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(54) **Method for preparing strain tolerant coatings from a green material**

(57) Methods for coating substrates arc provided. A method for coating a substrate comprises disposing a coating on a substrate, where the coating exhibits a first strain tolerance; and treating the coating to enhance the strain tolerance of the coating to a second strain tolerance. The second strain tolerance is more strain tolerant strain than the first strain tolerance. Further, the step of treating comprises at least one of mechanical treating, chemically treating, thermally treating, and combinations thereof.



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## Description

BACKGROUND OF THE INVENTION

**[0001]** The invention relates to methods, and the articles produced thereby, for preparing strain tolerant coatings. In particular, the invention relates to methods, and the articles produced thereby, for preparing strain tolerant coatings, where the coatings have a "green" state. Moreover, the invention relates to methods, and the articles produced thereby, for preparing strain tolerant coatings, which have a green state, where the coatings can be used for thermal barrier coatings.

**[0002]** Metals can oxidize, corrode, and become brittle if they are exposed to relatively high temperatures (i.e., greater than or equal to about 700°C) and especially if they are present in oxidative environments. Environments, such as these with temperatures and oxidizing environments, can be produced in gas turbines, such as gas turbines used for power generation applications. It is recognized in the power generation technology area that a thermal barrier coating (TBC), when applied to metal turbine components, can reduce the effects that high-temperature, oxidative environments have on the metal components.

**[0003]** Thermal barrier coatings typically comprise at least two components, a metallic bond coating and a ceramic coating. The metallic bond coating can contain oxidation protection and or corrosion protection materials, such as, but not limited to, at least one of aluminum and chromium. For example, the metallic bond coating can comprise chromium, aluminum, yttrium, or combinations of the forgoing, such as MCrAlY where M is nickel, cobalt, or iron (U.S. Patent No. 4,034,142 to Hecht, and U.S. Patent No. 4,585,481 to Gupta et al. describe some coating materials). Metallic bond coatings can be applied by thermal spraying techniques (Gupta et al. describe the coating materials comprising silicon and hafnium particles being applied by plasma spraying).

**[0004]** Moreover, a ceramic coating of a thermal barrier coating can be applied to the metallic bond coating. The method of applying include known methods, such as, but not limited to, air plasma spray (APS) or electron beam physical vapor deposition (EB-PVD).

**[0005]** A "green" state, as defined in this application, refers to the state in which the chemistry/properties of the coating, regardless of the number of components and layers, has been applied, is "un-finished" or not finally treated to be in final desired form with the desired chemistry/properties, but requires subsequent active processing to achieve the desired chemistry/properties. The subsequent active processing is conducted to achieve the final desired properties of the resultant coating. Subsequent processing is defined herein to comprise further steps that are desired to "finish" the coating.

**[0006]** All coatings, which have a green state, are vulnerable when in this un-finished or "green" state. When in the green state, these coatings may not possess the same properties as they do in their final state. These properties include optical and/or mechanical and/or chemical and/or thermal properties of the coating. It is this vulnerability that allows the coatings to be altered, sometimes altered permanently, by conditions that would not generally affect the coatings if the coatings were in their final state. If a TBC is attempted to be applied using a material that exhibits a green state, the final desired properties are not achieved.

**[0007]** Traditional coating methods to obtain a strain tolerant TBC can be very expensive and/or very difficult to produce. Coatings produced through the EB-PVD method produce a structure, which is very strain tolerant, yet the process is expensive and can be impractical, especially for components that have large or unique geometries. Further, coatings with strain tolerance are modified either in-situ or after final processing, which is both expensive and difficult. Moreover, known coating methods to obtain a strain tolerant TBC do not address the need to process green coatings creating strain tolerance.

**[0008]** Therefore, a need for a method to apply a strain tolerant TBC to metal turbine components and other structures that could benefit from the presence of a TBC exists. Further, a need to provide coating method to obtain a strain tolerant TBC that processes green coatings to isolate creating strain tolerance in the coating is needed.

SUMMARY OF THE INVENTION

**[0009]** A method for coating a substrate, as embodied by the invention, comprises disposing a coating on a substrate, where the coating exhibits a first strain tolerance; and treating the coating to enhance the strain tolerance of the coating to a second strain tolerance. The second strain tolerance is more strain tolerant strain than the first strain tolerance. Further, the step of treating comprises at least one of mechanical treating, chemically treating, thermally treating, and combinations thereof.

**[0010]** The above described and other features are exemplified by the following detailed description.

DETAILED DESCRIPTION

**[0011]** Disclosed herein are processes for producing strain tolerant coatings from a first coating material that exhibits a green or non-final state. The term green has been referred to as the state of a material before being treated, such as treated by heat, mechanical means, and/or chemical means. A common, but not limiting, heat treating for a green material is sintering.

**[0012]** The coating from a material that exhibits a green state, as embodied by the invention, could be any of the following coatings, however, not limited to these coatings: sol-gel, slurry, and paste. The methods of forming the coating from a material that exhibits a green state includes, but is not limited to, suspension methods, painting methods, dipping processes, spraying, and deposition methods. Electro-plating processing is another method for forming the coating from a material that exhibits a green state, as embodied by the invention.

**[0013]** The spraying can comprise most conventional spray processes, such as, but not limited to, thermal spray, APS, VPS, LPPS, HVOF, Flame, Arc Wire, Detonation, and cold spraying methods. Further, the deposition methods, as embodied by the invention, can comprise physical vapor deposition, as well as evaporative, sputtering, and pulsed laser deposition processes.

**[0014]** Furthermore, as embodied by the invention, the deposition can comprise chemical vapor deposition (CVD). The chemical vapor deposition, as embodied by the invention, can include atomic layer, aerosol assisted, hot wire assisted, microwave plasma assisted chemical vapor deposition processing.

**[0015]** Generally, the method of preparing the strain tolerant thermal barrier coating on a metal substrate comprises the following: disposing a green coating on a metal substrate; and treating the green coating to form a strain tolerant coating. The treating, as embodied by the invention, comprises at least one of mechanical treating, chemically treating, thermally treating, and combinations thereof. The resulting coating provides oxidation protection to the metallic bond coating and the substrate.

**[0016]** In the process, as embodied by the invention, the treating of the coating enhances the strain tolerance of the green coating, from a first strain tolerance to a second strain tolerance. Here, the second strain tolerance being more strain tolerant strain than the first strain tolerance.

**[0017]** In one embodiment, to minimize the potential of cracks forming in the coating, the first/green coating can undergo a hot-isostatic pressing process prior to, or during, the sintering step. Such a step allows for thicker coatings to be dried and sintered without uncontrolled or undesired cracking.

**[0018]** The step of treating, as embodied by the invention, can comprise mechanical treatment. The mechanical treatment comprises at least one of scratching; imprinting; screening; cutting; applying a removable, non-wetting pattern or mesh; or combinations comprising at least one of the foregoing.

**[0019]** The step of treating, as embodied by the invention, can comprise chemical treatment. The chemical treatment can comprise at least one of application of a non-wetting pattern or inclusion of a binder to result in controlled cracking of the coating during treating.

**[0020]** Further, the step of treating, as embodied by the invention, can comprise thermal treatment. The treatment if thermally treating comprises applying at least one of a laser or an electron beam.

**[0021]** The metal substrate can be any one of various components that would benefit from the addition of a barrier coating, such as, for example, combustion liners or transition pieces, buckets, nozzles, blades, vanes, shrouds, as well as other components, for example, components that will be disposed in a hot gas stream in a turbine engine. This metal substrate can comprise various metals employed in such applications including nickel, cobalt, iron, combinations comprising at least one of the foregoing, as well as alloys comprising at least one of the foregoing, such as a nickel-base superalloy, and/or a cobalt-based superalloy.

**[0022]** The metallic bond coating material(s) to form the barrier coatings, as embodied by the invention, can include nickel (Ni), cobalt (Co), iron (Fe), chromium (Cr), aluminum (Al), yttrium (Y), alloys comprising at least one of the foregoing, as well as combinations comprising at least one of the foregoing. For example, and in no way limiting of the application, the metallic bond coating can comprises MCrAlY (where M consists of nickel, cobalt, iron, and combinations comprising at least one of the forgoing). An MCrAlY coating can further comprise elements such as silicon (Si), ruthenium (Ru), iridium (Ir), osmium (Os), gold (Au), silver (Ag), tantalum (Ta), palladium (Pd), rhenium (Re), hafnium (Hf), platinum (Pt), rhodium (Rh), tungsten (W), alloys comprising at least one of the foregoing, as well as combinations comprising at least one of the foregoing. For example, but not limited to, the metallic bond coat can comprise sufficient aluminum to form an alumina scale on the surface of the metallic bond coating. The aluminum can be in the form of an aluminide that optionally comprises ruthenium (Ru), iridium (Ir), osmium (Os), gold (Au), silver (Ag), palladium (Pd), platinum (Pt), rhodium (Rh), alloys comprising at least one of the foregoing, as well as combinations comprising at least one of the foregoing.

**[0023]** Application of the green, metallic bond coating to the substrate, which can be accomplished in a single or multiple stages, can be accomplished in various fashions as embodied by the invention. These application of coating processes include, but are not limited to, vapor deposition (e.g., electron beam physical vapor deposition (EB-PVD), chemical vapor deposition (CVD), electroplating, ion plasma deposition (IPD), plasma spray (for example, vacuum plasma spray (VPS), low pressure plasma spray (LPPS), air plasma spray (APS), and so forth), thermal deposition (for example, high velocity oxidation fuel (HVOF) deposition, and the like, as well as combinations comprising at least one of the foregoing processes. For example, metallic bond coating components can be combined (for example, by induction melting, and the like), powderized (for example, by powder atomization), or a plasma sprayed onto the substrate. Alternatively, or in addition, the metallic bond coating elements can be incorporated into a target and ion plasma deposited. Where multiple stages are employed, the same or different elements can be applied to the substrate during each phase. As an example, a precious metal (for example, platinum) can be applied by a technique that reduces waste, followed by another process to apply the remaining elements. Therefore, the precious metal can be electroplated onto the substrate surface, and the other elements can be applied by the thermal deposition (for example, by HVOF) of a powder composition. Aluminizing can then be carried out, to attain intermixing of the precious metal with the rest of the coating composition.

**[0024]** For example, metal material, such as in the form of wire, rod, and similar forms can be applied to a substrate. The metal material could be feed fed into an oxyacetylene flame. The flame melts the metal material and atomizes the particle melt with an auxiliary stream of high-pressure air that deposits the material as a coating on the substrate. Flameless spray apparatus can also be employed, such as those disclosed in U.S. Patent No. 5,285,967 to Weidman. The HVOF process produces smooth coatings, e.g., a coating having a $R_a$ of less than or equal to about 1 micrometer (50 microinches), which, of course, is desirable.

**[0025]** The thickness of the metallic bond coating depends upon the application in which the coated component is used and the application technique. The coating can be applied to turbine components at a thickness of about 50 micrometers to about 625 micrometers, or, more specifically, about 75 micrometers to about 425 micrometers. The metallic bond coating can be treated to roughen the surface prior to the application of the sol-gel coating. Specifically the metallic bond coating can be roughened in the order of about 100 to about 400 micro inches (about 2.54 to about 10.16 micrometers) surface roughness average (Ra) to provide adequate bonding for the application of the coating.

**[0026]** In an exemplary embodiment, however, not intended to limit the invention in any manner, a metal substrate is coated with a "green" strain tolerant TBC using a sol-gel type process. A metal substrate is first coated with a metallic bond coating by any number of processes including, for example, HVOF or VPS. A sol containing inorganic metal oxide powders is then coated on the metallic bond coating to the surface opposite to the metal substrate. The sol coating is treated to induce removal of the liquid and other volatile components of the "green" sol. The final step includes treating by sintering the "green"coating to form a strain tolerant TBC on the metal substrate. This strain tolerance can act to inhibit the coating to form and propagate cracks and spallation during an engine service interval of a turbine engine component.

**[0027]** Also, as embodied by the invention, the "green" coating can be; hot-isostatically pressed before or during sintering the coating to form a strain tolerant coating. The coating can be a thermal barrier coating, an erosion resistant coating or any other desirable coating for the intended application.

**[0028]** A process for producing strain tolerant coatings from a material that exhibits a green state using a sol-gel type process can be used to produce thermal barrier coatings. This process is disclosed in US Patent Application 11/386424, filed March 22, 2006, and assigned to the instant Assignee of this application. A further explanation of the sol-gel type process is omitted for ease of description. Reference can be made to US Patent Application 11/386424 for the description.

**[0029]** The process description herein is merely exemplary in purpose, and is not intended to limit the application in any manner. Such a process allows for the convenient preparation of coated articles having intricate and large geometries, such as turbine components, as the thermal barrier coatings can be applied using techniques. These techniques include, but not limited to, dip coating, spray coating, roll coating, inkjet printing, spin coating, painting, and the like. The following description will be directed to the coating and the process with respect to a thermal barrier coating; however, this application of a TBC coating and process are merely exemplary and are not intended to limit the invention in any manner. The coating could be used for erosion resistance, or any other like function. Also, the process can be used to apply a coating to any suitable substrate for any appropriate application.

**[0030]** The terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another, and the terms "a" and "an" herein do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context, (e.g., includes the degree of error associated with measurement of the particular quantity). The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including one or more of that term (e.g., the metal(s) includes one or more metals). Ranges disclosed herein are inclusive and independently combinable (e.g., ranges of "up to about 25 wt%, or, more specifically, about 5 wt% to about 20 wt %", is inclusive of the endpoints and all intermediate values of the ranges of "about 5 wt% to about 25 wt%," etc).

**[0031]** Once the green coating has formed, a pattern can be induced on or in the coating, where the patterning can occur before or after treatment. As used herein, "inducing a pattern" means altering the surface morphology and coating. The process of inducing a pattern is not particularly limited and can be selected by one of ordinary skill in the art without undue experimentation using the guidelines provided. The process of inducing a pattern may be provided by various mechanical, chemical, or thermal methods.

**[0032]** Mechanical methods can include means such as scratching, imprinting, screening, cutting, or utilizing a peelable mesh that would inhibit coating in desired locations on the substrate and be physically removed after the coating process is complete or burned out during if heat treated. Imprinting can include pressing a mold to the surface impart a pattern, where the mold contains a negative of the desired pattern. Chemical means can include methods such as application of a non-wetting pattern or inclusion of a specialized binder. Thermal modification can be achieved using means such as a laser or electronbeam (EB) etching. The resulting pattern, regardless of the method by which it is achieved, can enhance and better tolerate thermal expansion changes of the coated components.

**[0033]** While various embodiments are described herein, it will be appreciated from the specification that various combinations of elements, variations or improvements therein may be made by those skilled in the art, and are within the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

## Claims

**1.** A method for coating a substrate, comprising:

disposing a first coating on a substrate, where the first coating exhibits a first strain tolerance; and
treating the first coating to enhance the strain tolerance of the first coating to a second strain tolerance, the second strain tolerance being more strain tolerant strain than the first strain tolerance,

wherein the step of treating comprises at least one of mechanical treating, chemically treating, thermally treating, and combinations thereof.

**2.** The method of claim 1, further comprising disposing a metallic bond coating on the metal substrate, wherein the first coating is disposed on the metallic bond coating surface opposite to the metal substrate.

**3.** The method according to claim 1 or claim 2, further comprising a step of drying the first coating after inducing a pattern on or in the first coating.

**4.** The method according to any of claims 1, 2, or 3, wherein the step of treating comprising mechanically treating comprises at least one of scratching; imprinting; screening; cutting; applying a removable, non-wetting pattern or mesh; or combinations comprising at least one of the foregoing or
comprises at least one of application of a non-wetting pattern or inclusion of a binder to result in controlled cracking of the coating during treating, or
comprises applying at least one of a laser or an electron beam.

**5.** The method according to any of the preceding claims, wherein the step of disposing of the first coating on the substrate comprises at least one of dip coating, spray coating, roll coating, inkjet printing, spin coating, painting, or a combination comprising at least one of the foregoing methods.

**6.** The method according to any of the preceding claims, further comprising at least one of removing volatile components of the coating, or
providing a pattern on or in the coating, or
hot-isostatically pressing the coating, or
sintering the coating.

**7.** The method according to any of the preceding claims, wherein disposing the metallic bond coating comprises vapor deposition, electroplating, ion plasma deposition, plasma spray, thermal deposition or combinations comprising at least one of the foregoing of metallic bond coating elements onto the metal substrate.

**8.** The method according to any of claims 2-7, wherein the metallic bond coating comprises MCrAlY, wherein M is selected from the group consisting of nickel, cobalt, iron, and combinations comprising at least one of the foregoing, and wherein the metallic bond coating further comprises an element selected from the group consisting of silicon, ruthenium, iridium, osmium, gold, silver, tantalum, palladium, rhenium, hafnium, platinum, rhodium, tungsten, alloys comprising at least one of the foregoing, and combinations comprising at least one of the foregoing.

**9.** The method according to any of the preceding claims, further comprising forming the coating on the substrate into a thermal barrier coating.

**10.** The method according to any of the preceding claims, further comprising forming the coating on the substrate into an erosion resistant coating.

## REFERENCES CITED IN THE DESCRIPTION



### Patent documents cited in the description

- US 4034142 A, Hecht **[0003]**
- US 4585481 A, Gupta **[0003]**
- US 5285967 A, Weidman **[0024]**
- US 11386424 B **[0028] [0028]**