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ELECTROLYTIC DESCALING OF TITANIUM AND ITS ALLOYS

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This invention relates to electrolytic methods and solutions for descaling titanium and its alloys and is also effective in use on ferrous alloys including metals such as nickel, chromium, cobalt, tungsten, vanadium and molybdenum. Articles formed of these metals and alloys generally are heat treated to facilitate forming and to bring out and develop maximum mechanical properties and characteristics required in the end use of the articles. As a result of such heat treatment, refractory pyrolytic oxides (scale) are formed on the surfaces of the articles. These pyrolytic refractory oxides are insoluble in acids and are therefore extremely difficult to remove by a chemical immersion process.

Heretofore it has been the practice, in accordance with certain prior art descaling methods, to convert the acid insoluble refractory oxides to lower state acid soluble forms thereof as by the use of hot hydride baths or caustic solutions operated at elevated temperatures. After conversion, the lower state oxides typically are removed in an acidic solution such as a nitric-hydrofluoric acid bath.

While the prior art descaling methods and solutions have been satisfactory to some extent there are many disadvantages inherent in their use for the purpose. The preliminary scale conditioning or conversion method, for example, is both dangerous and expensive to use. The hot caustic bath presents a constant danger to operating personnel through exposure to the caustic by accidental physical contact therewith and possible serious injury from burns. The caustic bath, moreover, to be functional, must be held at the elevated temperature to maintain the liquid state and this makes the process expensive both because of the energy required and the need for replenishment of raw materials making up the bath.

The acid bath for removing the lower state oxides, according to the prior art methods, has the disadvantage of introducing nascent hydrogen which is absorbed by titanium and causes embrittlement of the metal. Hydrogen embrittlement frequently occurs, for example, in the use of the nitric-hydrofluoric acid bath.

The caustic-acid prior art descale process is also objectionable in that the conversion to the lower state oxides often times is not uniform and this permits a so-called "preferential attack" of the acids on the bare basis metal with resultant step-etching of the articles being descaled. In the hot forming of titanium it is customary, for example, to use some form of a sprayed-on heat barrier to prevent excessive oxidation of the substrate metal. When this cover becomes abraded in certain areas, due to some metal working operation such as may be caused by dies, to thus expose the substrate metal, the exposed metal surfaces become oxidized to a higher state than those areas protected by the heat barrier cover. Any attempt to fully descale the higher oxidized areas inevitably produces a stepped-etching of the basis metal underlying the lesser oxidized areas, which having been protected by the heat barrier, respond normally to the caustic-acid descale treatment. The readily descaled areas are thus subjected to an etchant action of the acids on the basis metal during prolonged immersion and/or re-immersion of the articles as required to remove the higher oxidized areas.

Certain of the aforedescribed difficulties of the prior art caustic-acid descale process are obviated by use of the electrolytic process disclosed in Patent No. 2,780,594 to John J. Dailey wherein the titanium part to be descaled is made the cathode in an electrolytic system which employs an aqueous acid bath operated at ambient temperature. The anode in the electrolytic system is either titanium or a suitable ferrous metal, and the direct current is reversed at intervals to effect loosening and removal of the oxide from the substrate. Such an electrolytic method has the advantage of avoiding the high cost and hazards inherent in the operation of the caustic baths at high temperatures, but the process is objectionable in that the aqueous acid bath produces copious quantities of nascent hydrogen at the cathode which is intolerable from the standpoint of hydrogen embrittlement of the part being descaled. Evolution of the hydrogen, moreover, evidences an undesired attack on the metal, and this becomes many times greater when the current is removed due to the fact that the acids ionize readily in the highly aqueous medium. The aqueous electrolytic process and bath of the Dailey patent is also objectionable because of the color effects which it produces on the surfaces of the titanium articles descaled in its use. It is well known that titanium will exhibit many different colors when subjected to the influence of an impressed voltage within the confines of an aqueous electrolytic medium.

In accordance with the electrolytic descaling method and bath of the present invention, the difficulties and limitations of the prior art methods and baths are largely obviated by making the titanium article to be descaled the anode in an electrolytic system in which the electrolyte is substantially non-aqueous except for the water already included in the hydrofluoric acid, sulfuric and glacial acetic acid components and provides a small acidic ion which, under current flow, attacks and penetrates the scale to forcibly release its tenacious attachment to the substrate metal. The electrolytic bath also provides buffer materials for averting pitting of the titanium surfaces in the event that the current should become inadvertently high, and further contains inhibitor materials for preventing direct acid attack on the metal in the event the current flow is discontinued. To this end, the electrolytic bath comprises hydrofluoric acid which provides the acidic attack ion, concentrated sulfuric acid which serves as the buffer, acetic acid which provides a substantially non-aqueous carrier in lieu of the water carrier of the aqueous bath of the Dailey patent, aforesaid, and a mixture of amides and an acetylenic alcohol, which mixture serves as the inhibitor in the bath. In addition, the bath preferably includes an an-ionic wetting agent which will not break down in the presence of the highly acidic materials of the bath, and the surface of the bath preferably is covered with a layer of mineral oil to suppress fumes emanating from the acetic acid and also to reduce evaporation of the hydrofluoric acid.

In the anodically operated electrolytic descaling process of the present invention which is operated at ambient temperature, a cathode formed of a suitable material such as copper is employed and low current densities ranging from 0.1 to 5.0 amperes per square foot are used which effectively remove refractory oxides in from 2 to 30 minutes, the specific processing time in a given case being dictated by the temperature to which the titanium article has been subjected in the hot forming or heat treat operations thereon. Under the influence of the impressed voltage, the nascent hydrogen collects at the cathode to thus avoid hydrogen pickup and embrittlement of the titanium articles undergoing the descaling operation. The process, moreover, is characterized as one having the property of reducing the amount of embrit-

tling hydrogen which was present in the titanium article prior to the removal of the scale therefrom.

The constituents of the highly acid bath have the property of being mutually miscible whereby the entire bath is formed readily by materials on hand at the descaling site, or the materials at hand may be limited to the bulky acetic and sulfuric acids to which are added the remaining bath constituents in the form of a purchasable additive.

It is an object of the present invention therefor to provide an electrolytic process and bath for descaling articles formed of titanium and its alloys which may be operated safely at ambient temperature levels and at low cost and without resultant hydrogen embrittlement, alteration of mechanical properties, or metal loss.

Another object is to provide an anodically operative electrolytic process for descaling articles formed of titanium and its alloys.

Another object is to provide a non-aqueous electrolytic bath for descaling articles formed of titanium and its alloys in which a miscible organic acid serves as a liquid carrier for the other materials in the bath.

Still another object is an electrolytic descale process and bath as aforedescribed is to prevent acid attack on the articles being descaled in the event either of an increase in the current flow or a discontinuation thereof.

Yet another object resides in the provision of a descale electrolytic bath as aforedescribed which contains no chlorides to promote stress corrosion cracking.

Still a further object is to provide an anodically operated electrolytic descale bath effective to descale titanium and its alloys at low current density levels.

An additional object is to provide an electrolytic descale bath as aforedescribed in which certain constituents of the bath may be packaged and sold as an additive to major constituents of the bath.

Yet another object is to provide an electrolytic descale process in which the period of descale is timed according to the thermal exposure of the articles being descaled.

Still other objects, features and advantages of the present invention will appear as the description of the preferred embodiment thereof proceeds with reference to specific proportions of the bath ingredients and specific operative conditions of the bath which give satisfactory results.

Titanium is categorized as a "reactive" metal owing to its affinity for non-metallic elements such as oxygen, nitrogen, sulfur and others. When exposed to elevated temperatures in the presence of air, titanium readily combines with oxygen to produce an oxide of the metal. The chemical structure of the oxide (scale) is completely dependent for its formation on the surrounding temperature and the availability of oxygen. The oxides which are formed on the surface of titanium by exposing the metal to temperatures of from 700° to 900° F. are readily soluble in acid. It is considerably more difficult to remove scale from the metal by acid attack when exposure temperatures fall within the range of 1,000°–1,150° F., and temperatures in excess of 1,150° F. produce scale so highly refractory in composition that acid attack is futile. Other means must therefore be resorted to for removal of the refractory oxides.

It has been standard practice for many years to treat the metal scale to fifty percent aqueous sodium hydroxide at a temperature of 275° F. either alone or in combination with oxidizing agents such as sodium dichromate, potassium permanganate or sodium nitrate. A solution of the concentrated caustic with a small percentage of copper sulfate is sometimes used to aid in scale removal. This mode of treatment supposedly creates a softening or conditioning of the oxide to such an extent that it is somewhat more readily removed by acid attack. The acid in most instances, as aforementioned, is a combination of nitric and hydrofluoric acids.

Conditioning is also accomplished by sodium hydride treatment at 700° F. and by other processes operative at high temperatures and known commercially by the tradenames Kolene and Virgo. Each of the processes is a precursor to the final acid attack for scale removal. Each is extremely hazardous and expensive to operate.

The electrolytic removal of scale from titanium has been practiced heretofore as described in the Dailey patent, aforesaid. The patent states that efficient removal of scale in an aqueous acidic solution is possible by a process in which the scale is attacked "cathodically." This, however, inevitably leads to intersititial deposition of hydrogen with undesirable embrittlement of the metal. Excessive metal loss is also attendant with this process in the event of current failure.

The descale process of the present invention may be used effectively on the following exemplary materials:

Titanium:
- (Commercially pure)
- 6Al–4V (6–4)
- 8Al–1V–1Mo (8–1–1)
- 6Al–6V–2Sn (6–6–2)

Ferrous alloys:
- Stainless steels—300 Series
- Precipitation hardening steels (17–7) (pH 15–7 Mo)
- Inconel
- Hastelloy

These materials are cleaned prior to thermal exposure by immersion in one of the following baths which are suitable for the purpose.

Cold alkaline cleaner—528 B of Greater Mountain Chemical Company of Los Angeles, Calif.

Hot alkaline cleaner—6470A of B & B Chemical Company of Hialeah, Fla.

Acid cleaner—WEBCO 1315 of W. E. Brantner Company of San Diego, Calif.

Of these cleaners, the acid cleaner removes all contaminants upon immersion of the articles therein for a time period of the order of about one minute, and its use is preferred. This cleaner is a mixture of chromic and sulfuric acids and is also used to strip epoxy coatings as disclosed and claimed in the copending patent application of Earl W. Kendall for Process and Composition for Removing Protective Paint Films, Ser. No. 507,671, filed Nov. 15, 1965 now U.S. Patent 3,379,645, issued Apr. 23, 1968.

It has been found in practice and as a result of extensive experimentation that the surfaces of titanium must be meticulously clean before exposure to high temperatures. The presence of fingerprints, oil, dirt, mill markings or any contaminant foreign to the metal will carbonize under elevated thermal conditions and become an integral part of the surface structure. Subsequent removal is extremely difficult.

The cleaned titanium or ferrous articles, as the case may be, may be coated prior to thermal exposure with a spray-applied heat cover suitable for the purpose such, for example, as the commercially known Turco Pretreat material. Whether protected against oxidation by such a heat barrier material or exposed to the high temperature without the protective cover, the heated articles after hot forming, or heat treatment as the case may be, are immersed and connected as the anode in the electrolytic bath of the present invention, this bath having the following formulation of ingredients and proportions.

ELECTROLYTIC BATH

	Percent by weight	Percent by volume
Acetic acid (glacial)	57–73	55–70
Sulfuric acid (concentrated)	34–51	20–30
Hydrofluoric acid (48–50%)	6–9	10–15
Inhibitor		0.3–0.5
Wetting agent		0.2–0.3
Mineral oil		

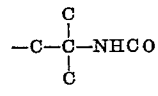
A D.C. voltage is impressed across the anode and a suitable cathode, this voltage being adequate to provide a current density therebetween of the order of 0.1 to 5.0 amperes per square foot. After a time period of the order of 2–30 minutes, the voltage is removed. The articles are then removed from the electrolytic bath and the loosened scale (refractory oxides) are simply washed away in a water rinse.

The cathode may be formed of any one of a group of suitable conductor materials including copper, aluminum, stainless steel, titanium and carbon, the copper being preferred when taking into account various significant factors and parameters such as electrical conductivity, cathodic corrosion, and vitiation of bath composition. Aluminum has a tendency to corrode in contact with the electrolyte, and the stainless steel has a tendency to cause staining of titanium articles after the scale has become softened or removed in the bath. Titanium offers too much electrical resistance to be economical, and carbon tends to disintegrate and foul the bath solution.

The bath is non-aqueous and the acetic acid serves as the carrier. Formic acid which is another of a group of miscible liquid organic acids may also be used for the purpose, but acetic acid is preferred. In the formation of the bath, the acetic and sulfuric acids which are mixed first, generate considerable heat which is believed to be due to the pickup by the sulfuric acid of the small water content of the glacial acetic acid. This ionization of the sulfuric acid is believed to aid in the electrolytic process.

The hydrofluoric acid, inhibitor and wetting agent preferably are mixed separately and suitably packaged, as a liquid or in the form of a paste, for sale as an additive for mixing on-site with the initially mixed acetic and sulfuric acids. In either form of the additive, its content is largely hydrofluoric acid which makes the paste form preferable from the standpoint of ease and safety of handling, and for additional reasons. In the preparation of the paste a suitable thickener such as sub-microscopic pyrogenic silica ("Cabosil") may be employed for the purpose.

The sulfuric acid serves as a buffer to limit the metal attack of the hydrofluoric acid on the metallic articles in the bath, particularly in the event of an inadvertent increase in the current flow. The inhibitor, on the other hand, limits the hydrofluoric acid attack in the event the current is inadvertently discontinued. The inhibitor for this purpose is a mixture of amides and acetylenic alcohol in which the amides contain the general structure



of which the alkyl group approximates the C_{12-14} range. This inhibitor mixture preferably is composed of 65% by volume of the amides and 35% by volume of propargyl alcohol.

A preferred wetting agent is Benax 2A1 of Dow Chemical Company, of Midland, Mich. This is an anionic surfactant completely effective in a high acidic medium and identified as dodecylated oxydibenzene disulfonate sodium salt.

A cover layer of mineral oil such as liquid paraffin of the order of ¼ to 1 inch thick is maintained at the surface of the bath. The oil cover does not enter into any of the reactions of the electrolytic bath medium. The cover, however, serves effectively to reduce the volatilization of the hydrofluoric acid and to prevent escape of the noxious fumes of the acetic acid.

When the scale has been removed, the descaled articles preferably are immersed for from 1 to 5 minutes in the following aqueous brightener bath operated at ambient temperature of the order of 70° to 90° F. to increase the lustre and improve the metallic appearance.

Brightener:	Percent by weight
Ammonium bifluoride	0.1–0.2
Citric acid	1.5–3.0
Ammonium persulfate	4.0–8.0
Water (deionized)	Balance

The fluoride ion attacks the metal articles, the attack, however, being buffered somewhat by the citric acid as disclosed in Patent No. 3,003,896 issued to Earl W. Kendall on Oct. 10, 1961. The ammonium persulfate addition to the patented ammonium bifluoride-citric acid composition serves to inhibit the attack of the fluoride ion while permitting a passivation and oxidation action in the brightener which produces the desired lustre and metallic appearance.

Current densities

Optimum clean surface conditions of the descaled articles are obtained when anode current densities are employed in accordance with the thermal exposure of the articles. A mottled surface condition results, for example, when the anode current density is held constant at 5 amperes per square foot regardless of the thermal exposure conditions. The desired variation of the anode current density to produce a clean surface on an exemplary specimen for different exposure temperatures is given in the following table.

Temperature, degrees F.:	Anode current density, amperes per square foot
1200	1.0
1300	2.0
1400	3.5
1500	4.75
1600	5.00
1700	5.00

Surface cleanliness

Three panels of titanium 8Al–1V–1Mo were prepared for test. Panel No. 1 was used "as received" with no preparatory treatment. Panel No. 2 was cleaned in an alkaline medium for 10 minutes. Panel No. 3 was cleaned in the aforesaid acid cleaner for 1 minute. All three panels were protected by Turco Pretreat and then exposed to heat at 1100° F. for 15 minutes. After descaling by the hereinbefore described electrolytic process and bath of the present invention, followed by water rinsing, and immersion for 3 minutes in the aforedisclosed brightener, the panels were inspected for cleanliness.

Panel No. 1 clearly evidenced a carbonizing and "burning" thereinto of fingerprints, oil and other contaminants. Panel No. 2 which evidenced a "water-break free" surface prior to heat exposure and application of the Turco Pretreat, when observed after descaling, evidenced the presence of carbonized contaminants, thereby suggesting that the so-called "water-break free" surface test is a fallacious indication of surface cleanliness and cannot be completely relied upon. Panel No. 3 evidenced no trace of carbonized materials, thereby attesting to the effectiveness of the acid cleaner in completely removing all surface contaminants.

Rate of scale removal

Sixteen specimen panels of titanium 8Al–1V–1Mo, 10" x 3" x 0.020", were cleaned in a cold alkaline cleaner. The panels were then divided into two groups of eight panels each and thermally exposed. One group was numbered 10 through 17 and the other 10T through 17T to designate by the added letter T that the panels of the second group prior to thermal exposure had each been protected by an approximately 0.6 mil thick layer of Turco Pretreat, the aforementioned spray-applied heat cover. Each number of each group represented the temperature of exposure in hundreds of degrees Fahrenheit to which the panel had been exposed. Panels 10–17 were not protected by a heat cover. Using an anode to cathode

separation of 1 inch and a current density of 1 ampere per square foot, the panels where then descaled in the electrolytic bath of the present invention, followed by a water rinse and immersion in the brightener, to disclose comparatively in terms of time of descale required, the ease of effecting scale removal in the use of a heat barrier. The results of the tests tabulated below disclose that the presence of an oxidation-resistant barrier on the surface of titanium is beneficial from the standpoint of reducing the time required for scale removal when the metal is exposed to temperatures upwards of 1300° F.

Panel No.	Exposure temperature, degrees F.	Descale time, minutes
10	1,000	2
10T		2
11	1,100	3
11T		3
12	1,200	5
12T		5
13	1,300	5
13T		5
14	1,400	20
14T		10
15	1,500	25
15T		15
16	1,600	35
16T		15
17	1,700	40
17T		15

Hydrogen embrittlement

Specimen panels 10" x 2" x .020" of titanium 8Al–1V–1Mo were stamped respectively with the numbers 1–8, each panel being stamped at both ends with the same number. All panels were thoroughly cleaned in an alkaline medium, and a ½ inch numbered strip then removed from the end of each of the panels and analyzed for hydrogen content, these strips being referred to hereinafter as the "as received" specimens.

The surfaces of the remaining portions of the 8 panels were then coated with Turco Pretreat and exposed to heat at 1450° F. for a period of 15 minutes. All panels were descaled by the process of the present invention using a current density of 4.5 amperes per square foot, and threafter, following rinsing, were treated in the brightener bath for 3 minutes. After descaling, a ½ inch numbered test strip was removed from each of the descaled panels and analyzed for hydrogen content, these test strips being referred to hereinafter as the "descaled" specimens.

The non-embrittling properties of the hereindisclosed anodically functional electrolytic bath is disclosed in the table set forth hereinbelow wherein the hydrogen content of the "as received" and "descaled," numbered strip specimens are compared.

In the table, the "as received" specimens are numbered 1 to 8, and the "descaled" specimens are numbered 1D to 8D.

Specimen:	Hydrogen content, parts per million
1	63
1D	60
2	62
2D	59
3	63
3D	61
4	65
4D	65
5	69
5D	67
6	64
6D	66
7	73
7D	51
8	67
8D	52

With the exception of the number 6 specimens, it will be apparent from the foregoing table that the descale process does not result in an increase in hydrogen content, but on the contrary, in each case, with the exception of the number 4 specimens, actually results in a decrease. Extensive tests have shown that a hydrogen decrease is a characteristic feature of this process and that a measured increase can be attributed to an error of analylsis.

In another series of comparative tests for hydrogen content, one set of 14 panels numbered 1–14 was descaled by the aforementioned prior art caustic-acid descale process involving scale conditioning by immersion in an aqueous 50 percent sodium hydroxide solution operating at 275° F. followed by scale removal in a nitric-hydrofluoric acid bath. A second 14 panel set of panels identical with the first set and numbered 1K–14K (Kendall), was descaled by the electrolytic process of the present invention (the Kendall process). The hydrogen content of the panels of each set was determined following descale.

For the purpose of these tests, four panels of commercially pure titanium (C.P.), four panels of titanium-6Al-6V-2Sn (6–6–2), and six panels of titanium-6Al-4V (6–4), were used in each set of 14 panels and exposed to temperatures of 1200°, 1300°, 1500°, 1600° and 1700° F. Prior to thermal exposure, the panels were deliberately vitiated with fingerprints, grease, and shop soil. No cleaning of any nature of the panels was attempted. In each set of 14 panels two panels of pure titanium, two panels of 6–6–2 alloy, and three panels of the 6–4 alloy were each coated with a forming lubricant hereinafter designated E and known commercially as Everlube T50, and two panels of pure titanium, two panels of 6–6–2 alloy, and three panels of 6–4 alloy were each coated with the aforesaid Turco Pretreat herein designated T.

The results of these tests are given in the following table from which it is manifest that the specimens descaled by the herein disclosed and claimed Kendall process, in each of the pairs of specimens compared, has a lower content of embrittling hydrogen than the specimens descaled by the prior art caustic-acid process, as evidenced in the table by the negative difference tabulated in each case.

Titanium composition	Coating	Exposure temp., degrees F.	Hydrogen content parts per million (p.p.m.)				
			Caustic-acid process		Kendall process		
			Panel	P.p.m.	Panel	P.p.m.	Difference
C.P.	E	1,200	1	58	1K	48	−10
C.P.	E	1,300	2	49	2K	42	−7
C.P.	T	1,200	3	47	3K	44	−3
C.P.	T	1,300	4	43	4K	42	−1
6-6-2	E	1,300	5	109	5K	69	−40
6-6-2	E	1,600	6	95	6K	92	−3
6-6-2	T	1,300	7	123	7K	72	−51
6-6-2	T	1,600	8	122	8K	104	−18
6-4	E	1,300	9	97	9K	73	−24
6-4	E	1,500	10	102	10K	83	−19
6-4	E	1,700	11	185	11K	148	−37
6-4	T	1,300	12	96	12K	71	−25
6-4	T	1,500	13	98	13K	86	−12
6-4	T	1,700	14	123	14K	77	−46

Etch rate (electrolytic)

A series of tests were made at various current density levels to determine the rate of attack of the herein disclosed anodically operated Kendall descale bath on the substrate metal. Six panels of titanium-6Al-4V, 3" x 4", were thoroughly cleaned in a cold alkaline medium, rinsed in deionized water, and dried. All panels were identified by metal stamping (1–6) and weighed to the fourth decimal place. These panels were subjected to the following six current density levels of 0.43, 0.48, 0.80, 1.38, 1.60 and 1.80 amperes per square foot for periods of time extending from 10 to 25 minutes. The panels were then weighed and compared with the initial weight measurements, the results being given in the following table.

ELECTROLYTIC ETCH LOSS AND RATE

Panel No.	Current density, amperes/ft.²	Weight in grams			Etch	
		Initial	Final	Loss	Time, min.	Rate, mg./ft.²/min.
1	0.43	26.0087	26.0055	.0032	20	.77
2	0.48	26.5285	26.5248	.0037	20	.89
3	0.80	43.9417	43.9320	.0097	25	3.1
4	1.38	43.7994	43.7856	.0138	10	11.0
5	1.60	44.1420	44.1212	.0208	10	16.6
6	1.80	15.1207	15.0776	.0431	10	25.9

Etch rate (chemical)

Two panels of titanium-6Al-4V, 1" x 2", were thoroughly cleaned and weighed to the fourth decimal place. Both panels were then completely submerged in the electrolytic bath of the present invention for 24 hours and without current flow. After rinsing and drying, the panels were again weighed to the fourth decimal place and the losses calculated. The results are given in the following table from which it may be noted that the loss due to chemical etch is 0.0063 gram which, calculated from the square foot area and etch time employed, corresponds to an etch rate of 9.5 milligrams per square foot per hour (mg./ft.²/hr.).

CHEMICAL ETCH LOSS AND RATE

Panel No.	Weight in grams			Etch	
	Initial	Final	Loss	Time, hours	Rate, mg./ft.²/hr
1	4.2796	4.2726	0.0070	2	10.5
2	4.2726	4.2610	0.0057	2	8.55
Average	4.2731	4.2668	0.0063		9.5

It will be noted that both the electrolytic and chemical tests were made using specimens of titanium-6Al-4V, and it will further be noted that the electrolytic etch rate of .77 mg./ft.²/min. for the lowest current density employed corresponds to 46.2 mg./ft.²/hr. which is considerably greater than the calculated chemical etch rate of 9.5 mg./ft.²/hr., this being due to the enhanced ionization accompanying the current flow. The chemical etch rate, on the other hand is low due in part to the non-aqueous nature of the electrolytic bath and the buffering action of the sulfuric acid and the inhibiting action of the amides and acetylenic alcohol.

Bend tests

Ten panels of titanium-8Al-1V-1Mo, 4" x 2½" x .016", were cleaned and prepared for bend tests. Five of the ten panels were left in the "as cleaned" condition, and the other five were coated with Turco Pretreat and exposed to heat at 1450° F. for 15 minutes. Subsequent to this exposure, the five panels were descaled in the hereindisclosed electrolytic bath and brightener. The five "as cleaned" and the five "descaled" panels were then subjected to 5T and 1.5T bends which were accomplished equally well by both sets, thereby indicating comparatively that no adverse structural effects are introduced by the descale process.

Tensile tests

Five tensile specimens of titanium-8Al-1V-1Mo, .020 gage, were duplex annealed at 1450° F. After cooling to ambient temperature of 70°–75° F., the specimens were descaled in the electrolytic process of the present invention including the brightener. Mechanical properties of ultimate yield and percent elongation were subsequently determined and tabulated in the following table from which it may be ascertained by reference to Military Specifications MIL–T–9046 that the mechanical properties are not adversely affected by the electrolytic descale process.

MECHANICAL PROPERTIES

Specimen No.	Ultimate load, lbs.	Yield point 0.2% lbs.	Percent elongation, 2"
1	145,000	132,000	14.0
2	145,300	134,000	13.0
3	147,000	133,500	14.6
4	148,500	134,200	12.0
5	145,000	132,200	12.3
Average	146,100	133,200	13.2

The desirability of precleaning titanium surfaces which are to be descale subsequent to thermal exposure has been emphasized herein in order to provide a highly efficient and economical industrial process. It will be understood, however, that the hereindisclosed anodically operated electrolytic descale bath is effective to produce clean surfaces in the presence of severe contamination such as fingerprints and shop soil, oxidation barriers such as Turco Pretreat, and/or forming lubricants such as Everlube T50. This was the condition deliberately established in the aforedescribed series of tests for determining hydrogen content. While the surfaces of the descaled panels were acceptably clean, a greater period of current flow in the electrolytic process was required to remove the evidences of contamination.

The novel principles of this invention transcend the scope of the invention as suggested or implied by the foregoing disclosure thereof, and the invention may be embodied in other forms or carried out in other ways which have been conceived and reduced to practice during the course of this development, without departing from the spirit or essential characteristics of the invention. The invention disclosed herein therefore is 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 comes within the meaning and range of equivalency of the claims are intended to be embraced therein.

Having thus described the invention, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. The method of descaling an article formed of titanium and its alloys comprising the steps of immersing said article as an anode in an electrolytic bath and passing an electric current between said article and a cathode, said bath consisting essentially of hydrofluoric acid (48–50) and concentrated sulfuric dissolved in glacial acetic acid as the carrier.

2. The method as in claim 1 and wherein the hydrofluoric acid is 48–50% acid and wherein the acetic, sulfuric, and hydrofluoric acids respectively comprise from 57–73, 34–51, and 6–9% by weight of the electrolytic bath.

3. The method as in claim 1 and wherein the cathode is an electrical conductor selected from the group consisting of carbon, titanium, aluminum, copper, and stainless steel.

4. The method as in claim 1 and wherein the current flow is continued for a period of from 2–30 minutes.

5. The method as in claim 1 wherein said current is passed at a current density level of from 0.1 to 5.0 amperes per square foot of the anode surface.

6. The method as in claim 1 and wherein a layer of mineral oil is placed on the surface of the bath to prevent loss by vaporization of the hydrofluoric acid and to contain fumes from the acetic acid.

7. A two bath treatment for thermally exposed articles formed of titanium and its alloys comprising the steps of electrolytically descaling a titanium article immersed as the anode in a bath consisting essentially of hydrofluoric acid (48–50) and concentrated sulfuric dissolved in glacial acetic acid as the carrier and passing a current of from 0.1 to 5.0 amperes per square foot from the anode to the cathod in the bath for a time period of from 2 to 30 minutes sufficient to soften refractory oxides on the surface of said article, rinsing with water to wash away the loosened scale, and immersing the descaled article for from 1 to 5 minutes in an aqueous brightener

bath operated at ambient temperature of the order of 70°–90° F. consisting of 0.1 to 0.2% by weight of ammonium bifluoride, 1.5 to 3.0 by weight of citric acid, 4.0 to 8.0 by weight of ammonium persulfate, and the balance water.

8. A two bath treatment as in claim 7 and wherein the cathode is selected from a group of conductor materials including copper, aluminum, titanium, stainless steel, and carbon.

9. A two bath treatment as in claim 7 and wherein the hydrofluoric acid comprises 48–50% water and the acetic, sulfuric, and hydrofluoric acids respectively comprise from 57–73, 34–51, and 6–9% by weight of the electrolytic bath.

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