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PROCESS OF DEOXIDIZING TITANIUM AND ITS ALLOYS

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12 Claims

ABSTRACT OF THE DISCLOSURE

A process of deoxidizing and cleaning titanium and titanium-based alloy surfaces using a treatment bath containing nitric acid, sulfuric acid and a material which supplies the acid fluoride ion. Water and phosphoric acid can be included in the bath.

This invention relates to processes for cleaning, deoxidizing and brightening titanium and its alloys.

Titanium and titanium alloys develop a resistant oxide scale during manufacturing processes involving heat treatment and fabrication. Proper finishing requires that this adherent oxide be removed with minimum or no adverse effects to the article.

Several conventional methods are known for deoxidizing titanium and its alloys. The most common are abrasive blasting, a molten salt bath and pickling in an aqueous solution of nitric acid and hydrofluoric acid.

Pickling in an aqueous solution of nitric acid, hydrochloric acid, hydrofluoric acid and water results in a dark rough etched surface quite susceptible to hydrogen embrittlement and intergranular corrosion.

Abrasive blasting also roughens the surface, produces uneven metal removal and its use is limited to regular shapes. Articles having complex surfaces with hidden areas cannot be completely deoxidized using this method.

Molten salt baths require extremely high temperatures and normally produce a stained surface. The stain is usually removed with a post-treatment to complete the process. It is impractical to descale large articles with this process.

Hydrogen embrittlement represents a major problem in treating titanium and its alloys after heat treating, welding and other scale forming processes. Removing the heavy oxide with the standard aqueous hydrofluoric acid, nitric acid and hydrochloric acid baths produces hydrogen absorption. Hydrogen absorption into the titanium intergranular structure produces hydrogen embrittlement causing structural cracks and failure under stress. This absorption of hydrogen is irreversible. It cannot be baked out, as with high strength steels.

Provided by this invention is a process for cleaning and deoxidizing titanium and its alloys which produces a stain free, smooth bright surface with inhibition of hydrogen absorption and consequent embrittlement. The process also gives substantially or essentially smut free surfaces even with titanium alloys which normally produce smutty surfaces with other processes.

It has been found according to the present invention that the surfaces of titanium and titanium-based alloys can be deoxidized and cleaned by bringing the surface into contact with a bath of the following composition:

	Percent by wt.
Nitric acid	30-52
Sulfuric acid	10-75
Hydrofluoric acid	1-30
Phosphoric acid	0-25
Water	0-25

Except for water, the percentages are on an anhydrous basis. For the purpose of this application, the term "hydrofluoric acid" is considered to encompass hydrofluoric acid as well as the resulting acids formed by the utilization of salts in the solutions to provide the needed hydrofluoric acid and/or the equivalent acid fluoride ion. Thus, some of the salts which can be used are the alkali metal silicofluorides such as sodium or potassium silicofluoride, ammonium bifluoride, calcium bifluoride, and alkali metal bifluorides such as sodium or potassium bifluoride, an alkali metal fluoride and particularly sodium, potassium or lithium fluoride, or fluoro boric acid. The bath can also be used with a mixture of such hydrofluoric acid or acid fluoride ion supplying materials.

The described baths dissolve or remove surface oxides from titanium and titanium-based alloys without etching the surface, leaving it clean and bright, with low hydrogen absorption thus minimizing or eliminating hydrogen embrittlement. The process is also characterized by an essential lack of smut adherence on the surface. The surfaces also seem to be made passive by the treatment.

Although the presence of phosphoric acid in the bath is not essential, its inclusion gives better cleaning and deoxidizing than without it. Phosphoric acid also serves to suppress etching. It is accordingly usually beneficial to include at least 5% phosphoric acid in the bath.

Although up to 25% of water can be in the bath, it is advisable to employ 10% or less of water to suppress hydrogen absorption and resulting embrittlement of the metal.

A particularly useful deoxidizing bath for titanium and its alloys can have 0-25% water, 10-55% sulfuric acid, 30-52% nitric acid, 0-25% phosphoric acid and 1-10% ammonium bifluoride with the percentages of the acids and bifluoride being on an anhydrous basis.

It is acceptable, but generally unnecessary, to include one or more surfactants in the deoxidizing bath. Some surfactants which can be used are metal sulfates such as alkali metal alkyl sulfates such as sodium lauryl sulfate and sodium nonyl sulfate, and sulfated alcohols such as sulfated tridecyl alcohol. From about 0.01% to 5% of a surfactant can be included if advisable.

Deoxidizing, cleaning and/or brightening of titanium and its alloys is readily effected by contacting the metal surface with the bath. Although this can be done successfully with the bath at ambient temperature, it is usually more satisfactory to employ the bath at about 30-140° F. Contact times of about 30 seconds to 25 minutes are often adequate for effecting the desired treatment.

Following the deoxidation, cleaning and/or brightening, the titanium or titanium alloy surface can be rinsed with cold water and air dried.

The following examples are presented to illustrate the invention.

EXAMPLE 1

Unalloyed titanium, Ti75A, was treated in a solution consisting of 23.4% sulfuric acid, 37.9% nitric acid, 20.9% phosphoric acid, 5.9% ammonium bifluoride, 3.9% sodium silicofluoride and the remainder water. This treatment at 75° F., for 5 minutes produced a bright oxide free surface. Analysis revealed hydrogen absorption was in the order of 78 p.p.m.

EXAMPLE 2

Unalloyed titanium, heat treated at 1000° F., was treated as described in Example 1 for three minutes at 80° F. The treated titanium surface was bright, clean and oxide free. On analysis, the hydrogen absorption was found to be 69 p.p.m.

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EXAMPLE 3

Unalloyed titanium, Ti100A, contaminated with a molybdenum disulfide soil was treated as described in Example 1 for 10 minutes at 65° F., with gentle part agitation. After this treatment, the titanium surface was clean, bright and free of the lubricant molybdenum disulfide. Chemical analysis revealed the hydrogen absorption was 95 p.p.m.

EXAMPLE 4

Example 1 was repeated adding 0.5% sodium lauryl sulfate surfactant to the solution. After 1 minute at 78° F., the surface was clean and bright. Chemical analysis revealed hydrogen absorption was in the order of 66 p.p.m.

EXAMPLE 5

Unalloyed titanium, Ti-35A was treated in a solution consisting of 43.9% nitric acid, 28.9% sulfuric acid, 2.3% hydrofluoric acid and 24.9% phosphoric acid at 60° F. for 2 minutes. The treatment produced a clean bright surface. Chemical analysis revealed the hydrogen absorption to be 68 p.p.m.

EXAMPLE 6

Example 1 was repeated using 3.9% calcium fluoride in place of 3.9% sodium silicofluoride. This treatment produced a bright, clean oxide free surface.

EXAMPLE 7

Example 1 was repeated using the alloy Ti-8Al-1Mo-1V consisting of 8% aluminum, 1% molybdenum, 1% vanadium and the remainder titanium. Microscopic analysis of the bright clean surface revealed no titanium hydride formation. In contrast, treating the alloy with the standard bath of 1 part hydrofluoric acid and 10 parts nitric acid, used under the same conditions, produced a dark, rough surface showing titanium hydride formation sufficient to produce hydrogen embrittlement.

EXAMPLE 8

Example 1 was repeated using the alpha-beta alloy Ti-6Al-4V consisting of 6% aluminum, 4% vanadium and the remainder titanium. The heavy marking ink on the surface was removed and a bright clean surface was produced.

EXAMPLE 9

Example 6 was repeated with an annealed sheet of alpha-beta alloy Ti-8Mn containing 8% manganese as its principal alloying constituent. Black marking ink stencil was removed and a bright clean surface produced. Analysis revealed no titanium hydride formation.

EXAMPLE 10

Example 5 was repeated with a titanium alpha alloy forging RS-110C containing 5% aluminum and 2.5% tin as the principal alloying constituents. A clean bright smut-free surface was produced. By contrast, a nitric acid-hydrofluoric acid bath consisting of 5% hydrofluoric acid, 10% nitric acid and the remainder water at room temperature for 3 minutes produced a dark smutty surface.

EXAMPLE 11

Example 1 was repeated using a titanium alpha alloy sheet Ti-5Al-2.5Sn containing 5% aluminum and 2.5% tin as the principal alloying constituents. A bright clean surface having less than 0.0001 inch per side dimensional change was produced. By contrast, a conventional bath consisting of 20% nitric acid, 20% hydrochloric acid, 5% hydrofluoric acid and the remainder water produced a rough smutty surface with a dimensional change of 0.003 inch per side.

EXAMPLE 12

Unalloyed titanium alloy Ti65, having a nominal composition of 99% titanium was treated in a bath consisting

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of 55% sulfuric acid, 40% nitric acid and 5% ammonium bifluoride at 80° F., for 10 minutes. A green marking ink was removed and a bright, oxide free surface was produced. This deoxidized article retained its bright satin finish for several days. By contrast, the same alloy deoxidized in a bath consisting of 10% nitric acid, 1% hydrofluoric acid and the remainder water produced a rough surface with smut and failed to remove the marking ink. Standing overnight, the treated surface developed a bluish stain or discoloration.

EXAMPLE 13

Unalloyed titanium Ti65 was treated with the first bath described in Example 12, at 120° F. for 5 minutes, instead of 80° F. for 10 minutes. A bright smut free surface was produced. By contrast, a 10% nitric acid, 1% hydrofluoric acid bath at 120° F. produced deep etching, heavy gasing and a dark smut.

EXAMPLE 14

Titanium alloy RS-70 consisting nominally of 99% titanium was treated in a bath consisting of 25% sulfuric acid, 5% phosphoric acid, 40% nitric acid, 5% ammonium bifluoride and 25% water for 10 minutes at 75° F. A bright smut free surface was produced. By contrast, a bath consisting of 10% nitric acid, 1% hydrofluoric acid and the remainder water produced a rough dark surface under the same conditions.

EXAMPLE 15

Titanium alloy RS-70 was treated in the bath described in Example 14 at 120° F. for 5 minutes, instead of 75° F. for 10 minutes. A bright smut free surface was produced. By contrast, a bath of 10% nitric acid, 1% hydrochloric acid and the remainder water at 100° F. for 3 minutes produced a dark rough finish.

EXAMPLE 16

Titanium alloy Ti65 nominally consisting of 99 %titanium was treated in a bath consisting of 40% sulfuric acid, 20% phosphoric acid, 30% nitric acid, 5% water and 5% ammonium bifluoride at 120° F. for 10 minutes. A bright, smut free surface was produced. By contrast, a bath consisting of 30% nitric acid, 3% hydrofluoric acid and the remainder water at 120° F. for 5 minutes produced a dark rough surface.

The foregoing detailed description has been given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications will be obvious to those skilled in the art.

What is claimed is:

1. The method of deoxidizing and cleaning a titanium or titanium-based alloy surface which comprises contacting the surface with a bath consisting essentially of:

	Percent by wt.
Nitric acid	30-52
Sulfuric acid	10-75
Hydrofluoric acid	1-30
Phosphoric acid	0-25
Water	0-25

2. The method of claim 1 in which the bath is at a temperature of 30-140° F. in contact with the metal surface.

3. The method of claim 1 in which the bath and metal surface are in contact with each other for about 30 seconds to 25 minutes.

4. The method of claim 1 in which the maximum water content is 10%.

5. The method of claim 1 in which the minimum phosphoric acid content is 5%.

6. The method of claim 1 in which the bath contains about 0.01 to 5% by weight of a surfactant of the group consisting of metal alkyl sulfates or sulfated alcohols.

7. The method of deoxidizing and cleaning a titanium or titanium-based alloy surface which comprises contact-

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ing the surface with a bath consisting essentially of 10-50% by weight of sulfuric acid, 30-52% by weight of nitric acid, 0-25% by weight of phosphoric acid, 0-25% by weight of water and 1-30% by weight of ammonium bifluoride, calcium bifluoride, an alkali metal fluoride or an alkali metal fluoro boric acid.

8. The method of claim 7 in which the bath consists essentially of 23.4% sulfuric acid, 37.9% nitric acid, 20.9% phosphoric acid, 5.9% ammonium bifluoride, 3.9% sodium silicofluoride and the balance water.

9. The method of claim 7 in which the bath consists essentially of 43.9% nitric acid, 28.9% sulfuric acid, 2.3% hydrofluoric acid and 24.9% phosphoric acid.

10. The method of claim 7 in which the bath consists essentially of 55% sulfuric acid, 40% nitric acid and 5% ammonium bifluoride.

11. The method of claim 7 in which the bath consists essentially of 25% sulfuric acid, 5% phosphoric acid, 40% nitric acid, 5% ammonium bifluoride and 25% water.

12. The method of claim 7 in which the bath consists

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essentially of 40% sulfuric acid, 20% phosphoric acid, 30% nitric acid, 5% water and 5% ammonium bifluoride.

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