METHODS FOR CLEANING SUBSTRATES

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ABSTRACT

A method for removing sand particles from a substrate is described. The method includes the step of treating the substrate with an acid solution comprising H₃AF₅, wherein A is selected from the group consisting of Si, Ge, Ti, Zr, Al, and Ga; and wherein H₃AF₅ is present at a concentration in the range from about 5 weight percent to about 40 weight percent.
FIG. 1

Treating the substrate with an $H_x AF_6$ acid solution having a concentration in the range from about 5 weight percent to about 40 weight percent

Rinsing the substrate with water prior to treatment with the wetting agent

Treating the substrate with a wetting agent

Rinsing the substrate with water after treatment with the $H_x AF_6$ acid solution

FIG. 2
METHODS FOR CLEANING SUBSTRATES

BACKGROUND

[0001] The invention relates to cleaning substrate surfaces, and more particularly to the removal of sand particles from turbine engine surfaces, such as airfoils.

[0002] Sand fouling has recently emerged as a key factor significantly degrading performance in turbine components. For example, aircraft engines flying domestic routes often experience significant sand fouling due to heavy sand intake during flight idle, take-off, and landing. It has been determined that the primary mechanism for fouling is the increased roughness of compressor blades due to sand ingestion. Specifically, this increased roughness results from the formation of micropits due to particle impact. Subsequently, sand particles with sizes less than 10 microns accumulate in these pits to form the fouling layers. High temperatures in the downstream stages of the compressor result in baking of the sand particles, which increases the airfoil-sand adhesion. Consequently, water wash treatments, which are frequently used to clean the turbine components, are often not successful in removing the accumulated sand particles.

[0003] Accordingly, there remains a need in the art for a method to remove sand particles and sand-fouling layers from turbine engine components, for example, while having minimal or no effect on the airfoil surface underneath, or on any protective coatings on such a surface.

BRIEF DESCRIPTION

[0004] A primary embodiment of this invention is directed to a method for removing sand particles from a substrate. The method includes the step of treating the substrate with an acid solution comprising $H_{2}A_{2}$ wherein A is selected from the group consisting of Si, Ge, Ti, Zr, Al, and Ga; and wherein $H_{2}A_{2}$ is present at a concentration in the range from about 5 weight percent to about 40 weight percent.

DRAWINGS

[0005] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawings, wherein:

[0006] FIG. 1 is a cross sectional view of a portion of a turbine engine component; and

[0007] FIG. 2 illustrates a method for removing sand particles from a substrate.

DETAILED DESCRIPTION

[0008] Embodiments of the present invention relate to a method for removing sand particles from a substrate. The method includes the step of treating the substrate with an $H_{2}A_{2}$ acid solution having a concentration in the range from about 5 weight percent to about 40 weight percent. As will be described in detail below, typically, milder processing conditions, such as lower concentrations of $H_{2}A_{2}$ acid in the aqueous solution, lower temperatures, and shorter treatment times, are preferred to remove the sand particles from the substrate without causing substantial damage to the underlying coating.

[0009] As used herein, “sand” can generally be defined as a naturally occurring granular material composed of finely divided rock and mineral particles. The most common constituent of sand is often silica (silicon dioxide, or $SiO_2$), typically in the form of quartz. However, the composition of sand can vary widely. In some embodiments, the term “sand” is meant to specifically refer to “CMAS” materials, which are materials based on a mixture of calcia, magnesia, alumina and silica. The particle size of the sand particles is usually submicron. In one embodiment, the average particle size of the sand particles is in a range from about 0.5 micron to about 10 microns.

[0010] It has been found that sand fouling often takes place in aircraft engines flying in geographical locations that have desert areas. Airfoils in the compressor sections of such aircraft engines show significant accumulations of fine sand. Surfaces of the turbine components, such as blades, can accumulate sand, resulting in reduced air flow, and a significant increase in specific fuel consumption (SFC). The accumulation of sand exists in both particulate form, as well as glassy layers.

[0011] Sand particles with sizes less than 10 microns accumulate on the airfoils of the compressor. High temperatures in the downstream stages of the compressor result in baking of the sand particles, which increases the airfoil-sand adhesion. The baking of the sand particles forms a cement-like layer of the sand particles on the airfoil. Consequently, a water wash that is frequently effective in cleaning the turbine components is often not successful in removing the accumulated sand particles.

[0012] The process includes treating the substrate with a mild aqueous solution of $H_{2}A_{2}$ acid at a selected temperature for a selected period of time, and then rinsing the turbine engine component in an aqueous medium. As used herein, the term “mild aqueous solution of $H_{2}A_{2}$ acid” refers to an aqueous solution of $H_{2}A_{2}$ acid that is substantially free of strong acids, such as phosphoric acid. The process of this invention employs fluosilicic acid or its derivatives, having the formula $H_{2}A_{2}.$ In this formula, A is selected from the group consisting of Si, Ge, Ti, Zr, Al, and Ga. The subscript “x” is a quantity from 1 to 6, and more typically, from 1 to 3. Materials of this type are available commercially, or can be prepared without undue effort. The preferred acid is $H_{2}SiF_{x}$. It is referred to by various names, such as “hydrofluorsilicic acid”, “fluoro silicic acid”, “fluosilicic acid”, “hexafluoro silicic acid”, and “HFS.” Materials of this type are described in U.S. Pat. No. 6,599,416 (Kool et al.), which is incorporated herein by reference.

[0013] As described herein, the use of the $H_{2}A_{2}$ compound provides considerable advantages for the sand-removal process. In many instances, such a process is very suitable, e.g., when there is a need for high removal rates. Surprisingly it has been found that by employing the aqueous solution of fluosilicic acid and/or the derivatives of the fluosilicic acid, the sand particles can be removed from the surface of the airfoils without damaging the underlying metal alloy surface, or any intervening coating, as described below.

[0014] Precursors to the $H_{2}A_{2}$ acid may also be used. As used herein, a “precursor” refers to any compound or group of compounds which can be combined to form the acid or its dianion $A_{2}^{2-}$, or which can be transformed into the acid or its dianion under reactive conditions, e.g. the action of heat, agitation, catalysts, and the like. Thus, the acid can be formed, in situ, in a reaction vessel, for example.

[0015] As one illustration, the precursor may sometimes be a metal salt, inorganic salt, or an organic salt in which the dianion is ionically bound. Non-limiting examples include
salts of Ag, Na, Ni, and K, as well as organic salts, such as a quaternary ammonium salt. Dissociation of the salts in an aqueous solution often yields the acid. In the case of H$_2$SiF$_6$, a convenient salt which can be employed is Na$_2$SiF$_6$.

**[0016]** Those skilled in the art are familiar with the use of compounds which cause the formation of H$_2$AF$_6$ within an aqueous composition. For example, H$_2$SiF$_6$ can be formed in situ by the reaction of a silicon-containing compound with a fluorine-containing compound. An exemplary silicon-containing compound is SiO$_2$, while an exemplary fluorine-containing compound is hydrofluoric acid (i.e., aqueous hydrogen fluoride).

**[0017]** Referring now to FIG. 1, there is depicted a cross-sectional view of a portion of an exemplary turbine engine component generally designated by reference numeral 10. The turbine engine component is an airfoil in this instance. The component 10 includes a concave surface 12 and a convex surface 14. The sand particles can be removed from either surface, or from passageways, indentations, or various cavities in those surfaces.

**[0018]** The type of turbine engine component is not intended to be limited, and can vary among a shroud, blade, nozzle or vane, diaphragm component, seal component, valve stem, nozzle box, nozzle plate, or the like. The terms “blade” and “bucket” can be used interchangeably. Generally a blade is a rotating airfoil of an aircraft turbine engine, and a bucket is a rotating airfoil of a land-based power generation turbine engine. Also the term “nozzle”; which generally refers to a stationary vane in a steam or gas turbine, can be used interchangeably with the term “vane”.

**[0019]** The turbine engine component, e.g., substrate 12, may generally comprise a variety of metallic alloys, e.g., steel or alloys thereof; or titanium alloys (e.g., Ti-6Al-4V). In some preferred embodiments, the turbine engine component is formed from superalloys, which can be used at high temperatures, often in excess of about 0.7 of the absolute melting temperature. The superalloys are based on nickel, cobalt, iron, or some combination thereof. Many are described in the above-referenced patent to Kool et al.

**[0020]** As those skilled in the art understand, turbine engine components are most often provided with one or more protective coatings. Therefore, the present invention contemplate the removal of sand from the surfaces of these coatings, as well as the removal of sand from an uncoated substrate. Many different types of protective coatings are typically used, e.g., diffusion coatings or overlay coatings, as described in the Kool patent. Moreover, overlay coatings like the “MerAl (X)” materials (considered to be metallic coatings) may be coated by thermal barrier coatings (TBC’s). Non-limiting examples of the latter include ceramic coatings such as yttria-stabilized zirconia. Some of the TBC’s are described in U.S. Pat. No. 6,921,586 (Zhao et al), which is incorporated herein by reference. The thickness of the protective coating(s) will depend on various factors, such as the type of article being coated, the composition of the substrate, and the environmental conditions to which the article will be subjected.

**[0021]** FIG. 2 is an illustrative flow chart for an exemplary, non-limiting method of removing sand particles from a substrate. At block 20, the substrate is treated with an H$_2$AF$_6$ acid solution having a concentration in the range from about 5 weight percent to about 40 weight percent. For example, the substrate can be treated by at least partially immersing the substrate in a bath of the H$_2$AF$_6$ acid solution. The bath may be mechanically agitated during treatment.

**[0022]** The preferred level of H$_2$AF$_6$ acid which is employed will depend on various factors. They include the type and amount of sand being removed; the location of the sand on a substrate; the type of substrate; the thermal history of the substrate and sand material (e.g., how tightly adherent the sand is to the substrate); the time and temperature used for treatment; and the stability of the acid in the treatment solution.

**[0023]** As a general rule, the H$_2$AF$_6$ acid is present in a treatment composition at a level in the range of about 5 weight percent to about 40 weight percent. Usually, the level is in the range of about 10 weight percent to about 30 weight percent. In the case of H$_2$SiF$_6$, a preferred concentration (here in molar units) is about 0.2M to about 2.2M, Adjustment of the amount of H$_2$AF$_6$ acid, and of other components described below, can readily be made by considering stoichiometric parameters, and by observing the effect of particular compositions on sand-removal from the substrate.

**[0024]** The temperature of the H$_2$AF$_6$ acid solution can usually be maintained up to about 100°C. In some specific embodiments, the temperature is maintained below about 50°C. In some especially preferred embodiments, the temperature range is from about 50°C to about 80°C. Typically, ambient pressure is suitable while treating the substrate with the H$_2$AF$_6$ acid.

**[0025]** The time required for removing the sand particles (i.e., the immersion time within the aqueous composition) may vary considerably. Factors which influence the selection of an appropriate time include the particular composition of the sand-based material being removed; as well as its density and thickness. The time may also vary with the temperature of the H$_2$AF$_6$ acid solution. For example, for a higher temprature of the fluosilicic acid solution, the treatment time may be shorter, and vice versa. Usually, the substrate is at least partially immersed in a bath of the wetting agent for treatment, for a period of time in a range from about 1 minute to about 36 hours, and preferably, from about 5 minutes to about 8 hours. In some instances, an especially preferred immersion time is in the range of about 10 minutes to about 2 hours. The immersion time for the substrate in the bath usually depends on the temperature of the bath and the type of protective coating on the substrate. For example, longer immersion times are acceptable for substrates having protective coatings, such as MCRAF and TBC, because of the total nature of such protective coatings towards the H$_2$AF$_6$ acid solution. Accordingly, in the case of such protective coatings, the underlying substrate remains mostly unharmed—even after prolonged immersion of the substrate in the H$_2$AF$_6$ acid solution.

**[0026]** The aqueous composition used for the present invention may include various other additives that serve a variety of functions. Non-limiting examples of these additives are inhibitors, dispersants, surfactants, chelating agents, wetting agents, deflocculants, stabilizers, anti-settling agents, and anti-foam agents. Those of ordinary skill in the art are familiar with specific types of such additives, and with effective levels for their use. An example of an inhibitor for the composition is a relatively weak acid like acetic acid, mentioned above. Such a material tends to lower the activity of the primary acid in the composition. This is desirable in some instances, e.g., to decrease the possibility of any damage to the underlying coating(s) or substrate surface.

**[0027]** The aqueous solution of the H$_2$AF$_6$ acid of the present invention is not only effective at removing the deposit containing the sand particles on the substrate, but is also
usually benign to the underlying metal of the airfoil, and to any of the protective coatings. In other words, with proper monitoring of the treatment process, the underlying surfaces are not adversely affected.

[0028] Optionally, as illustrated in block 22, the substrate is treated with a wetting agent, such as a surfactant, prior to treatment with the $\text{H}_3\text{AF}_6$, acid solution. The treatment with the wetting agent can facilitate better interaction between the sand particles and the $\text{H}_3\text{AF}_6$ acid to facilitate removal of the coating.

[0029] Non-limiting examples of suitable surfactants include detergents, acid stable surfactants, non-acid stable surfactants, or combinations thereof. An example of an acid-stable surfactant may include polyethylene oxide, which is commercially available as Triton x-100™ (manufactured by Research Chemicals Limited [CAS No. 9002-93-1]). An example of non-acid stable surfactant includes trisodium phosphate, which is commercially available as Alconox TSPT™

[0030] Optionally, as illustrated in block 24, the substrate is rinsed with water, prior to treatment with the wetting agent. Rinsing the substrate with water removes any dirt particles or loose sand particles from the surface of the substrate.

[0031] Optionally, at block 26, the substrate may be rinsed with water or another liquid after treatment with the $\text{H}_3\text{AF}_6$ acid solution, to remove any debris or undesired chemicals from the surface of the substrate. In one embodiment, rinsing may be done by applying a water jet.

[0032] In addition to (or in lieu of) the rinsing step 26, treatment of the sand-fouled surface may also include at least one subsequent step, to remove any remaining residue—sand or otherwise. As described in the referenced Kool patent, a post-cleaning or “de-smutting” operation can be undertaken. It may be in the form of an abrasion step which minimizes damage to the substrate or protective coatings. As one example, a grit-blasting can be carried out by directing a pressurized air stream containing aluminum oxide particles across the surface. The air pressure is usually less than about 100 psi. The grit-blasting is carried out for a time period sufficient to remove any residual material. Other known techniques for abrading the surface may be used in lieu of grit-blasting. Many of these are described in U.S. Pat. No. 5,976,265, incorporated herein by reference. For example, the surface can be manually scrubbed with a fiber pad, e.g. a pad with polymeric, metallic, or ceramic fibers. Alternatively, the surface can be polished with a flexible wheel or belt in which alumina or silicon carbide particles have been embedded. Liquid abrasive materials may alternatively be used on the wheels or belts. These alternative techniques would be controlled in a manner that maintained a contact force against the surface that was no greater than the force used in the grit-blasting technique discussed above.

[0033] Other techniques (or combinations of techniques) could be employed in place of abrasion, to remove any residual material. Examples include tumbling of the article (e.g., water-tumbling), or laser ablation of its surface. Alternatively, the residual material could be scraped off the surface. As still another alternative, sound waves (e.g., ultrasonic) could be directed against the surface, causing vibrations which can shake loose the degraded material. For each of these alternative techniques, those skilled in the art would be familiar with operating adjustments which are made to control the relevant force applied against the surface of the article (as in the case of the abrasion technique), to minimize damage to the substrate or overlying protective coatings. The article is sometimes rinsed after this step, e.g., using water or a combination of water and a wetting agent.

[0034] The bath may be mechanically agitated during this residue-removal step. For example, the bath may be mechanically agitated (as described previously) while treating the substrate in the $\text{H}_3\text{AF}_6$ acid solution. In one embodiment, the bath may be mechanically agitated while treating the substrate with a wetting agent.

[0035] As mentioned previously, the present invention can also be used to efficiently remove sand from any internal region or cavity in an article, e.g., indentations, hollow regions, passages, or holes. In the case of a turbine airfoil, the internal region is often in the form of radial cooling holes or serpentine passageways. The process of the present technique produces a synergistic effect, and results in an extremely effective cleaning method for airfoils and other turbine engine parts which contain tightly-adherent sand particles.

[0036] While only certain features of the invention have been illustrated and described herein, many modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all such modifications and changes as fall within the scope of the invention.

1. A method for removing sand particles from a substrate, comprising the step of treating the substrate with an acid solution comprising $\text{H}_3\text{AF}_6$, wherein A is selected from the group consisting of Si, Ge, Ti, Zr, Al, and Ga; and wherein $\text{H}_3\text{AF}_6$ is present at a concentration in the range from about 5 weight percent to about 40 weight percent.

2. The method of claim 1, wherein the $\text{H}_3\text{AF}_6$ acid solution is an aqueous solution.

3. The method of claim 1, wherein the concentration of the $\text{H}_3\text{AF}_6$ acid is in a range from about 10 weight percent to about 30 weight percent.

4. The method of claim 2, wherein the $\text{H}_3\text{AF}_6$ acid solution is maintained at a temperature no greater than about 100°C during treatment.

5. The method of claim 1, wherein the substrate is treated with a wetting agent, prior to treatment with the fluosilicic acid solution.

6. The method of claim 5, wherein the wetting agent comprises a surfactant.

7. The method of claim 5, further comprising rinsing the substrate with water prior to treatment with the wetting agent.

8. The method of claim 1, further comprising rinsing the substrate with water after treatment with the $\text{H}_3\text{AF}_6$ acid solution.

9. The method of claim 1, wherein the treatment with the $\text{H}_3\text{AF}_6$ acid solution is carried out for a time period in a range from about 10 minutes to about 2 hours.

10. The method of claim 1, wherein treatment with the $\text{H}_3\text{AF}_6$ acid solution is carried out at a temperature in a range from about 20 degrees Celsius to about 100 degrees Celsius.

11. The method of claim 10, wherein the temperature is in a range from about 50 degrees Celsius to about 80 degrees Celsius.

12. The method of claim 1, wherein the substrate is at least partially immersed in a bath of the $\text{H}_3\text{AF}_6$ acid solution during treatment.

13. The method of claim 12, wherein the bath is mechanically agitated during treatment.
14. The method of claim 5, wherein the substrate is at least partially immersed in a bath of the wetting agent for treatment, for a period of time in a range from about 10 minutes to about 2 hours.

15. The method of claim 1, wherein the substrate is a section of a turbine engine component.

16. The method of claim 15, wherein the turbine engine component is an airfoil.

17. The method of claim 1, wherein the sand particles have an average particle size in the range of about 0.5 micron to about 10 microns.

18. The method of claim 15, wherein the turbine engine component is formed of a material which comprises a steel, a superalloy, a titanium alloy, or a combination thereof.

19. The method of claim 18, wherein the turbine engine component comprises a shroud, a bucket, a blade, a nozzle, a vane, a diaphragm component, a seal component, or a valve stem.

20. The method of claim 18, wherein the coating comprises CMAS (calcium-magnesia-alumina-silicate).

21. The method of claim 1, wherein at least one protective coating is disposed over the substrate; and the sand particles being removed are those which adhere to a surface of the protective coating.

22. The method of claim 21, wherein the protective coating comprises a diffusion coating or an overlay coating.

23. The method of claim 21, wherein the protective coating comprises an underlying metallic coating, and an overlying ceramic barrier coating.

24. A method for removing sand particles from a surface of at least one protective coating disposed on a superalloy substrate, comprising the step of treating the coated substrate with an acid solution comprising H₄AF₆, wherein A is selected from the group consisting of Si, Ge, Ti, Zr, Al, and Ga; and wherein H₄AF₆ is present at a concentration in the range from about 5 weight percent to about 40 weight percent.

25. The method of claim 24, wherein the protective coating is a thermal barrier coating.

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