

1

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DESCALING TITANIUM AND TITANIUM BASE ALLOY ARTICLES

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This invention relates to a method for descaling the surfaces of articles manufactured of titanium and titanium base alloys, and more particularly to a low temperature descaling method 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 treating scale on the surface of titanium and titanium base alloy articles. Another object of this invention is to provide a method for descaling the surface of titanium and titanium base alloy articles that may be operated at low temperature, and which is more economical, rapid, and convenient than methods heretofore proposed. Yet another object of this invention is to provide a method of descaling titanium and titanium base alloy articles without detrimental attack on the metal itself and yet at the same time providing efficient removal of heavy and refractory scales. A still further object of this invention is to provide a method of descaling titanium and titanium base alloy articles without appreciably raising the hydrogen content of the metal of which such articles are composed.

This invention in its broadest aspects contemplates a method for treating scale on the surface of an article of

2

titanium or titanium base alloy which comprises immersing said article in a sulfuric acid electrolyte and passing electric current between said article as an anode and a cathode immersed in or contacting said electrolyte until the scale has been loosened or removed, and an anodic film has been formed on the exposed metal surface. The article is then removed from the electrolyte and the anodic film is removed from its surface, resulting in a bright, clean and completely descaled titanium or titanium base alloy article.

The sulfuric acid electrolyte may be of convenient concentration, and may be an aqueous solution containing at least 1% H₂SO₄ by volume and may be as strong as essentially 100% H₂SO₄. It is preferred to employ as an electrolyte an aqueous solution containing between 40% and 80% sulfuric acid by volume. Concentrations below 40% will be effective but the time required for complete action in the electrolytic descaling step will be unnecessarily lengthened. Concentrations higher than 80% sulfuric acid are not desirable due to the evolution of corrosive sulfur oxide fumes, and will provide little additional reaction speed. The electrolytic descaling step may be carried out at any temperature, from room temperature to the boiling point of the electrolyte. It is preferred to operate in the range between 80° and 130° C., depending on the acid concentration, since this provides adequate reaction speed without excessive loss of electrolyte constituents.

The cell in which the electrolyte is contained may be of convenient construction and manufactured of material suitably resistant to the corrosive effect of the sulfuric acid electrolyte. The cathode employed in the cell may be fabricated of similarly acid resistant metal or material, such as platinum, tantalum, lead, or graphite. If desired, the cell lining itself may be arranged to act as a cathode, and a graphite liner, which will be acid resistant and a suitable and desirable cathode, may be advantageously employed.

Any suitable conventional and convenient source of direct electric current may be employed to produce the electrolytic action. The positive pole of the current source is connected to the article to be descaled which, under such conditions, will be the anode in the cell. Suitable connection is also made from the negative pole of the power supply to the cell cathode. Current to the anode and cathode is supplied to provide a current density over the total immersed surface of the article to be descaled of between 2 and 100 amperes per square foot, and the voltage may vary between 3 and 60 volts. At least 2 amperes per square foot current density is necessary to provide an anodic protective film and more than 100 amperes per square foot is not desirable because of equipment requirements to supply currents of this magnitude and at current densities much above 100 amperes per square foot the acid content of the electrolyte has a tendency to decompose. Preferably the current density should be between 5 and 50 amperes per square foot, to provide efficient current utilization and rapid and effective loosening and removal of the scale.

It is preferred, particularly when employing more concentrated electrolytes within the defined range, to connect the alloy article and the cathode of the cell to the electric current supply prior to immersing the article in the electrolyte. Also, when removing the article from the electrolyte, to insure that the electric current remains connected until the article is removed from the electrolyte. During the electrolytic treating step, the article itself suffers no detrimental attack by the acid electrolyte. This advantageous condition maintains only during the time that electric current is passing between the anode and cathode in the cell, and if the article being descaled should remain in strong sulfuric acid electrolyte without

passage of current between the anode and the cathode some attack by the electrolytic acid could result in corrosion and pitting of its surface.

The electrolytic action in the cell operated as described above results in loosening or removal of scale, and the formation on the metal surface of an anodic film. Such anodic film is itself a form of oxidic coating but quite different in character from the original scale. It is a unique feature of this invention, however, that such anodic film is formed as a result of electrolytic action which loosens or removes the scale. It protects the surface while current passage is maintained to prevent detrimental attack by the electrolyte acid. At the same time, since the article being descaled is employed as the anode during electrolysis, oxygen will be generated and released by electrolytic action and decomposition of the electrolyte from its surface. Hydrogen will be correspondingly released at the cathode. Since the article is anodic, no hydrogen will be formed at or near its surface and no hydrogen will therefore be absorbed by the metal of the article as a result of the descaling action.

Electrolysis in the cell is continued for at least one minute and until the scale is effectively loosened or removed and the anodic film as described is formed on the surface of the immersed article. Since the original scale and the anodic film present a completely different appearance, completion of descaling may be determined by visual inspection. In any event the time of treatment in the cell will vary between about one minute and about one hour, when the preferred operating condition of between 5 and 50 amperes current density is employed. Current densities lower than the preferred range stated will require correspondingly longer time. Excess time in the cell will do no harm but will not provide improved results. Light scales may be removed in a short time, that is, up to 3 to 5 minutes, medium scales may take 5 to 10 minutes and the heaviest and most refractory scales may take as long as about 15 minutes. After the scale has been effectively loosened or removed, the article is removed from the electrolyte. The electric current supply is disconnected and residual electrolyte adhering to its surface preferably removed, conveniently by a water rinse. If any loosened scale remains on the article surface that has not been dislodged during the electrolytic process, it may be separated by wiping, brushing, or other simple mechanical action.

Removal of the anodic film and loosened scale from the article surface may be readily accomplished by mechanical abrasion such as sanding, wire brushing or grinding, or by chemical means such as immersion in pickling acid for an appropriate time. It is preferred to remove the anodic film by immersion in a pickling acid for a period of between about one and about five minutes at a temperature not higher than about 80° C. The character of the anodic film is quite different from that of the oxidic compounds of the original scale which are loosened and removed during the electrolytic step. The anodic film is readily soluble in acid solutions containing a fluoride, and a solution of 10% nitric and 2% hydrofluoric acids will be found effective and advantageous. Aqueous solutions of other acids such as hydrochloric, acetic, or sulfuric, in combination with hydrofluoric acid, may also be employed. Immersion in such acid will result in removal of the scale and anodic film and an incidental amount of the metal itself to provide a bright, clean descaled surface.

Treatment to remove the anodic film may be intensified as by immersion for a longer period of time, employment of more concentrated pickling solution, or at more elevated temperatures. This can result in dissolution of a small but appreciable thickness of metal at the surface of the article. In so doing the top layer which is contaminated to a small or greater extent by a dissolved oxide content is thereby removed. Such treatment provides surface metal which will be essentially uniform with

the interior metal and thus avoid detrimental effect on mechanical properties caused by high oxygen content metal at the surface.

Such purposeful and useful removal of gage should be distinguished from uncontrolled and detrimental corrosion, pitting, and similar effects caused by employment of strong acids in heretofore proposed treatments for removal or loosening of scale.

Articles whose surfaces are descaled by the process of this invention may be of any size or shape commensurate, of course, with size limitations of apparatus, such as tanks and baths. Fabricated articles, castings, and forgings, as well as semi-fabricated products, such as plate, sheet, bars, rods, wire, tubing, and other shapes, may be advantageously descaled. The method of this invention is useful for descaling articles of commercially pure metallic titanium as well as any of the known commercially useful titanium base alloys such as, for example, Ti—4% Al—3% Mo—1% V, Ti—6% Al—4% V, Ti—13% V—11% Cr—3% Al, Ti—8 Mn and Ti—2% Fe—2% Mo—2% Cr. It will readily and effectively descale the surfaces of articles of titanium base alloys containing relatively high percentages of chromium and molybdenum which are difficult, if not impossible, to conveniently and readily descale by previously known methods.

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

Example 1

An electrolyte consisting of a solution of essentially 100% sulfuric acid was contained in a small glass tank and maintained at a temperature of between 80° and 100° C. A platinum wire cathode was immersed in the electrolyte and connected to the negative pole of a D.C. power source. A section of sheet of titanium base alloy containing 4% aluminum, 3% molybdenum and 1% vanadium and having a medium scaled surface resulting from solution heat treatment, was connected to the positive pole of the D.C. power source and immersed as the anode in the electrolyte. A current density of about 25 amperes per square foot of total surface was maintained by adjusting the power input and the voltage varied between 10 and 50 volts. After 15 minutes immersion under these conditions, the surface appearance of the sheet had radically changed and the scale had been replaced by an anodic film. The sheet section was then removed from the electrolyte, the power source disconnected therefrom and residual electrolyte washed off by means of a water rinse. The sheet section was then immersed in an aqueous solution containing 10% nitric and 2% hydrofluoric acids by volume, for two minutes, at a temperature of about 50° C. After removal from this solution, residual acid was rinsed off with water and the sheet surface appeared bright, clean and free from scale or oxide coating. No appreciable metal thickness was removed and the hydrogen content of the sheet after treatment was determined to be 0.0045% compared to 0.0048% before descaling.

Example 2

The same general process steps as those described for Example 1 were employed on the same type of scaled sheet except that the electrolyte was composed of an aqueous solution containing 5% sulfuric acid. Amperage was maintained at about 85 amperes per square foot of sheet surface and voltage varied from 4 to 54. After 15 minutes in the electrolytic bath at between 83° and 92° C., the sheet was removed, rinsed, and wiped with a cloth to separate loose scale. The sheet was then immersed in a pickling bath similar to that of Example 1, for two minutes and subsequently showed a similar surface bright, clean and free from scale or oxide coating. The hydrogen content of the sheet metal was not increased.

5

Example 3

The same general process steps as those described for Example 1 were employed on the same type of scaled sheet except that the electrolyte was composed of an aqueous solution containing 60% sulfuric acid. Amperage was maintained at about 30 amperes per square foot of sheet surface and voltage varied from 6 to 23. After 10 minutes in the electrolytic bath at between 94° and 96° C., the sheet was removed and rinsed to remove adhering electrolyte. The sheet was then immersed in a pickling bath similar to that of Example 1, for 2 minutes and subsequently showed a similar surface, bright, clean and free from scale or oxide coating. The hydrogen content of the metal was not increased.

Example 4

An electrolyte consisting of an aqueous solution containing 60% sulfuric acid was contained in a small glass tank and maintained at a temperature between 90° and 95° C. A platinum wire cathode was immersed in the electrolyte and connected to the negative pole of a D.C. power source. A section of sheet of commercially pure titanium, having light scale resulting from exposure during annealing, was connected to the positive pole of the D.C. power source, and immersed as the anode in the electrolyte. A current density of about 25 amperes per square foot of total surface was maintained by adjusting the power input and the voltage varied from 30 to 52 volts. After 5 minutes immersion under these conditions the surface appearance of the sheet had radically changed and the scale had been replaced by an anodic film. The sheet was then removed from the electrolyte, the power source disconnected therefrom and residual electrolyte washed off by means of a water rinse. The sheet section was then immersed in an aqueous solution containing 10% nitric and 2% hydrofluoric acids by volume for 2 minutes at a temperature of about 50° C. After removal from this solution, residual acid was rinsed off with water and the sheet surface appeared bright, clean and free from scale or oxide coating. No appreciable metal thickness was removed and the hydrogen content of the sheet metal was not increased.

Example 5

An electrolyte consisting of an aqueous solution containing 60% sulfuric acid was contained in a small glass tank and maintained at a temperature between 114° and 117° C. A graphite rod cathode was immersed in the electrolyte and connected to the negative pole of a D.C. power source. A section of sheet of titanium base alloy containing 6% aluminum and 4% vanadium, having a medium mill scaled surface, was connected to the positive pole of the D.C. power source and immersed as the anode in the electrolyte. A current density of about 45 amperes per square foot of total surface, was maintained by adjusting the power input, and the voltage varied between 4 and 6 volts. After 15 minutes immersion under these conditions the surface appearance of the sheet had radically changed and the scale had been replaced by an anodic film. The sheet section was then removed from the electrolyte, the power source disconnected therefrom, and residual electrolyte washed off by means of a water rinse. A sander was then employed to remove the anodic film which was readily ground off by light sanding to provide a sheet surface which appeared bright, clean and free from scale or oxide coating. Only a slight amount of metal thickness was removed during the sanding operation and the hydrogen content of the sheet metal was not increased.

Example 6

An electrolyte consisting of an aqueous solution containing 60% sulfuric acid was contained in a small glass tank and maintained at a temperature between 118° and 128° C. A platinum wire cathode was immersed in the

6

electrolyte and connected to the negative pole of a D.C. power source. A section of sheet of titanium base alloy containing 5% aluminum and 2½% tin and having a heavy mill scaled surface, was connected to the positive pole of the D.C. power source, and immersed as the anode in the electrolyte. A current density of about 45 amperes per square foot of total surface was maintained by adjusting the power input and the voltage varied between 4 and 15 volts. After 12 minutes immersion under these conditions, the surface appearance of the sheet had radically changed and the scale had been replaced by an anodic film. The sheet section was then removed from the electrolyte, the power source disconnected therefrom, and residual electrolyte washed off by means of a water rinse. The sheet section was then immersed in an aqueous solution containing 10% acetic and 5% hydrofluoric acids by volume, for 3 minutes at a temperature of 50° C. This treatment removed the anodic film and also dissolved about 2 mils gage from each side of the sheet. After removal from this solution, residual acid was rinsed off with water and the sheet surface appeared bright, clean and free from scale or oxide coating. A strip sample taken from the so-treated sheet, showed bend properties indicating ductile metal at the surface. The hydrogen content of sheet metal was not appreciably increased.

Example 7

An electrolyte consisting of an aqueous solution containing 60% sulfuric acid was contained in a small glass tank and maintained at a temperature between 85° and 100° C. A platinum wire cathode was immersed in the electrolyte and connected to the negative pole of a D.C. power source. A section of sheet of titanium base alloy containing 13% vanadium, 11% chromium and 3% aluminum and having a heavy mill scaled surface was connected to the positive pole of the D.C. power source and immersed as the anode in the electrolyte. A current density of about 50 amperes per square foot of total surface, was maintained by adjusting the power input and the voltage varied between 10 and 38 volts. After 15 minutes immersion under these conditions the surface appearance of the sheet had radically changed and the scale had been replaced by an anodic film. The sheet section was then removed from the electrolyte, the power source disconnected therefrom, and residual electrolyte washed off by means of a water rinse. The sheet section was then immersed in an aqueous solution containing 10% nitric and 2% hydrofluoric acids by volume for 2 minutes at a temperature of about 50° C. After removal from this solution residual acid was rinsed off with water and the sheet surface appeared bright, clean and free from scale or oxide coating. No appreciable metal thickness was removed and the hydrogen content of the sheet was not increased.

The mechanism by which the scale is loosened or removed in the electrolytic treatment is not clearly understood. It is theorized that possibly the scale is to some extent porous or reactive with the electrolyte allowing the electrolyte acid to penetrate the film and to release oxygen on contact with sub-scale metal. The oxygen may mechanically loosen and separate the scale or react with it chemically to destroy its cohesive and adhesive characteristics. At the same time an anodic film, which is, as is well known, a type of oxide coating, is formed on the metal surface protecting it against any detrimental attack by the electrolyte acid. Thus the method of this invention provides a process for treating scale on the surface of a titanium or titanium base alloy article in which tenacious and refractory scale oxide is converted to an easily removable oxide by immersing in an acid bath while maintaining anodic protection of the metal surface. The process is operated at low temperature, compared to those of molten alkali baths previously employed to attack stubborn scale, and the sulfuric acid and power em-

played are relatively inexpensive. The electrolyte is more convenient and safer than molten alkalis. The process of this invention will remove the heaviest and most resistant scales on titanium metal or any type of titanium base alloy without detrimental attack on the metal itself, and the characteristic efficiency of this action without raising the hydrogen content of the metal is extremely advantageous.

I claim:

1. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulfuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof.

2. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration between 40% and 80% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof.

3. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 5 and about 50 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof.

4. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of between about one minute and about one hour, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form

on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof.

5. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof by immersion in a pickling acid.

6. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof by immersion in an aqueous solution containing about 10% nitric and about 2% hydrofluoric acids by volume for a period of from one to five minutes at a temperature up to about 80° C.

7. A method for descaling the surface of an article of metal selected from the group consisting of titanium and titanium base alloys which comprises; immersing and maintaining said article as an anode in a sulphuric acid electrolyte of concentration more than 1% H_2SO_4 by volume, meanwhile passing electric current at between 3 and 60 volts between said article and a cathode to provide a current density of between about 2 and about 100 amperes per square foot of said surface for a period of at least one minute, at a temperature of between room temperature and the boiling point of said electrolyte, thereby to loosen and remove scale from said surface of said article and to form on said surface an anodic film, removing said article from said electrolyte and removing said anodic film from said surface thereof by mechanical abrasion.

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