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ELECTROLYTIC PICKLING OF TITANIUM AND TITANIUM BASE ALLOY ARTICLES

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This application is a continuation-in-part of my co-pending application Serial No. 65,301, filed October 27, 1960, and now abandoned.

This invention relates to a method for pickling a surface of a titanium or titanium base alloy article.

Titanium and titanium base alloy articles, such as mill products, casting or forgings, are often exposed to elevated temperature during manufacture or fabrication. Oxidation of the metal surface results, and a higher than desirable oxygen content may be present in an outer layer of the metal. This layer of contaminated metal can be removed by pickling so that fresh, new, uncontaminated metal is exposed. Pickling is also useful to remove a layer of surface metal to eliminate surface imperfections, for example, pits and scratches caused by a previous grinding operation. Pickling can be additionally useful, if the metal removal process can be accurately controlled, to remove a predetermined thickness of surface metal to control dimensions of the article. Thus, titanium or titanium base alloy sheet may be processed to an oversize thickness and then pickled to reduce its thickness to desired finish gauge.

Pickling has generally heretofore been accomplished by immersing the article to be pickled in a strong acid solution. Such treatment can effectively dissolve titanium and its alloys, but the dissolution action is often difficult to control since powerful acids and elevated temperatures are often required. The acid strength and temperature necessary for metal attack may result in rapid and, to an extent, uncontrollable reaction. A much more serious result of acid pickling is its effect on the hydrogen content of the metal. Solution of titanium in acid, like other metals, results in evolution of hydrogen at the metal surface. This hydrogen is readily absorbed by titanium, particularly when the pickling acid is at elevated temperature. A hydrogen content above a minute level, measured in parts per million, will adversely affect the properties of titanium and titanium base alloys, resulting in loss of ductility which could lead to catastrophic failure in service.

Titanium and titanium base alloy articles during fabrication at elevated temperature may, in addition to absorbing oxygen in the metal itself, become covered with a layer of scale. This scale is generally composed of fused oxides of titanium and is not ordinarily soluble in strong acids such as those used for pickling. Molten caustic baths have been employed with some success for descaling titanium and its alloys, and this has been found to loosen the scale so it can readily be removed from the metal surface. Following scale removal, however, a pickling step is still necessary to remove a high oxygen-content outer layer of titanium.

Electrolytic descaling processes have been proposed, but those in which the titanium article is connected as the cathode have not proved successful because hydrogen is inevitably liberated at the cathode and, as previously described, hydrogen can be readily absorbed by titanium and titanium base alloys, resulting in deleterious effects on their mechanical properties. Descaling methods in which the article to be descaled is connected as an anode have also been proposed; however, when employing electrolytes ordinarily used, while the scale can be loosened and removed, a layer of titanium oxide, referred to as an anodic film, remains on its surface after descaling. Also, as with other methods in which a separate descaling step is employed, an additional pickling operation is necessary to produce a clean, uncontaminated metal surface.

It is a principal object of this invention to provide an improved electrolytic process for pickling a surface of a titanium or titanium base alloy article. Another object of this invention is to provide a process for pickling a surface of a titanium or titanium base alloy article to remove metal at a predetermined rate. Another object of this invention is to provide an electrolytic process for pickling and at the same time descaling a titanium or titanium base alloy article. Yet another object of this invention is to provide a process for pickling a titanium or titanium base alloy article to produce a bright, polished surface finish on said article. These and other objects of this invention will be apparent from the following description thereof.

This invention in its broad aspects contemplates a method for pickling a surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises immersing said article in an electrolyte as described while passing an electric current between said article as anode and a cathode.

The electrolyte is an important feature of this invention. It will consist essentially of:

A compound selected from the group consisting of H_2SO_4, Na_2SO_4 and $(NH_4)_2SO_4$	0.125 to 1 mole per liter.
A soluble dichromate salt	Up to 0.33 mole per liter.
HF	0.5 to 1.5 moles per liter.
Balance	Substantially water.

The soluble dichromate salt will be selected from the group consisting of ammonium, potassium and sodium dichromate, and a preferred range for the dichromate salt content is from 0.05 to 0.33 mole per liter. A preferred and advantageous electrolyte composition consists essentially of about 0.25 mole per liter of sulphate compound, advantageously ammonium sulphate, about 0.1 mole per liter of sodium dichromate and about 0.75 mole per liter of hydrofluoric acid, balance water. The electrolyte is conveniently prepared by dissolving and mixing the ammonium sulphate, and dichromate salt, if used, as commercially available salts, with 48 to 51% hydrofluoric acid, in which form it may readily be obtained commerically, with a proper amount of water to produce the required concentration of electrolyte constituents.

The constituents of the electrolyte employed in the practice of this invention appear to perform functions which in combination in a one-step process produce the unique and excellent results obtained. The sulphate is considered to produce an ionized electrolyte when dissolved in water, which, under the influence of the electric current, removes or loosens the oxide layer or scale if present. Hydrofluoric acid is a good solvent for titanium metal and it also dissolves any anodic oxide formed during the electrolytic pickling step. The presence of hydrofluoric acid in the electrolyte also promotes the pickling action during electrolysis to remove a surface layer of titanium or titanium alloy metal. The dichromate content, when employed, provides an oxidizing element in the electrolyte to prevent hydrogen contamination of the titanium or titanium base alloy article being pickled. In addition, an electrolyte as described containing a soluble dichromate, promotes formation of a bright, polished surface on the titanium or titanium base alloy article. The process will descale and pickle in the same electrolyte and in the same operation while not appreciably increasing the hydrogen content of the titanium or ti-

tanium base alloy article being treated. The electrolytic action is carried on with excellent efficiency of the current used, and the amount of metal dissolved and removed can be predetermined and controlled within reasonably accurate limits to produce a bright, polished surface on the pickled article.

The composition of the electrolyte is critical, and the various constituents should be employed within the ranges disclosed above. Of the sulphates employed, ammonium sulphate and sodium sulphate are preferred. These salts are effective, are available at comparatively low price, and provide an electrolyte which is not unreasonably corrosive. Ammonium sulphate has the additional advantage of lower molecular weight than the sodium or potassium salt, thus providing more ions in solution per weight unit. Potassium sulphate is effective as an electrolyte constituent but is somewhat higher priced than the ammonium or sodium salt. Sulphuric acid may be employed without adverse effect on the pickling action and is reasonably priced, but its use results in a more acid electrolyte which intensifies equipment corrosion problems. Although they may produce a conductive electrolyte, nitrates and chlorides cannot be employed to replace the sulphates in the electrolyte employed in the process of this invention. When used in place of sulphate, nitrates and chlorides result in severe and undesirable pitting or roughening of the metal surface. Phosphates have been tried, but I have found that these promote an anodizing effect and current efficiency measured by metal removed per ampere minute is low. If less than 0.125 mole per liter of sulphate compound is employed, the electrolyte will not be sufficiently electrically conductive. If more than 1 mole per liter of sulphate compound is employed, the pickling action will tend to be uneven and the uniformity of the surface of the pickled article will be adversely affected.

The soluble dichromate salt may be employed in amounts up to 0.33 mole per liter. The electrolyte will function without the presence of a soluble dichromate, but its inclusion is preferred in order to prevent hydrogen absorption by the titanium or titanium base alloy being pickled and to produce a bright, polished finish on the metal surface. Up to 0.05 mole per liter of a soluble dichromate is useful to act as an oxidizing agent to prevent hydrogen absorption. When present in amount from 0.05 mole to 0.33 mole per liter, the soluble dichromate, in addition to preventing hydrogen absorption, promotes pickling to produce a bright, polished surface on the pickled article. If more than 0.33 mole per liter of soluble dichromate is employed in the electrolyte, the pickled metal surface will tend to be oxidized and discolored.

Ammonium dichromate, sodium dichromate, and potassium dichromate are the common soluble dichromates. Sodium dichromate is preferred as a constituent of the electrolyte according to this invention since it is readily available and comparatively inexpensive.

The hydrofluoric acid is preferably employed at the higher end of its range, that is, from about 0.75 to 1.5 moles per liter to provide rapid and efficient pickling. A concentration of more than 1.5 moles per liter will result in a smutty surface on the pickled metal. If the hydrofluoric acid concentration is less than 0.5 mole per liter, the reaction rate will be slowed to the point where efficient pickling cannot be obtained in a reasonable time, even with excessively high voltage impressed.

Titanium and titanium base alloy articles which can be pickled by the method of this invention may be of any shape or size, and will include forgings and castings as well as mill products such as bars, rods, tubes, wire, plate, sheet, and strip. Large articles will, of course, require correspondingly large apparatus such as tanks, handling equipment, and power supply. Elongated sheet or strip can be processed as described in more detail hereinafter. Such articles may be fabricated of titanium, that is commercially pure titanium, or titanium base alloy, that is an alloy comprising a major part at least titanium plus alloying elements such as aluminum, tin, zirconium, molybdenum, vanadium, iron, chromium, manganese, columbium, tantalum, tungsten, nickel, copper, cobalt, silicon, and beryllium, individually or in various combinations. Examples of such alloys will include those of the so-called alpha-beta type as:

6% Al, 4% V, balance Ti
8% Al, 1% Mo, 1% V, balance Ti
8% Mn, balance Ti
4% Al, 3% Mo, 1% V, balance Ti

and the so-called beta type as:

13% V, 11% Cr, 3% Al, balance Ti

and the so-called alpha type as:

5% Al, 2.5%, Sn, balance Ti
5% Al, 5% Sn, 5% Zr, balance Ti
2.5% Al, 11% Sn, 5% Zr, 1% Mo, 0.25% Si, balance Ti,

all of which are commercially available titanium base alloys. Articles of titanium of all such alloys can be successfully pickled, employing the method of this invention, and at the same time descaled with the exception sometimes of large sheets and strips of tin-containing alloys from which it is difficult to remove refractory and tightly adhering hot mill scale. It is thought that possibly the tin content may affect the refractory nature of such scale to form an uneven scale deposit on large surfaces. Lighter anneal scale may successfully and readily be removed by the method of this invention from such tin-containing alloys, as well as others, and even mill scale from small areas of the tin-containing alloys.

In the method of this invention, the article to be pickled is employed as an anode and therefore connected to the positive pole of a source of direct electric current. A suitable cathode is also immersed in the electrolyte and may be fabricated of stainless steel, titanium, or other metal or electrically conductive material which is not unduly attacked by the electrolyte solution. It is often convenient when pickling castings, forgings or small articles, for example, to employ the electrolyte container as the cathode, and a stainless steel tank or vessel is admirably suited for this purpose when connected to the negative pole of the D.C. electric current supply. Under such conditions the article to be pickled is simply suspended in such a tank containing the electrolyte and maintained without physical contact with the walls or bottom thereof. The electrolyte container surrounding the article to be pickled will provide cathode surface facing, and at least co-extensive with, the surfaces of the article being pickled. When articles of irregular shape are being handled in this manner, it will be found that the spacing between the cathode and the article surface is not critical, and adequate and even pickling may be obtained providing sufficient amperage at high enough voltage is employed. In the case of flat rolled products such as strip, plate, and sheet, a cathode which is itself flat corresponding to the surface to be pickled may be employed; and to obtain best current efficiency, this should be closely spaced and advantageously no further than one-inch from the titanium or titanium alloy surface. In the case of a strip product being continuously passed through the electrolyte, and which immersed surface may be curved, a cathode surface shaped and curved to correspond with the immersed surface of the strip is employed to preserve a uniform spacing over the area of that portion of the strip which is immersed. The cathode area should be co-extensive with the immersed article area so that electrolytic action is obtained over the entire surface of the titanium or titanium base article in contact with the electrolyte. Therefore, if the cathode is arranged to face only one surface of the article to be pickled, or a selected portion of such surface or surfaces, then the surface or

surfaces not facing the cathode must be protected from contact with the electrolyte in order to prevent corrosive attack of these surfaces by the electrolyte.

The titanium or titanium base alloy article is maintained as the anode during the entire pickling operation since reversal of the current connections making the titanium article the cathode would create serious danger of hydrogen absorption. It is also important that passage of current be maintained while the article is immersed in the electrolyte so that electrolytic action under the pickling conditions of the method of this invention is maintained during the immersion period. Titanium and titanium alloys in contact with the electrolyte without electrolytic action may be seriously corroded. It is necessary, therefore, in order to obtain best results when practicing the method of this invention to make sure that current is passed while the article remains immersed in the electrolyte, that is, from the time it is initially immersed until it is withdrawn from the electrolyte. In the case of elongated strip, particularly strip wound as a coil and which is to be treated by successive immersion of portions thereof by being passed continuously through the electrolyte, the matter of current passage will apply to that portion of the strip immersed in the electrolyte at any moment, and precautions should be taken that the cathode is substantially co-extensive with the portion of the strip so immersed.

Electric current is passed between the article as anode and the cathode at a current density based on the anode surface area of between about 0.55 and 8.5 amperes per square inch, and the voltage required will vary, depending on the cell and the scale characteristics, between about 5 and 70 volts. Temperature of the electrolyte affects the voltage required, higher temperatures with the range specified promoting faster pickling action at lower voltage. The electrolyte composition also affects voltage with higher sulphate and HF contents also tending to reduce the voltage required. The higher current densities within the range are useful for attacking and dissolving the heaviest and most refractory scales. Current densities in the lower portion of the range are useful in treating articles having somewhat lighter scale or oxide coatings and have the additional advantage that the pickling action, that is the rate of metal removal, may be somewhat more conveniently controlled.

I have found that a current density between 0.55 and 8.5 amperes per square inch base on the exposed anode surface area will provide proper pickling and also descaling; and when the current density is within this range, a predictable metal removal rate may be obtained. This metal removal rate will be about 120 amperes minutes per gram of titanium metal removed and dissolved by the pickling process. This metal removal rate may vary somewhat from the optimum of 120 ampere minutes per gram and will generally be within the range of 110 to 130 ampere minutes per gram. Thus the current passed in a given time may be employed to control the amount of metal removed within comparatively precise limits, and this is an important and significant advantage.

If the current density on the anode is too low, that is, below about 0.55 ampere per square inch, then the current and metal removal interdependency no longer holds. Under these conditions, pickling is accomplished to an appreciable extent by chemical action, that is, by reaction between the electrolyte and the metal. This is disadvantageous because hydrogen may be liberated at the metal surface and additionally the pickled surface is frosty and discolored. Therefore, to obtain essentially electrolytic action with freedom from hydrogen pick-up and best surface characteristics, the anode current density should be maintained above 0.55 ampere per square inch.

Current densities on the anode of over 8.5 amperes per square inch should not be employed because undesirable heating of the electrolyte will occur and also such high currents will be approaching, or may exceed, the current-carrying capacity of the electrolyte. High current densities approaching 8.5 amperes per square foot are, however, useful for producing an extremely bright and even brilliant mirror-like finish; and, also, I have found that the rapid metal removal rate produces a greater planing effect to remove or level out surface imperfections and blemishes.

Articles of titanium and titanium base alloys may be connected in any convenient and suitable manner to the positive pole of a source of direct electric current. A power lead wire may be attached by a clamp or bolted connector to provide sufficient contact and current-carrying capacity to transmit the amperage employed. For articles of more or less uniform dimensions, as castings, forgings, blocks, rods, sheets and plates of small area and comparatively great thickness, the transmission of current from the connection to the surface or surfaces facing the anode will not be a problem. For thin section articles, however, such as flat-rolled products, which term includes sheet, thin plate and strip, small thickness and relatively large area dimensions may require special consideration. It is preferred when pickling such products to make a current connection over a substantial portion of the area of the article immersed in the electrolyte. This avoids a long current travel path through a thin product of relatively high resistance. For pickling large size sheets of stripe it will be found advantageous to pickle one surface (or face) at a time and to make current contact over an appreciable area of the back of the sheet or strip, preferably an area greater than one-third of the face area and centrally located. This provides a short current path diametrically through the sheet and only to some slight extent laterally out toward the edges to provide good electrical contact and current distribution. The back surface of the article, that is the surface or face opposite to that facing the cathode and the side to which electrical connection is made, must be protected from contact by the electrolyte as by application of an impervious coating of a plastic or film, or sealing means of rubber-like material maintained in sealing engagement with the back surface.

The fact that in the process of this invention the metal pickled off and removed is proportional to the current used per unit of time is extremely important. This provides an operating control so that the amount of metal to be removed can be predetermined, and removal accomplished by control of the current flow and time, with reasonable accuracy. In order to remove a desired thickness of metal from the surface of an article being descaled and pickled, it is only necessary to calculate the weight of metal to be removed and then to pass current for the required time at the selected amperage to provide about 120 ampere minutes of current for each gram of metal desired to be dissolved by the pickling process. In actual practice, the weight of metal dissolved has been found to be close to the predetermined value and most generally at least within 10 percent plus or minus. This is very close control when the minute thicknesses involved, most often of the order of thousandths of an inch, are considered.

The electrolytic process of this invention may be operated at room or ambient temperature. Increased attack on refractory oxide and scale may be obtained by operating at elevated temperatures up to about 100° C. The rate of metal removal may be slightly increased at the higher temperatures within this range, but this factor is principally governed as pointed out hereinbefore by the ampere minutes of electric current used. However, it will be found that at the higher elevated temperatures, the reactivity of the electrolyte is greater and at temperatures of 90 to 100° C. less voltage is required for passage of high amperage.

Operation at temperatures from 90 to 100° C. may be accompanied, however, by some fuming of the electrolyte and temperatures within a range of 50 to 100° C. can be used to provide good pickling action with those in the lower part of this range avoiding the fume problem.

It will be understood that a desirable combination of electrolyte composition, temperature of operation, and voltage and current used can be employed for each type of product to be pickled. For pickling irregular castings, for example, where cathode spacing will generally not be close or uniform, a higher voltage will be required than for pickling strip with a closely spaced cathode, and the current density will probably not be as high. Pickling efficiency and desirable surface finish will, nevertheless, be obtained.

When pickling strip, or sheet, and where one surface is protected from contact with the electrolyte, it will be obvious that only one surface will be pickled. To pickle both sides, the strip will be turned over and the process repeated with the previously protected surface now exposed to the electrolyte.

The following examples will illustrate the practice of the process of this invention. Examples 1–4 inclusive illustrate employment of various sulphate compounds in the electrolyte.

Example 1

An electrolyte consisting essentially of 33 grams per liter of $(NH_4)_2SO_4$, 24.5 grams per liter of $K_2Cr_2O_7$ and 30 milliliters per liter of 48–51% HF solution, balance water, was placed in an open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.25 mole of $(NH_4)_2SO_4$, 0.083 mole of $K_2Cr_2O_7$ and 0.90 mole of HF per liter.

A section of unalloyed titanium sheet, having a surface area of 8 square inches, was suspended in the electrolyte, free from the container bottom and sidewalls and was connected to the positive pole of the D.C. current source to act as an anode. Electric current was passed between anode and cathode at 5 amperes (.6 amperes per square inch) and with the voltage varying from 2 to 9 volts. Temperature of the electrolyte was 75° C. At the end of 10 minutes under these conditions the electric current supply was shut off and the sheet section removed from the electrolyte and rinsed with water. Titanium had been removed from each surface in amount to reduce the gauge or thickness of the sheet by 0.001 inch. The weight loss in the sheet section was found to be 0.4321 gram corresponding to a metal removal rate per 100 ampere minutes of 0.8642 gram (115 ampere minutes per gram).

The pickled sheet surface was bright and clean without pits or other imperfections and thickness measurements over its area indicated the gauge had been evenly diminished. Its hydrogen content was not appreciably raised as a result of the pickling treatment.

Example 2

An electrolyte consisting essentially of 35 grams per liter of Na_2SO_4, 25 grams per liter of $Na_2Cr_2O_7 \cdot 2H_2O$ and 25 milliliters per liter of 48–51% HF solution, balance water, was placed in an open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.25 mole of Na_2SO_4, 0.083 mole of $Na_2Cr_2O_7$ and 0.75 mole of HF per liter.

A section of unalloyed titanium sheet having a surface area of 10 square inches was suspended in the electrolyte free from the container bottom and sidewalls and was connected to the positive pole of the D.C. current source to act as an anode. Electric current was passed between anode and cathode at 15 amperes (1.3 amperes per square inch) and with the voltage about 30 volts. Temperature of the electrolyte was 70° C. At the end of 5 minutes under these conditions the electric current supply was shut off and the sheet section removed from the electrolyte and rinsed with water. Titanium had been removed from each surface in amount to reduce a gauge of thickness of the sheet by 0.0021 inch. The weight loss in the sheet was found to be 0.6173 gram corresponding to a metal removal rate of 121 ampere minutes per gram.

The pickled surface was smooth and clean without pits or other imperfections, and its gauge had been evenly diminished.

Example 3

The electrolyte of this test was similar to that of Example 2 except that it contained 44 grams per liter of K_2SO_4 instead of Na_2SO_4. The electrolyte composition corresponds to 0.25 mole K_2SO_4, with the same proportions of $Na_2Cr_2O_7$ and HF as Example 2. The specimen of unalloyed titanium pickled was similar. Temperature of the pickling operation was 78° C. Voltage was 29 and amperage was 15 for similar current density of 1.3 amperes per square inch. Apparatus and procedure were similar to Example 2.

At the end of 5 minutes pickling, 0.6134 gram of metal had been removed for a removal rate of 122 ampere minutes per gram. The product was similar to that of Example 2.

Example 4

The electrolyte of this example was similar to that of Example 2 except that it contained 45 grams per liter of H_2SO_4 instead of Na_2SO_4. The electrolyte composition corresponds to 0.46 mole of H_2SO_4 with the same proportions of $Na_2Cr_2O_7$ and HF as Example 2. The specimen of unalloyed titanium pickled was similar. Temperature of the pickling operation was 78° C. Voltage was 28 and amperage was 15 for a similar current density of 1.3 amperes per square inch. Apparatus and procedure were similar to Example 2.

At the end of 5 minutes pickling, 0.6444 gram of metal had been removed for a removal rate of 116 ampere minutes per gram. The product had a bright and shiny surface and was otherwise similar to that of Example 2.

The following Examples 5, 6 and 7 illustrate the effect of variations in the proportions of the constituents of the electrolyte:

Example 5

An electrolyte consisting of 100 grams per liter of $(NH_4)_2SO_4$, 25 grams per liter of $Na_2Cr_2O_7 \cdot 2H_2O$, 25 milliliters per liter of 48–51% HF solution, balance water, was placed in an open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.75 mole of

$(NH_4)_2SO_4$

0.083 mole of $Na_2Cr_2O_7$ and 0.75 mole of HF per liter.

A strip of unalloyed titanium sheet 1-inch by 7¼-inches long was suspended in the electrolyte free from the container bottom and sidewalls and connected to the positive pole of the D.C. current source to act as an anode. Electric current was passed between anode and cathode at 15 amperes (1.0 ampere per square inch) with the voltage at about 40 volts. Temperature of the electrolyte was 45° C. At the end of 5 minutes under these conditions the electric current supply was shut off and the section of titanium strip was removed from the electrolyte and rinsed with water. Titanium had been removed from each surface in amount to reduce the gauge or thickness of the strip by 0.0011 inch. The weight loss in the strip section was found to be 0.6383 gram corresponding to a metal removal rate of 117 ampere minutes per gram.

The pickled strip surface was smooth and bright with a slight bluish discoloration. Hydrogen content of the strip was not increased by the pickling treatment.

Example 6

An electrolyte consisting of 33 grams per liter of $(NH_4)_2SO_4$, 80 grams per liter of $Na_2Cr_2O_7 \cdot 2H_2O$, 25 milliliters per liter of 48–51% HF solution, balance water, was placed in a stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.25 mole of $(NH_4)_2SO_4$, 0.27 mole of $Na_2Cr_2O_7$ and 0.75 mole of HF per liter.

A strip of unalloyed titanium similar to that employed in Example 5 was immersed in the electrolyte, which was maintained at 44° C. The unalloyed titanium strip was connected to the positive pole of the D.C. current source to act as an anode as before. Electric current was passed between anode and cathode at 15 amperes (1.0 ampere per square inch) at 4 volts for a period of 5 minutes. Then the unalloyed titanium strip was removed from the electrolyte, and it was determined that the thickness of the strip had been reduced by 0.0013 inch and the weight of metal removed was 0.6060 gram, corresponding to a metal removal rate of 123 ampere minutes per gram.

The pickled strip surface was smooth, bright and shiny, and gauge had been evenly reduced over its surface. Hydrogen content of the strip was not increased by the pickling treatment.

Example 7

An electrolyte consisting of 33 grams per liter of $(NH_4)_2SO_4$, 25 grams per liter of $Na_2Cr_2O_7 \cdot 2H_2O$, 40 milliliters per liter of 48–51% HF, balance water, was placed in the same type of open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode as in the previous examples. The electrolyte composition corresponds to 0.25 mole of $(NH_4)_2SO_4$, 0.083 mole of $Na_2Cr_2O_7$ and 1.2 moles of HF per liter.

A strip of unalloyed titanium 1-inch by 7¼-inches long was pickled in the electrolyte described in the previous parapgraph at a temperature of 40° C. employing a current density of 1.0 ampere per square inch at a voltage of 32 volts. In a time period of 5 minutes, the gauge of the strip had been reduced by 0.008 inch and the amount of metal removed was 0.6094 gram corresponding to a metal removal rate of 123 ampere minutes per gram. The pickled strip was smooth, bright and shiny and its hydrogen content had been raised only an insignificant 3 parts per million.

The following Examples 8 and 9 illustrate operation of the process of this invention employing an electrolyte containing no dichromate constituent; in addition, the effect of somewhat higher current density is shown by comparison of the surface finish results obtained in the test of Example 9 compared to that of Example 8:

Example 8

An electrolyte consisting of 33 grams per liter of $(NH_4)_2SO_4$, 23 millimeters per liter of 48% HF, balance water, was placed in an open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.25 mole of $(NH_4)_2SO_4$ and 0.69 mole of HF per liter.

A strip of unalloyed titanium 1-inch by 7¼-inches long was immersed in the electrolyte to provide an immersed anode surface area of ⅒ of a square foot. Electric current was passed between anode and cathode at a rate of 10 amperes at 35 volts for 5 minutes. This was equivalent to .7 ampere per square inch. The temperature of the electrolyte was 70° C. At the end of the 5-minute electrolytic pickling period, the electric current supply was shut off and the titanium strip was removed from the electrolyte and rinsed with water. Titanium had been removed from the titanium strip surface to provide a reduction in gauge of 0.0005 inch, the total amount of metal reduced being 0.4422 gram. The metal removal rate was equivalent to 111 ampere minutes of electric current per gram of metal removed.

The pickled strip surface was stained but was smooth and even. Thickness measurements over its area indicated uniform pickling action, although it did not have the bright finish which was produced when dichromate was included as an ingredient in the electrolyte.

Example 9

A specimen similar to that used in Example 8 was immersed in an electrolyte of the same composition but was so arranged that only one-half the previous surface area was immersed in the electrolyte. Other conditions were similar, except that 12 amperes of electric current were passed over a period of 5 minutes to provide a current density of 1.7 amperes per square inch. After electrolytic pickling had been completed, the strip specimen was removed and rinsed with water, and it was found that 0.5011 gram of metal had been removed, corresponding to a metal removal rate of 120 ampere minutes per gram.

The pickled strip surface was bright and shiny without pits or other imperfections, and thickness measurements over its area indicated that gauge had been evenly diminished. It will be noted that the higher current density compared to Example 8 resulted in a brighter and more polished surface on the titanium strip.

The following example illustrates the practice of the process of this invention to descale as well as pickle and also its use to treat a titanium base alloy sheet:

Example 10

An electrolyte consisting of 33 grams per liter of $(NH_4)_2SO_4$, 24.5 grams per liter of $Na_2Cr_2O_7 \cdot 2H_2O$ and 30 milliliters per liter of 48–51% HF solution, balance water, was placed on an open top stainless steel container which was connected to the negative pole of a source of D.C. electric current to act as a cathode. The electrolyte composition corresponds to 0.25 mole of $(NH_4)_2SO_4$, 0.081 mole of $Na_2Cr_2O_7$, and 0.90 mole of HF per liter.

A section of titanium alloy sheet of composition 4% aluminum, 3% vanadium, 1% molybdenum, balance titanium, and having a surface area of 12 square inches and with this surface covered by a layer of tightly adhering mill scale, was suspended in the electrolyte free from the container bottom and sidewalls and connected to the positive pole of the D.C. source to act as an anode. Electric current was passed between the anode and cathode at 20 amperes with the voltage varying from 10 to 18 volts (1.6 amperes per square inch). Temperature of the electrolyte was 80 to 95° C. At the end of 10 minutes under these conditions the electric current supply was shut off and the sheet section removed from the electrolyte and rinsed with water. The mill scale had been completely removed from the surface of the sheet and the titanium alloy had been removed from each surface in amount to reduce the gauge or thickness of the sheet by 0.0037 inch. The weight loss in the sheet section was found to be 1.8108 grams corresponding to a metal removal rate per 100 ampere minutes of 0.9054 gram (110 ampere minutes per gram).

The pickled sheet surface was bright and clean without pits or other imperfections and thickness measurements over its area indicated that gauge had been evenly diminished. Its hydrogen content was not appreciably raised as a result of the pickling treatment.

The following Examples 11 and 12 illustrate practice of this invention for pickling a flat rolled titanium metal product. In addition, Example 12 illustrates employment of a very high current density to provide the utmost in a brilliant and polished metal usrface.

Example 11

A coil of unalloyed titanium metal strip 36-inches wide and 0.040-inch thick was pickled by continuously passing

the strip through an electrolyte to immerse successive portions thereof. The strip was led around the lower portion of a rotatable drum partially immersed in the electrolyte, contact being made through the drum rim to the back side of the titanium strip. The electrical contact area of the drum rim was about one-half the area of the portion of the strip with which it was in contact, the outer portions of the back strip surface being snugly held against rubber collars. The edges of the titanium strip were thus sealed with respect to the drum rim to prevent contact of the electrolyte with the back surface of the strip. The drum rim was connected to the positive pole of a source of D.C. electric current. A cathode of arcuate shape corresponding to the curve of the metal strip following the rim of the contact drum was arranged spaced apart from the strip surface a uniform distance of about three-fourths of an inch.

An electrolyte consisting essentially of 600-pounds of $(NH_4)_2SO_4$, 400-pounds of $Na_2Cr_2O_7 \cdot 2H_2O$, 334-pounds of 70% HF, made up with 2,000 gallons of water, was continuously circulated through the space between the cathode and the exposed strip surface. The electrolyte composition corresponds to 0.26 mole per liter of $(NH_4)_2SO_4$, 0.09 mole per liter of $Na_2Cr_2O_7$ and 0.75 mole per liter of HF.

During passage of the sheet through the electrolyte, electric current was caused to flow between the exposed sheet surface and the cathode with a flow of 20,000 amperes at 14 volts. The sheet progressed through the electrolyte at a speed of 4 linear feet per minute with a total length of strip immersed at one time being 16 linear feet. By calculation, the current density on the anode (strip surface) was found to be 2.8 amperes per square inch. Temperature of the electrolyte was maintained at about 57° C.

After passage through the electrolyte, the titanium strip was rinsed with water and dried. Its surface appearance was bright and shiny and no hydrogen pickup would occur with this grade of material. The electrolytic pickling action had removed 0.0013 inch thickness of metal from the exposed face of the strip. The rate of metal removal calculated from the gauge loss was about 120 ampere minutes per gram.

The strip was then turned over and run through the process a second time with the previously protected back surface of the strip now exposed to electrolytic pickling action, and the pickled surface lying next to the drum and protected. The same operating conditions were employed and the same results in metal removal and surface were obtained. The finished strip product was pickled uniformly with a bright, shiny finish on both sides.

Example 12

The same type of apparatus and titanium strip pickled as in Example 10 was employed for this example. The electrolyte composition was the same, and the temperature of operation and electric current employed were the same. Voltage was slightly higher at 20 volts. The principal difference was in the total length of strip immersed at any one time, which was 5 to 6 feet compared to 16 feet in the process illustrated in Example 11. This was arranged by lowering the level of the electrolyte in its container around the lower part of the contact drum. This increased the current density on the anode from about 2.8 amperes per square inch to about 8.4 amperes per square inch.

As a result of the high current density, the pickled surface of the titanium metal strip was characterized by a brilliant mirror-like polish.

As would be expected, the amount of metal removed per unit area was about 3 times that of the practice of Example 11, and amounted to 0.004 inch gauge removal.

The pickling process of this invention is versatile and under good control. A variety of metal shapes may be effectively pickled and simultaneously descaled if desirable or necessary. The amount of metal pickled and removed is related dependably to the current and time employed so that a predetermined amount of metal may be removed with very reasonable accuracy. Additionally, a range of surface finishes may be produced. Metal may be removed to produce an even, flat finish or, as described, a brightly polished surface may be obtained. At the highest current levels, an extremely bright, mirror-like finish can be produced.

I claim:

1. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

2. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of sulphuric acid, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

3. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of sodium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

4. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of potassium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hrydrofluoric acid, balance substantially water.

5. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

6. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an elec-

trolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate salt, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

7. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate salt, from 0.75 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

8. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of about 0.25 mole per liter of a compound selected from the group consisting of sulphur acid, sodium sulphate, potassium sulphate and ammonium sulphate, about 0.1 mole per liter of sodium dichromate, about 0.75 mole per liter of hydrofluoric acid, balance substantially water.

9. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte maintained at between about 50 and 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate salt, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

10. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte maintained at between about 90 and 100° C., while passing electric current between said article as anode and a cathode at a current density based on the immersed anode surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate salt, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

11. A method for pickling an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said article in an electrolyte at a temperature between room temperature and up to about 100° C., while passing electric current between said article as anode and a cathode in amount of about 120 ampere minutes for each gram of metal to be dissolved by the pickling process, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate salt, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

12. A method for pickling a flat rolled product of metal selected from the group consisting of titanium and tinaium base alloys which comprises; immersing said product in an electrolyte at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as anode and a cathode co-extensive with and facing the other and unprotected face of said product at a current density based on an anode immersed and unprotected surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting esentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

13. A method for pickling a flat roller product of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said product in an electrolyte at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as anode and a cathode co-extensive with and facing the other and unprotected face of said product at a current density based on an anode immersed and unprotected surface area of between about 0.55 and 8.5 amperes per square inch, said cathode being spaced apart from said product as anode a uniform distance of not more than about one-inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

14. A method for pickling a flat rolled product of metal selected from the group consisting of titanium and titanium base alloys which comprises; continuously passing said flat rolled product through an electrolyte to successively immerse portions thereof at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as anode and a cathode co-extensive with and facing the other and unprotected face of the immersed portion of said product at a current density based on an anode immersed and unprotected immersed surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water.

15. A method for pickling a flat rolled product of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing said product in an electrolyte at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as anode and a cathode co-existensive with and facing the other and unprotected face of said product at a current density based on an anode immersed and unpro-

tected surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water, meanwhile circulating said electrolyte between said flat rolled product and said cathode.

16. A method for pickling a flat rolled product of metal selected from the group consisting of titanium and titanium base alloys which comprises; continuously passing said flat rolled product through an electrolyte to successively immerse portions thereof at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as anode and a cathode co-extensive with and facing the other and unprotected face of the immersed portion of said product at a current density based on an anode unprotected immersed surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, up to 0.33 mole per liter of a soluble dichromate, from 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water, said electric current being connected to the said protected face of said product.

17. A method for pickling a flat rolled product of metal selected from the group consisting of titanium and titanium base alloys which comprises; continuously passing said flat rolled product through an electrolyte to successively imerse portions thereof at a temperature between room temperature and up to about 100° C. while protecting one face of said product from contact with said electrolyte while passing electric current between said product as an anode and a cathode co-extensive with and facing the other and unprotected face of the immersed portion of said product at a current density based on an anode unprotected immersed surface area of between about 0.55 and 8.5 amperes per square inch, said electrolyte consisting essentially of from 0.125 to 1 mole per liter of a compound selected from the group consisting of sulphuric acid, sodium sulphate, potassium sulphate and ammonium sulphate, from 0.05 to 0.33 mole per liter of a soluble dichromate and 0.5 to 1.5 moles per liter of hydrofluoric acid, balance substantially water, said electric current being connected to the said protected face of said product by contact with a current conductor over at least one-third of the area of said protected face.

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