the further metal loss. With removal of the desired amount of metal, a total of about 10 mils off the diameter, the coils were washed down with water under pressure and then set aside to dry.

Further batches of coils were treated in like manner.

Now in our process, we find that the reaction of the hydrofluoric acid component of the bath on the wire being treated generates a considerable amount of heat. And as a result, the temperature of the treating bath is inclined to creep upwards. In order, then, that excessive operating temperatures be forestalled, we customarily stop the processing when the bath temperature reaches about 135° F. For we find, as previously indicated, that where the temperature exceeds some 140° F., there is great danger of excessive hydrogen absorption. When the bath has cooled to about 120° F., we continue with the processing as noted.

Where desired, as where the volume of business, that is the tonnage of metal to be treated, warrants the same, the temperature of the bath may be maintained relatively constant, as from about 130° to 140° F., by means of refrigerating equipment. Such equipment employs a vat for containing the bath in which refrigerating tubing is embedded in the side walls thereof.

Now in processing significant tonnage of the titanium or titanium alloy metal, we find that the dissolved titanium, that is the metal removed during the course of

TABLE III

The Effect of Continuous Additions of Hydrofluoric Acid and Dissolved Titanium on the Chem Milling of Ti-6Al-4V in Phosphoric Acid Solutions

	Solution No. 1 (10% H_3PO_4 10% HF)	Solution No. 2 (No. 1 plus 12% HF)	Solution No. 3 (No. 2 plus 13% HF)	Solution No. 4 (No. 3 plus 10% HF)	Solution No. 5 (No. 4 plus 10% HF)
Titanium dissolved, gm	14.6678	16.6886	16.1225	11.9971	13.6918
Total Ti in solution, gm	14.6678	31.3564	47.4789	59.4760	73.1678
Avg. diameter loss, inches (6 samples)	.056	.071	.062	.046	.056
Avg.* hydrogen absorption, p.p.m. (6 samples)	31	25	26	25	32

*Determined by subtracting 26 p.p.m., the average starting hydrogen value, from the average final hydrogen value.

the treatment, precipitates out in the form of titanium phosphate. Actually, about 3 pounds of titanium phosphate sludge accumulates at the bottom of the bath for every pound of titanium removed from the metal being treated. This sludge, for effective bath life, is removed by scooping it out from time to time. Where desired, however, suitable filtering equipment or suitable centrifuge equipment may be employed for sludge removal. With the removal of sludge, the necessity for bath replacement is effectively minimized. For effective bath life, not only are there required additions of hydrofluoric acid from time to time, as noted, but also there are required additions of phosphoric acid, this to compensate for the loss by the formation of the titanium phosphate precipitated.

The coils treated in accordance with our invention, when dried following treatment and wash, reveal a surface of satin-like quality, free of pitting. The amount of metal removed from the surface is found to be uniform throughout the product. Hair cracks and fissures either are eliminated or are so flattened out, with edges rounded off, as to give a smooth, crack-free surface upon further processing, as by cold-drawing, for example.

Thus, it will be seen that we provide in our invention a method for treating titanium and titanium alloys, and bath employed therein, in which the various objects hereinbefore set forth are effectively had. The method is simple and effective. The bath is comparatively inexpensive. Metal is removed at a desired high rate, yet with a minimum of hydrogen absorption. There is had a surface which is comparatively free of cracks, fissures or other discontinuities. Moreover, the surface is of a dull satin finish free of pitting. Titanium and titanium alloys treated in accordance with the provisions of our invention are then admirably suited to the application of common lubricants and processing, as by cold-drawing, extrusion, piercing or the like.

Inasmuch as many embodiments may be made of our invention and inasmuch as various changes may be made in the embodiments set out above, it is to be understood that all matter described herein is to be interpreted as being illustrative and not by way of limitation.

We claim:

1. Method of chemically removing metal from hot-worked titanium products such as bar, rod, wire which comprises subjecting the same to molten sodium hydroxide; washing in water; and then subjecting to a solution essentially consisting of about 5 percent to 15 percent by volume hydrofluoric acid with remainder phosphoric acid in amount not exceeding about 25 percent by volume, and water at least about 60 percent by volume.

2. Method of chemically removing metal from hot-worked titanium products such as bar, rod, wire which comprises subjecting the same to molten sodium hydroxide; washing in water; and then subjecting to a solution essentially consisting of about 5 percent to 15 percent by volume of hydrofluoric acid, about 5 percent to about 25 percent by volume of phosphoric acid, and water at least about 60 percent by volume.

3. The method of chemically removing metal from the surface of titanium products which comprises treating the products in a bath essentially consisting of about 5 percent to about 15 percent by volume hydrofluoric acid, about 5 percent to about 25 percent by volume phosphoric acid, and water at least about 60 percent by volume while maintaining the bath at a temperature of at least about 115° F. but not exceeding about 145° F.

4. The method of chemically removing hairlines, surface cracks, fissures and surface metal generally from titanium products which comprises treating the products in an aqueous bath essentially consisting of about 10 percent to about 15 percent by volume hydrofluoric acid, about 5 percent to about 15 percent by volume phosphoric acid, and water at least about 60 percent by volume while maintaining the bath at a temperature of about 120° F. to about 140° F. for such time as to remove a desired quantity of metal and give a surface of dull satin finish without either pitting or polish.

5. The method of chemically removing hairlines, surface cracks, fissures and surface metal generally from titanium products which comprises treating the products in an aqueous bath essentially consisting of about 7 percent to about 10 percent by volume hydrofluoric acid, about 5 percent to about 15 percent by volume phosphoric acid, and water at least about 60 percent by volume while the bath is maintained at a temperature of about 120° to 140° F. and for such time as to give a surface of dull satin finish without pitting or polish.

6. The method of chemically removing metal from the surface of titanium products with maximum rate of metal removal consistent with minimum hydrogen absorption which comprises treating the products in an aqueous bath essentially consisting of about 10 percent by volume hydrofluoric acid and about 10 percent by volume phosphoric acid, and water at least about 60 percent by volume while maintaining the bath at a temperature of about 120° F. to about 140° F.

7. The method of chemically removing metal from the surface of titanium products which comprises treating the products in an aqueous bath essentially consisting of about 5 percent to about 15 percent by volume hydrofluoric acid, about 5 percent to about 25 percent by volume phosphoric acid, and water at least about 60 percent by volume; maintaining the bath at a temperature of about 120° to about 140° F.; and when the rate of metal removal has slowed to a value less than about 0.5 mils per minute spiking the bath with hydrofluoric acid.

8. The method of chemically removing metal from the surface of titanium products which comprises treating the products in an aqueous bath essentially consisting of about 5 percent to about 15 percent by volume hydrofluoric acid, about 5 percent to about 25 percent by volume phosphoric acid, and water at least about 60 percent by volume while the bath is maintained at a temperature of about 120° F. to about 140° F. to achieve a surface of dull satin finish without pit or polish; and when the rate of metal removal falls below about 0.5 mils per minute, removing sludge from the bottom of the bath and spiking the same with hydrofluoric acid in the amount of about 2 percent to about 15 percent by volume.

9. A bath for chemically removing metal from titanium products essentially consisting of about 5 percent to about 15 percent by volume hydrofluoric acid, about 5 percent to about 25 percent by volume phosphoric acid, and water in the amount of at least 60 percent by volume.

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