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DESCALING TITANIUM AND TITANIUM ALLOY ARTICLES

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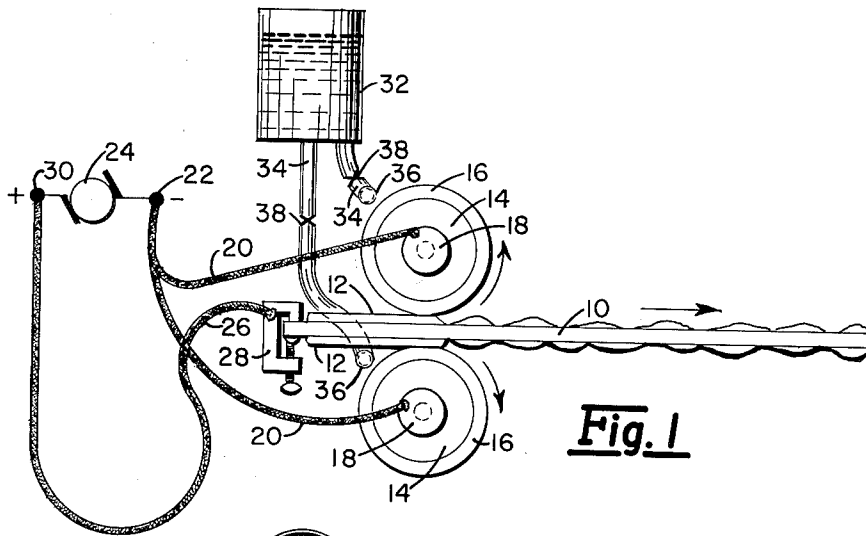


Fig. 1

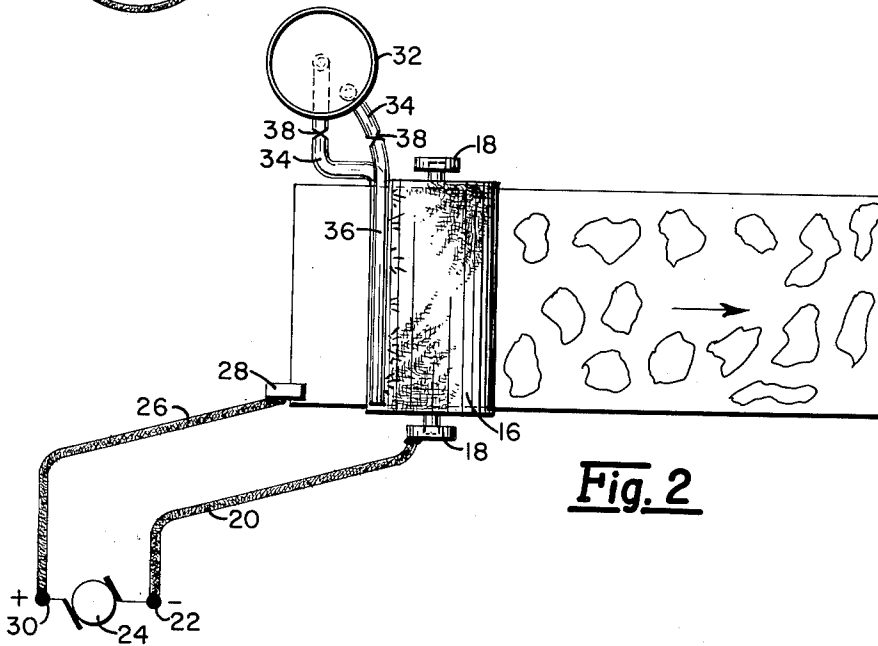


Fig. 2

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DESCALING TITANIUM AND TITANIUM
ALLOY ARTICLES

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This invention relates to a method for loosening scale on the surfaces of articles manufactured of titanium and titanium base alloys and more particularly to a process which will not raise the hydrogen content of the metal or alloy of which the article is composed.

In the manufacture and fabrication of titanium and titanium base alloy articles they are often exposed to high temperatures under conditions which result in formation of an adherent layer of refractory oxidic compounds, referred to as scale, on their surfaces. Further processing and ultimate usefulness require removal of such scale.

Several methods have heretofore been employed for descaling the surfaces of titanium and titanium base alloy articles. Baths of molten alkali compounds have been employed to a limited extent. Such baths apparently react with or loosen certain types of scale so that they may be subsequently removed by mechanical means or acid treatment. Such baths, however, are expensive to originally provide and to maintain, and must necessarily be used above the melting point of the constituent mixture which is generally of the order of 480° C. or higher. Such operating conditions are often dangerous and inconvenient, and in addition, such temperature may affect the mechanical properties of the metal immersed in such a bath. Moreover scale produced on the surface of certain titanium alloys does not appear to be amenable to removal by a treatment employing molten caustic. In treatment of any titanium article in such a bath a danger of hydrogen contamination exists.

Strong acid solutions such as for example, a mixture of nitric and hydrofluoric acid, have also been employed at elevated temperature. These, however, will not successfully loosen or act on heavy and refractory scale such as is often produced during mill processing and long exposure of titanium and titanium base alloy articles at high temperature. The acid strength, treatment temperature, and time necessary to provide attack on such scale often results in corrosive action on the metal itself, resulting in pitting and other detrimental surface defects. Acid solutions, employed at elevated temperature and for the extended period of contact time necessary to act on scale, inevitably raise the hydrogen content of the alloy of which an immersed article is composed, to an undesirably high level.

It is therefore a principal object of this invention to provide an improved method for loosening scale on the surface of titanium and titanium base alloy articles. Another object of this invention is to provide a method for loosening the scale on the surface of titanium and titanium base alloy articles, that may be operated at low temperatures and which is more economical, rapid and convenient than methods heretofore proposed. Yet another object of this invention is to provide a method for loosening scale on the surfaces of titanium and titanium base alloy articles without detrimental attack on the metal itself. A still further object of this invention is to provide a method for loosening scale on the surfaces of titanium and titanium base alloy articles which is safe and convenient. These and other objects of this invention will be apparent from the following description thereof.

This invention in its broadest aspects contemplates a method for loosening scale from a surface of an article

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made from titanium or titanium base alloys in which the article is connected to the positive pole of a source of direct electric current. A cylindrical electrode having an outer cover forming a pervious and preferably resilient pad is connected to the negative pole of the source of electric current and the electrode is rolled over the scaled surface of the titanium or titanium base alloy article with the electrode pad in contact with the scaled surface. While the electrode is being rolled over the scaled surface the cover pad of the electrode is maintained wet with an aqueous solution, preferably containing a soluble fluoride and a soluble phosphate, and electric current is passed between the article and the cylindrical electrode with the solution wetting the pad on the cylindrical electrode acting as an electrolyte.

The method of this invention will be more readily understood by referring to the annexed drawings in which:

FIG. 1 shows a side view of apparatus illustrating the manner in which the cylindrical electrodes are rolled over the surface of the titanium scaled article;

FIG. 2 shows a plan view of the apparatus illustrated in FIG. 1.

Referring now particularly to FIGS. 1 and 2, in which details of conventional construction and apparatus design have been omitted for ease of understanding of the process, a sheet of titanium is represented at 10 with a scaled surface at 12. Cylindrical electrodes of suitable electric current conducting material, are shown at 14, which are encircled by pervious and preferably resilient pads 16. The cylindrical electrodes are connected, through bearings 18 and connecting leads 20, to the negative terminal 22 of a suitable source of direct electric current, as generator 24. The titanium article 10, which in the embodiment illustrated is a flat rectangular sheet, is connected by fastening lead 26 by clamp 28 thereto, lead 26 at its other end being connected to the positive terminal 30 of the current source from generator 24.

An electrolyte tank 32 is provided, preferably elevated, from which transfer pipe lines 34 lead to distributing members 36, so that electrolyte contained in tank 32 may be applied to electrode cover pads 16 to maintain them wet. Suitable valves 38 may be placed in lines 34 to control the flow of the electrolyte therethrough.

It will be noted that the example illustrated in FIGS. 1 and 2 shows a pair of opposed padded electrodes, one above and one below the scaled sheet 10, and it will be understood that a single cylindrical electrode may be employed if desired to loosen scale from one surface only, whereas the opposed pair illustrated are convenient for simultaneously loosening scale from both side surfaces of an article such as the sheet shown. It is also to be understood that the apparatus may be suitably modified by provision, if desired, of a plurality of electrode rollers in tandem for contacting the scaled sheet as hereinbefore described.

Solutions suitable for use as the electrolyte may contain acids, bases or salts to provide the required ability to conduct electric current. Since the scale loosening process apparently involves formation of an anodic oxide film on the titanium surface, any electrolyte suitable for anodic deposition of such films may be employed. Aqueous solutions of sulphuric acid having H₂SO₄ concentration between 20% and 80% by volume, will provide effective scale loosening, as will solutions of hydrofluoric, nitric, and hydrochloric acids. Hydrofluoric acid has shown rapid and efficient action, as have soluble fluoride salts. Ammonium fluoride in concentrations between 50 and 200 grams per liter has been determined to be most advantageous, since it is essentially a neutral salt and appears to possess desirable rapid action in loosening scale. The formation of anodic oxide films on titanium is often advantageously conducted in an aqueous electro-

lyte containing a soluble phosphate, and the combination in aqueous solution of a soluble fluoride and a soluble phosphate has proved to be a desirable combination to form the electrolyte employed in the process of this invention. A combination of ammonium fluoride in concentration between 50 and 200 grams per liter and $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ in concentration between 5 and 200 grams per liter is preferred.

The pad encircling the cylindrical electrode is fabricated of material which is insulating, that is, will not itself conduct electric current, and also will not be subject to deleterious corrosion by the electrolyte solution employed. It must also be pervious, so that when wet the contained electrolyte will contact both the surface of the cylindrical electrode and the scaled surface of the titanium being treated. The pad should also be, to an extent, resilient so that there will be an appreciable pad area in contact with the scaled titanium surface when the cylindrical electrode is rolled over it. Fiberglass is a suitable material for pad construction especially when employing corrosive electrolytes such as stronger acid solutions, and a pad formed from a plurality of layers of glass cloth will be found effective. When using essentially neutral or non-corrosive electrolytes such as the ammonium fluoride complex phosphate electrolyte described above, a pad formed of cotton fabric such as cheesecloth will function very satisfactorily. A felted structure, produced from suitable fibers, may also be employed.

The cylindrical electrode is manufactured from any material capable of conducting electric current and having a surface, at least resistant to corrosion by the electrolyte under operating conditions. Constructional details may vary widely, according to known principles, to accomplish its purpose of conducting the electric current to its surface in contact with the electrolyte. Graphite, copper, lead, stainless steel as well as noble metals may be employed in its construction and it will be obvious that, if desired, it may be designed of composite or plated metals if desired, to properly accomplish its function.

The amount of electric current required to produce effective scale loosening will depend on the contact area of the pad on the scale surface and the speed with which the electrode is rolled over this surface. I have found that scale is effectively loosened when a current of density between about 300 and 10,000 amperes per square foot over the pad contact area is applied for a time period of between about 1 second and 10 minutes. I have also found that the current density may be proportionately reduced if the time is lengthened and vice versa. The average contact time of the pad with the scaled surface is that fraction of any given time period represented by the width of the contact area, that is the measurement transverse to the electrode axis, divided by the linear travel of the electrode in the given time period. For example, if an electrode rolls a linear distance of 6 inches across a scaled sheet in 1 minute and the width of the contact area is $\frac{1}{2}$ inch, then $\frac{1}{2}$ inch divided by 6 inches is $\frac{1}{12}$ and $\frac{1}{12}$ of 1 minute is 5 seconds, the average contact time. Obviously those skilled in the art will be able to arrange the desired speed of travel for any given electrode and pad design to provide the required contact time. It will also be apparent that the contact area of the pad on the scale titanium surface will be arranged by applying suitable pressure on the electrode to provide required flattening of the resilient pad at its contact with the scaled sheet.

The aqueous solution employed as an electrolyte in the process of this invention may be used at normal room temperature or may be employed, if desired, at elevated temperatures. Generally speaking, the high current densities which can be employed as a result of the relatively small contact area as the electrode pad is rolled over the sheet, do not require strong or elevated temperature electrolytes. The preferred solution containing sodium am-

monium hydrogen phosphate and ammonium fluoride is essentially neutral and functions satisfactorily at normal room temperatures. This is advantageous since the use of strong acid solutions, particularly at elevated temperatures as heretofore employed, almost inevitably has resulted in increasing the hydrogen content of the material being descaled.

After the scale has been loosened employing the process of this invention, a simple pickling solution will remove the scale together with the anodic film formed on the surface of the metal, to provide a completely descaled titanium surface. If desired, a portion or all of the loosened scale may be separated by mechanical action such as wire brushing, or other abrasion treatment prior to pickling. It appears that the process of this invention operates successfully due to replacement of the original hard and refractory scale by an anodic oxide coating on the titanium metal and this anodic oxide coating may be much more readily subsequently removed by a simple acid pickle than could the original refractory scale even by extended treatment at elevated temperature with strong and corrosive acids. Thus, it will be appreciated that the effective loosening of the scale is a most important feature, and that when this has been accomplished removal of the scale and the anodic oxide coating involves only a simple pickling step employing solutions known to the art. Preferred is a solution containing about 10% nitric acid and about 2% hydrofluoric acid and it has been found that immersion of a sheet with scale loosened in this solution for a period of not more than about 5 minutes at a temperature of not more than 80°C . will provide adequate pickling to completely remove the last vestiges of scale, and to produce a fine, bright, clean, pickled surface. Even though this is an acid treatment, exposure of the titanium is for a short time period only and the temperature should not be above 80°C . so that the hydrogen pickup resulting from this acid treatment will be negligible. Such subsequent acid treatment should be distinguished from an acid treatment for an original scale loosening or removal in which strong acids at elevated temperatures must be employed for extended periods of time to effect loosening and dissolution of a refractory scale. It is to be understood that in general terms the padded electrode is rolled over the scale sheet surface. This, as will be apparent, may be accomplished by any of several operations in which the sheet and the roll are actuated with relation to each other. Thus, the sheet may remain stationary and the roll may travel over its surface, or the electrode axis may remain stationary and the sheet moved with respect thereto. It will be convenient to provide an opposed pair of electrodes as shown in the embodiment illustrated in FIG. 1 and FIG. 2, in order to loosen scale simultaneously from both sides of a flat article, and to rotate these electrodes suitably either by hand or by some mechanical device so that the sheet is impelled through and between them. Alternatively, if desired, the pair of electrodes may be free wheeling and a scaled sheet interposed between them, and simply pulled through to provide the contact required.

The time of application of electric current required for effective scale loosening will vary according to the nature of the scale. The most refractory scales will require longer time periods at higher current densities. The longer time period required may be obtained by slowing down the relative motion of the scaled article with respect to the electrode which in effect slows down the rolling speed. Alternatively the scaled article may be subjected to a plurality of rolling passes in contact with the electrode or electrodes to accomplish the same purpose, as will be noted in the examples. Or if desired or more convenient, a plurality of electrodes in tandem may be arranged to provide a multiple of the time effect obtained by a single electrode rolling over a scaled surface. Thus, the mechanical apparatus and process arrangements may

be widely varied to provide operating conditions within the hereinbefore defined limits and ranges.

The following examples will illustrate selected embodiments of the practice of this invention.

Example 1

A section of sheet of a titanium base alloy containing 13% vanadium, 11% chromium, 3% aluminum and having a heavy mill scale on its surfaces, was treated employing apparatus of the general type illustrated in FIG. 1 and FIG. 2. The apparatus employed opposed cylindrical electrodes of approximately 2½ inches in diameter of a rubber base material which were covered first with a copper sheet to provide a current carrying surface and then with a quarter inch thick pad of cheesecloth encircling the copper outside surface. A sliding contact was arranged between the copper electrode surfaces and fixed bearings which were connected to the negative pole of a direct current supply. The titanium alloy sheet itself was connected to the positive pole of the same direct current supply.

Sufficient pressure was arranged on the padded electrodes so that the pads each established a contact area of ½ square inch on the scaled sheet surfaces. The electrolyte employed was an aqueous solution containing 10% ammonium fluoride (NH_4F) and 10% sodium ammonium hydrogen phosphate ($\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$).

The electrodes were rotated so that the sheet passed between them (thus effecting a rolling of the electrodes over the scaled surfaces) at a rate of 6 linear inches per minute to provide an average contact time of 5 seconds for the electrode contact areas. Meanwhile, the electrolyte, employed at room temperature, was distributed across the electrode pads so as to maintain the pads wet. Electric current was passed between the electrodes and the sheet at about 60 volts and at about 20 amperes to provide a current density over the areas of electrode pads in contact with the sheet of about 2,880 amperes per square foot.

After five passes through the electrodes under the conditions described, it was found that the scale had been loosened and could be readily removed by a two minute pickling operation in which the sheet, with loosened scale, was immersed in a solution containing 10% HNO_3 and 2% HF maintained at 70° C. Examination of the sheet after pickling and rinsing, showed complete descaling and an appreciable surface without pitting, or evidence of undesirable attack by the scale loosening or pickling operations. The hydrogen content of the titanium alloy prior to descaling was .0142% and after descaling as described above was .0139% showing substantially no hydrogen pick up as a result of the treatment according to this invention.

Example 2

A section of sheet of commercially pure unalloyed titanium with surfaces covered with a light scale from an annealing operation which involved exposure to air for five minutes at 1500° F., was used for this test. The apparatus employed was the same as that used in Example 1 and the same electrode pressure was arranged so that the contact area of ½ square inch on each electrode pad was obtained on the scaled sheet surfaces. The electrolyte employed was the same solution containing 10% ammonium fluoride and 10% sodium ammonium hydrogen phosphate. The electrodes were rotated so that the sheet passed between them at the same rate of 6 linear inches per minute to provide the average contact time of 5 seconds for the electrode pad contact areas.

Electric current was passed between the electrodes and the sheet at about 30 volts and 15 amperes to provide a current density over the areas of the electrode pads in contact with the sheet, of about 2,200 amperes per square foot.

After a single pass through the electrodes under the

conditions described it was found that the scale had been loosened, and the sheet was then pickled using the same solution and procedure described in Example 1. Examination of the sheet after pickling and rinsing showed complete descaling, and an acceptable surface, without pitting, or evidence of undesirable attack by the scale loosening or pickling operations. The hydrogen content of the descaled sheet was determined to be .0049% compared to .0047% before treatment, demonstrating that substantially no hydrogen pick up occurred as a result of treatment according to this invention.

It will be apparent that the lighter scale removed in the test described in this example was successfully loosened during one pass between the electrode pads, compared to the three passes required for the heavier scale loosened in the test of Example 1.

Example 3

A section of sheet of a titanium base alloy containing 6% aluminum and 4% vanadium with surfaces covered with a heavy scale developed from hot rolling, was used for this test. The apparatus employed was the same as that used in Example 1 and the same electrode pressure was arranged so that the contact area of ½ square inch on each electrode pad was obtained on the scaled sheet surfaces. The electrolyte employed was the same solution containing 10% ammonium fluoride and 10% sodium ammonium hydrogen phosphate. The electrodes were rotated so that the sheet passed between them at the same rate of 6 linear inches per minute to provide the average contact time of 5 seconds for the electrode pad contact areas.

Electric current was passed between the electrodes and the sheet at about 60 volts and 20 amperes to provide a current density over the areas of the electrode pads in contact with the sheet of about 2,880 amperes per square foot.

After four passes through the electrodes under the conditions described it was found that the scale had been loosened and the sheet was then pickled using the same solution and procedure described in Example 1. Examination of the sheet after pickling and rinsing showed complete descaling and an acceptable surface without pitting or evidence of undesirable attack by the scale loosening or pickling operations. The hydrogen content of the descaled sheet was determined to be .0077% compared to .0074% before treatment, demonstrating that substantially no hydrogen pick up occurred as a result of treatment according to this invention.

Example 4

A section of sheet of a titanium base alloy containing 13% vanadium, 11% chromium and 3% aluminum, with surfaces covered with a heavy mill scale was used for this test. The apparatus employed was the same as that used in Example 1 and the same electrode pressure was arranged so that the contact area of ½ square inch on each electrode pad was obtained on the scaled sheet surfaces. The electrolyte employed was a solution of 60% sulphuric acid by weight and the cotton pads used on the electrodes in Examples 1 and 2 were replaced with glass wool pads to resist the corrosive action of the sulphuric acid electrolyte. The electrodes were rotated so that the sheet passed between them at the same rate of 6 linear inches per minute to provide the average contact time of 5 seconds for the electrode pad contact areas.

Electric current was passed between the electrodes and the sheet at about 25 volts and 18 amperes to provide a current density over the areas of the electrode pads in contact with the sheet of about 2,600 amperes per square foot.

After seven passes through the electrodes under the conditions described it was found that the scale had been loosened and the sheet was then pickled using the same solution and procedure described in Example 1. Examination

tion of the sheet after pickling and rinsing showed complete descaling and an acceptable surface, without pitting or evidence of undesirable attack by the scale loosening or pickling operations. The hydrogen content of the descaled sheet was determined to be .0176% compared to .0132% before treatment demonstrating that only a small amount of hydrogen pick up occurred as a result of treatment according to this invention.

It will be apparent that the heavy scale on the alloy treated in this example required a greater number of passes between the electrode pads to obtain effective loosening of the scale. While the operation described in this example produced the results desired and satisfactory descaling was accomplished, a considerable amount of fuming resulted from employment of the sulphuric acid electrolyte.

Example 5

A section of sheet of a titanium base alloy containing 13% vanadium, 11% chromium and 3% aluminum with surfaces covered with a heavy mill scale, were used for this test. The apparatus employed was the same as that used in Example 1 and the same electrode pressure was arranged so that the contact area of $\frac{1}{2}$ square inch on each electrode pad was obtained on the scaled sheet surfaces. The electrolyte employed was an aqueous solution of 4% sodium fluoride by weight and the cheesecloth electrode pads used in the tests described in Examples 1, 2 and 3 were again used. The electrodes were rotated so that the sheet passed between them at the same rate of 6 linear inches per minute to provide the average contact time of 5 seconds for the electrode pad contact areas.

Electric current was passed between the electrodes and the sheet at about 25 volts and 18 amperes to provide a current density over the areas of the electrode pads in contact with the sheet of about 2,600 amperes per square foot.

After 10 passes through the electrodes under the conditions described it was found that the scale had been loosened, and the sheet was then pickled using the same solution and procedure described in Example 1. Examination of the sheet after pickling and rinsing showed complete descaling and acceptable surface without pitting or evidence of undesirable attack by the scale loosening or the pickling operations. The hydrogen content of the descaled sheet was approximately the same as that before treatment.

Example 6

A section of sheet of a titanium base alloy containing 13% vanadium, 11% chromium and 3% aluminum with surfaces covered with heavy mill scale was used for this test. The apparatus employed was the same as that used in Example 1 and the same electrode pressure was arranged so that the contact area of $\frac{1}{2}$ square inch on each electrode pad was obtained on the scaled sheet surfaces. The electrolyte employed was a saturated aqueous solution of sodium ammonium hydrogen phosphate and since this solution was not corrosive, the cheesecloth pads were again used around the electrodes. The electrodes were rotated so that the sheet passed between them at the same rate of 6 linear inches per minute to provide the average contact time of 5 seconds for the electrode pad contact areas.

Electric current was passed initially between the electrodes and the sheet at about 20 volts and 18 amperes and as the scale loosening process progressed and a heavy anodic oxide layer was built up on the surface of the sheet, it was necessary to gradually raise the voltage so that in the final stages current was being passed at 70 volts and about 2 amperes. The average current density over the time required for scale loosening was about 1,440 amperes per square foot of electrode pad contact area.

After twelve passes through the electrodes under the

conditions described it was found that the scale had been loosened and the sheet was then pickled using the same solution as described in Example 1, but using a 3 minute immersion time to insure removal of the heavier anodic oxide layer. Examination of the sheet after pickling and rinsing showed complete descaling and an acceptable surface without evidence of pitting or undesirable attack by the scale loosening or pickling operations. The hydrogen content of the sheet was not raised during the scale loosening and pickling treatment.

It will be apparent that a heavy mill scale can be successfully removed employing a phosphate electrolyte according to this example. The more rapid build-up of a heavy anodic oxide layer on the titanium surface increases the electrical resistivity so that higher voltage is required to pass appreciable current amperage.

The process of this invention provides a unique application of high density electric current through a relatively small electrode pad contact area, and this high current density is applied progressively over the area of the surface from which the scale is loosened. To obtain the same effect simultaneously over the surface area being treated would require an enormously high current amperage, and total immersion of the scaled article in the electrolyte or at least contact of the entire scaled surface therewith. Thus, the method of this invention represents a substantial improvement in economy, speed and convenience. An additional advantage is that, since high current density can be conveniently employed, the employment of hot corrosive electrolytes is not necessary and the preferred ammonium fluoride-sodium ammonium hydrogen phosphate solution is essentially neutral and used at room temperature. Under these conditions pitting and other detrimental attack resulting from extended treatment with hot and corrosive electrolytes is avoided.

I claim:

1. In a method for loosening scale from a surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises connecting said article to the positive pole of a source of direct electric current, connecting an electrode having a pervious and insulating padding to the negative pole of said source of electric current and rolling said electrode over a scaled surface of said article with said padding in contact with said scaled surface, meanwhile maintaining said padding wet with an electrolyte and meanwhile passing direct electric current between said article and said electrode, the improvements which comprise employing as said electrolyte a solution consisting essentially of 50 to 200 grams per liter of ammonium fluoride (NH_4F) and 50 to 200 grams per liter of sodium ammonium hydrogen phosphate ($\text{NaNH}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$) with the balance substantially all water, and the said direct electric current is passed in amount to provide a current density over the pad contact area of between about 300 and 10,000 amperes per square foot and is applied for a period of between about 1 second and 10 minutes.

2. The method of claim 1 carried out at substantially room temperature.

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