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(54) **Method of removing an alpha-case titanium layer from a beta-phase titanium alloy**

(57) A method of surface treating a metallic article (10) includes the step of chemically removing a surface layer (12) having titanium alloy alpha-phase precipitation to expose a core (14) having titanium alloy beta-phase.

In one example, the chemical removal includes using a first solution having nitric acid and hydrofluoric acid, and a second solution having nitric acid.

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Description

BACKGROUND OF THE INVENTION

[0001] This invention relates to chemically treating metallic articles and, more particularly, to chemically removing a surface layer to expose a core of the metallic article.

[0002] A metallic article is often manufactured from a raw work piece using a variety of steps. Typically, one or more of the steps includes heating the raw work piece to form it into a desired shape or to obtain desirable mechanical properties. One problem of using heat is that the heat may cause an undesirable surface layer to form on the raw work piece that diminishes the appearance or inhibits subsequent manufacturing steps. For example, heating a work piece made of titanium alloy may cause preferential alpha-phase precipitation at the surface of the work piece.

[0003] One proposed solution is to remove the surface layer in a removal step. However, conventional removal steps using a chemical treatment have been unsuccessful. For example, the treatment results in smut, such as oxides, intermetallics, or other impurities, on the surface that must subsequently be removed mechanically. Mechanical removal of the smut is labor intensive and often results in incomplete removal, which may subsequently be cause for rejection of the final article. Additionally, the treatment produces intergranular attack and thereby diminishes the mechanical integrity of the final article.

[0004] Therefore, what is needed is a treatment system and method for uniformly chemically removing the surface layer without need for mechanical removal. This invention addresses these needs while avoiding the shortcomings and drawbacks of the prior art.

SUMMARY OF THE INVENTION

[0005] An example method of surface treating a metallic article includes the step of chemically removing a surface layer having titanium alloy alpha-phase precipitation to expose a core having titanium alloy beta-phase. For example, the surface layer includes a higher volume fraction of titanium alloy alpha-phase and the core includes either single phase beta titanium or alpha precipitates in a beta titanium matrix.

[0006] An example solution system for chemically removing the surface layer includes a first solution having nitric acid and hydrofluoric acid; and a second solution having nitric acid. The first solution is to chemically remove a thin layer of titanium. The second solution is to prevent smut formation.

[0007] In one example, the first solution includes about 45 vol% - 50 vol% nitric acid that is at least 42° Baume (e.g., 70wt% or 1.42 g/cc reagent grade nitric acid), hydrofluoric acid in the range of from about 5.6-8.4 vol% at 70% grade to about 8-12% at 49% grade, and a remainder of water. This solution non-selectively removes the surface layer with no or minimal smut formation. The sec-

ond solution includes about 50 vol% - 60 vol% nitric acid that is at least 42° Baume and a remainder of water. This solution reacts with the surface to remove any created smut and prevent further smut formation in the final rinse.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The various features and advantages of this invention will become apparent to those skilled in the art from the following detailed description of the currently preferred embodiment. The drawing that accompanies the detailed description can be briefly described as follows.

[0009] Figure 1 illustrates selected portions of a work piece having a casing and a core, where the casing is chemically removed to expose the core.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0010] Figure 1 illustrates selected portions of an example metallic work piece 10, such as a sheet, stamping, forging, casting, or other type of pre-manufactured article. For example, the work piece 10 is used to manufacture an aircraft engine nozzle bracket, and aircraft nozzle honeycomb structure, or other type of article. The work piece 10 was previously heated in a known process, such as a vacuum heat treatment process, hot forming process, or other process that utilizes heat. The heating resulted in formation of a casing 12 (i.e., a surface layer) on a core 14 of the work piece 10. The casing 12 is uniformly chemically removed in a treatment process to expose the core 14 of treated work piece 10', as will be described below.

[0011] The work piece 10 is made of a titanium alloy. For example, the titanium alloy includes a nominal composition having about 14 wt% - 16 wt% molybdenum, about 2.5 wt% - 3.5 wt% aluminum, about 2.4 wt% - 3.2 wt% niobium, about 0.15 wt% - 0.25 wt% silicon, and a remainder titanium. The nominal composition also includes trace amounts of other elements. For example, the nominal composition also includes about 0.4 wt% iron, 0.05 wt% carbon, 0.1 wt% copper, 0.11 wt% - 0.17wt% oxygen, 0.05 wt% nitrogen, 150 ppm hydrogen, and 50ppm yttrium. In some examples, the trace amounts of the other elements are essential to obtaining desirable properties of the titanium alloy, such as processing properties and mechanical properties.

[0012] For the above example titanium alloy composition the casing 12 includes alpha-phase precipitation caused by the prior heating process, and the core 14 includes beta-phase titanium. For example, the casing 12 includes a higher volume fraction of titanium alloy alpha-phase and the core 14 includes either single phase beta titanium or alpha precipitates in a beta titanium matrix. If not removed, the alpha-phase precipitation in the casing 12 may compromise the mechanical integrity of an article produced from the work piece 10 or inhibit sub-

sequent manufacturing steps, such as forming or welding. Other titanium alloy compositions may also form alpha-phase casings.

[0013] The casing 12 is removed in a treatment process that utilizes a first solution that includes nitric acid and hydrofluoric acid, and a second solution that includes nitric acid. The first solution chemically removes the casing 12 to thereby expose the core 14 with minimal or no smut formation. The first solution reacts with the casing 12 to remove any pre-existing smut, and the second solution prevents further smut formation before a final rinse in water. Using the two solutions provides the benefit of removing the casing 12 with little or no hydrogen diffusion into the titanium alloy, without intergranular attack (i.e., selective oxidation between metallic microstructural grains of the work piece 10), and without smut remaining on the core 14.

[0014] In a first step, the treatment process includes wetting the casing 12 with the first solution, such as by immersing the work piece 10 in a container having the first solution. The first step is conducted at a temperature of about 75°F (24°C) for about one minute and thirty seconds, depending on the thickness of the casing 12 to be removed, for example. Given this description, one of ordinary skill in the art will, recognize that a higher temperature or a lower temperature than disclosed may be used.

[0015] In a second step, the work piece 10 is wetted with the second solution, such as by immersing the work piece 10 in a container having the second solution. The second step is conducted at a temperature of about 55°F - 120°F (13-49°C) for about thirty seconds, for example. Given this description, one of ordinary skill in the art will recognize that a higher temperature or a lower temperature than the disclosed range may be used.

[0016] The work piece 10 is maintained in a "wet" state between the steps of wetting with the first solution and wetting with the second solution. For example, the work piece 10 is moved from the first solution directly into the second solution within a short time, without rinsing. This prevents residual smut from setting and permanently bonding to the core 14, which would require mechanical removal. A short dwell time is permitted between the first solution and the second solution to allow drainage of the first solution off of the work piece 10. After the second solution, the work piece 10 is then rinsed in water.

[0017] In one example, the first solution and the second solution contain predetermined compositions to uniformly remove the casing 12. The following example solutions are described with reference to acid concentrations that are expressed in terms of density, specific gravity, or weight percent. However, it is to be understood that these conventions of expression may be converted into other conventions of expression.

[0018] The first solution includes about 45 vol% - 50 vol% nitric acid that is at least 42° Baume (e.g., 70wt% or 1.42 g/cc reagent grade nitric acid), about 5.6 vol% - 8.4 vol% hydrofluoric acid that is about 70% grade, and a remainder of water. The term "grade" as used in this

description refers to the concentration of the acid wherein the percentage is the weight percent of the acid in an "as received" technical or reagent acid solution. The second solution includes about 50 vol% - 60 vol% nitric acid that is at least 42° Baume and a remainder of water. Alternatively, the first solution includes about 45 vol% - 50 vol% of the nitric acid, about 8 vol% - 12 vol% hydrofluoric acid that is 49% grade, and a remainder of water. The term "about" as used in this description relative to percentages or compositions refers to possible variation in the compositional percentages, such as normally accepted variations or tolerances in the art. It is to be understood that other equivalent solution compositions than disclosed may be determined based on the purities of the acids.

[0019] Using the first solution and the second solution in two steps provides the benefits of removing the casing 12 with little or no hydrogen diffusion into the titanium alloy, little or no intergranular attack, and little or no smut remaining on the core 14. For example, using a more aggressive solution than disclosed (e.g., using stronger acids, or using greater volume percentages of the acids) to remove the casing 12 in a single step may result in non-uniform removal, intergranular attack, and promote hydrogen diffusion. Conversely, using a less aggressive solution (e.g., using weaker acids, or using lower volume percentages of the acids) to remove the casing 12 may result in incomplete removal of the casing 12. The disclosed treatment utilizing two steps and two different solutions avoids these drawbacks by removing the casing 12 in a controlled manner in the first step, and subsequently preventing further smut formation in the second step.

[0020] Although a preferred embodiment of this invention has been disclosed, a worker of ordinary skill in this art would recognize that certain modifications would come within the scope of this invention. For that reason, the following claims should be studied to determine the true scope and content of this invention.

Claims

1. A method of surface treating a metallic article, comprising the step:
chemically removing a surface layer having titanium alloy alpha-phase precipitation to expose a core having titanium alloy beta-phase.
2. The method as recited in claim 1, including chemically removing the surface layer using a first solution having nitric acid and hydrofluoric acid, and a second solution having nitric acid.
3. The method as recited in claim 1 or 2, including chemically removing the surface layer using a solution having unequal concentrations of nitric acid and hydrofluoric acid.

4. The method as recited in claim 1, 2 or 3, including wetting the surface layer with a first solution in a first step to remove at least a portion of the surface layer and expose the core, then wetting any remaining surface layer and the core with a second solution in a second step, and maintaining the surface layer and the core in a wet state between the first step and the second step. 5
5. The method as recited in claim 4, including performing the first step at a temperature of about 75° F (24°C) and performing the second step at a temperature of about 55° F - 120° F (13-49°C). 10
6. The method as recited in claim 4 or 5, wherein the first solution includes about 45 vol% - 50 vol% nitric acid that is at least 42° Baume, hydrofluoric acid in the range of from about 5.6-8.4 vol% at 70% grade to about 8-12% at 49% grade, and a remainder of water, and the second solution includes about 50 vol% - 60 vol% nitric acid that is at least 42° Baume, and a remainder of water. 15 20
7. The method as recited in any preceding claim, including wetting the surface layer with a first solution having about 45 vol% - 50 vol% nitric acid that is at least 42° Baume, about 8 vol% - 12 vol% hydrofluoric acid that is 49% grade, and a remainder of water. 25
8. The method as recited in any preceding claim, including wetting the surface layer with a first solution having about 45 vol% - 50 vol% nitric acid that is at least 42° Baume, about 5.6 vol% - 8.4 vol% hydrofluoric acid that is about 70% grade, and a remainder of water. 30 35
9. The method as recited in any preceding claim, including forming the surface layer and the core from a titanium alloy having a nominal composition that includes about 14 wt% - 16 wt% molybdenum, about 2.5 wt% - 3.5 wt% aluminum, about 2.4 wt% - 3.2 wt% niobium, about 0.15 wt% - 0.25 wt% silicon, and a remainder titanium. 40
10. The method as recited in any preceding claim, including uniformly removing the surface layer without hydrogen embrittlement and intergranular attack of the titanium alloy beta-phase. 45
11. A solution system for chemically removing a surface layer having titanium alloy alpha-phase precipitation to expose a core having titanium alloy beta-phase of a metallic article, comprising: 50
 - a first solution that includes nitric acid and hydrofluoric acid; and 55
 - a second solution that includes nitric acid, where the first solution and the second solution cooperate to remove the surface layer without smut formation to expose the core.
12. The solution system as recited in claim 11, wherein the first solution includes about 45 vol% - 50 vol% nitric acid that is at least 42° Baume, about 8 vol% - 12 vol% hydrofluoric acid that is about 49% grade, and a remainder of water.
13. The solution system as recited in claim 11, wherein the first solution includes about 45 vol% - 50 vol% nitric acid that is at least 42° Baume, about 5.6 vol% - 8.4 vol% hydrofluoric acid that is about 70% grade, and a remainder of water.
14. The solution system as recited in claim 11, 12 or 13, wherein the second solution includes about 50 vol% - 60 vol% nitric acid that is at least 42° Baume and a remainder of water.

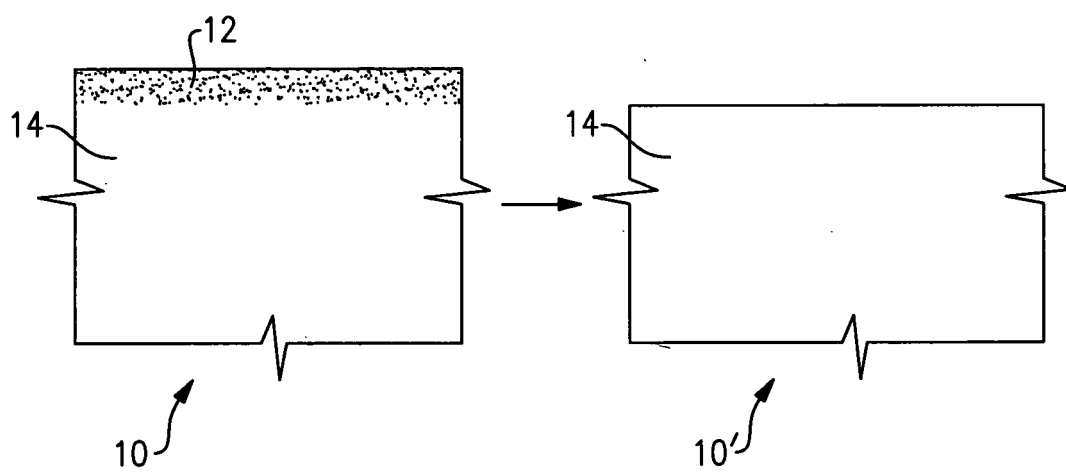


FIG.1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 08 25 0140

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	* page 3, paragraph 16 - page 4, paragraph 21 *		
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 15 April 2008	Examiner Handrea-Haller, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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