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# (54) PARTICULATE STRENGTHENED ALLOY ARTICLES AND METHODS OF FORMING

(57) An article and a method for forming the article are presented. The article includes a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the ma-

trix. The particulate phases include an oxide phase. Further embodiments include articles, such as turbomachinery components, fasteners, and pipes, for example, and methods for forming the articles.

EP 2 886 672 A2

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**BACKGROUND** 

[0001] The invention relates generally to nanostructured ferritic alloys. More particularly, the invention re-

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lates to articles formed of nanostructured ferritic alloys having non-uniformly distributed dispersions, and meth-

ods of forming thereof

[0002] Gas turbines operate in extreme environments, exposing the turbine components, especially those in the turbine hot section, to high operating temperatures and stresses. In order for the turbine components to endure these conditions, they are manufactured from a material capable of withstanding these severe conditions. As material limits are reached, one of two approaches is conventionally used in order to maintain the mechanical integrity of hot section components. In one approach, cooling air is used to reduce the part's effective temperature. In a second approach, the component size is increased to reduce the stresses. However, these approaches can reduce the efficiency of the turbine and increase the cost. [0003] In certain applications, superalloys have been used in these demanding applications because they maintain their strength at up to 90% of their melting temperature and have excellent environmental resistance. Nickel-based superalloys, in particular, have been used extensively throughout gas turbine engines, e.g., in turbine blade, nozzle, wheel, spacer, disk, spool, blisk, and shroud applications. In some lower temperature and stress applications, steels may be used for turbine components. However, use of conventional steels is often limited in high temperature and high stress applications because of not meeting the necessary mechanical property requirements and/or design requirements.

[0004] Nanostructured ferritic alloys (NFA) are an emerging class of alloys that are of considerable interest for the gas turbine rotors. These alloys (NFAs) exhibit exceptional high temperature properties, thought to be derived from nanometer-sized oxide clusters that precipitate during hot consolidation following a mechanical alloying step. These oxide clusters are present at high temperatures, providing a strong and stable microstructure during service. Moreover, unlike many nickel-based superalloys, that require the cast and wrought (C&W) process to be followed to obtain necessary properties, NFAs are manufactured via a different processing route that requires fewer melting steps.

[0005] While NFAs yield enhanced tensile and creep properties compared to conventional steels, additional benefits are sought for rotor applications. It should be noted that for the heavy duty gas turbine rotors, critical mechanical property requirements change from the bore to the rim of a wheel. For example, the bore is limited by burst strength, and hence would require a higher ultimate tensile strength, and the rim is limited by a material's

[0006] Accordingly, it is desirable to have a graded al-

loy article that exhibits improved mechanical integrity over various regions (locations) of the article with a proper balance of mechanical properties.

#### **BRIEF DESCRIPTION**

[0007] In one embodiment, an article is provided. The article includes a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix. The particulate phases include an oxide phase. Further embodiments include articles, such as turbomachinery components, fasteners, and pipes, for example.

[0008] One embodiment is a turbomachinery component. The component includes a radially symmetrical body having an inner surface proximate to a center of the body and an outer surface distal to the center of the body. The body includes a material comprising a metal matrix and a first population of particulate phases. The metal matrix includes iron and chromium. The first population of particulate phases includes an oxide phase that includes titanium and yttrium, and has a median size less than about 20 nanometers. A concentration of the first population of the particulate phases at the inner surface is less than a concentration of the first population of the particulate phases at the outer surface. The concentration of the first population of the particulate phases at the inner surface is in a range from about 0.1 volume percent to about 2 volume percent, and the concentration at the outer surface is in a range from about 0.7 volume percent to about 3 volume percent.

[0009] In one embodiment, a method includes joining a first composition comprising a first oxygen concentration to a second composition having a second oxygen concentration to form a material. The second oxygen concentration is different from the first oxygen concentration. The material includes a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix. The particulate phases include an oxide phase. The material is processed to provide an article.

[0010] In one embodiment, a method of forming a turbomachinery component is provided. The method includes steps of milling a first powder including iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, and thus forming a first composition having a first oxygen concentration; and milling a second powder including iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming a second composition having a second oxygen concentration that is greater than the first oxygen concentration. The powder having the first composition is disposed in a first region of a container, and the powder having the second composition is disposed in a second region of the container. These powders are consolidated to thereby join the first and second compositions at a temperature to precipitate an oxide phase comprising ti-

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tanium and yttrium within a matrix comprising iron and chromium. The first region of the container and the second region of the container respectively correspond to an inner surface and an outer surface of a radially symmetrical body of the turbomachinery component.

#### **DRAWINGS**

**[0011]** 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.

FIG. 1 is a schematic representation of an article, in accordance with one embodiment of the present invention:

FIG. 2 is a schematic representation of an article, in accordance with one embodiment of the present invention;

FIG. 3 is a schematic representation of a top-down cross-section of a turbomachinery component, in accordance with one embodiment of the present invention:

FIG. 4 is a schematic representation of a top-down cross-section of a turbomachinery component, in accordance with one embodiment of the present invention:

FIG. 5 schematically represents a container for forming an article, in accordance with one embodiment of the present invention.

### **DETAILED DESCRIPTION**

[0012] Embodiments of the invention described herein address the noted shortcomings of the state of the art. One or more specific embodiments of the present invention will be described below. In an effort to provide a concise description of these embodiments, all features of an actual implementation may not be described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure. [0013] When introducing elements of various embodiments of the present invention, the articles "a," "an," and "the," are intended to mean that there are one or more

of the elements. The terms "comprising," "including," and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements. Moreover, the use of "top," "bottom," "above," "below," and variations of these terms is made for convenience, but does not require any particular orientation of the components unless otherwise stated.

**[0014]** All ranges disclosed herein are inclusive of the endpoints, and the endpoints are combinable with each other. The terms "first," "second," and the like as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another.

[0015] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it may be about related. Accordingly, a value modified by a term such as "about" is not limited to the precise value specified. In some instances, the approximating language may correspond to the precision of an instrument for measuring the value.

**[0016]** Embodiments of the invention provide an article including a metal matrix and a first population of particulate phases that is macroscopically non-uniformly disposed within the metal matrix. The metal matrix may include nickel, iron, chromium, aluminum, cobalt, titanium, or a combination thereof. In one embodiment, the metal matrix includes an iron-containing alloy. The first population of particulate phases includes an oxide phase.

[0017] As used herein, "macroscopically non-uniform disposition" refers to heterogeneous dispersion of particulate phases over a length scale of at least 0.5 centimeter of the metal matrix. That is, a concentration of the particulate phases in a first portion of the article varies from a concentration of the particulate phases in a second portion, wherein the portions often extend over a length scale of at least about 0.5 centimeter. In some embodiments, the portions may extend to a length scale of up to about 200 centimeters. In certain embodiments, the portions may extend to a length scale of up to about 100 centimeters. As used herein, "disposed within the matrix" includes the dispersion of the particulate phases in the grains and grain boundaries of the matrix.

[0018] Some embodiments provide an article including a nanostructured ferritic alloy (NFA). Typically a nanostructured ferritic alloy includes an iron-containing alloy matrix that is strengthened by nanofeatures disposed in the matrix. The concentration of iron in the alloy matrix may be greater than about 50 weight percent. In one embodiment, the iron content in the alloy matrix is greater than about 70 weight percent. In one embodiment, the alloy matrix is in the form of the ferritic body-centered cubic (BCC) phase. As used herein, the term "nanofeatures" means particles of matter having a largest dimension less than about 20 nanometers in size. The nanofeatures of an NFA may have any shape, including, for example, spherical, cuboidal, lenticular, and other shapes.

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The nanofeatures used herein are typically in-situ formed in the NFA by the dissolution of at least a portion of the initial added oxide and the precipitation of nanometer sized particles of a modified oxide that can serve to pin the alloy structure, thus providing enhanced mechanical properties.

**[0019]** FIG. 1 illustrates an article 10 in accordance with some embodiments of the present invention. The article 10 includes a nanostructured ferritic alloy having a first population of particulate phases macroscopically non-uniformally disposed within the article, for example, from a first surface 12 to a second surface 14. In some embodiments, the article 10 has graded concentration of the first particulate phases from the first surface 12 towards the second surface 14. The gradation may be continuous or step wise.

**[0020]** In the illustrated embodiment, the article 10 includes a first region 18 extending from the first surface 12 to a predetermined surface 16, and a second region 20 extending from a second surface 14 to the predetermined surface 16. The first region 18 includes a first concentration of the first particulate phases, and the second region 20 includes a second concentration of the first particulate phases, where the first concentration of the first particulate phases in the first region 18 is not equal to the second concentration of the first particulate phases in the second region 20. In one embodiment, each of the first concentration in the first region 18 and the second concentration in the second region 20 is independently within a range from about 0.1 volume percent to about 5 volume percent.

[0021] In some embodiments, the article 10 may have more than two regions, wherein adjacent regions have different concentration of the first particulate phases. For example, the article 10 may have at least three regions, as illustrated in FIG. 2, with an intermediate region 22 extending from the predetermined surface 16 to another predetermined surface 26. The intermediate region 22 is disposed between the first region 18 and the second region 20. The concentration of the first particulate phases in the intermediate region 22 may be different from the first concentration of the first particulate phases in the first region 18 and the second concentration of the first particulate phases in the second region 20. In some embodiments, the concentration of the first particulate phases in the intermediate region 22 has a value between the first concentration and the second concentration. The article 10 may have a number of intermediate regions between the first region 18 and the second region 20. In one embodiment, the concentration of the first particulate phases in each intermediate region is between the concentrations of the particulate phases in adjacent regions. The concentrations of the first particulate phases may increase or decrease from the first region 18 towards the second region 20. In some embodiments, the alternate regions may have a same concentration of the first particulate phases. It should be noted herein that although the below material details are discussed with reference

to FIGS.1 and 2, the details are also equally applicable to the embodiment of FIGS. 3 and 4.

[0022] A metal matrix (may also be referred to as alloy matrix) of the NFA includes iron and chromium. Chromium is important for both phase stability and oxidation and/or corrosion resistance, and may thus be included in the NFA in amounts of at least about 5 weight percent. Amounts of up to about 30 weight percent may be included. In one embodiment, chromium is present in a range from about 9 weight percent to about 14 weight percent of the alloy. In some embodiments, the alloy may have titanium and yttrium. The titanium and yttrium may be present in the metallic or alloy form as a part of the matrix of the alloy, or may be present in the particulate phases of the alloy. They may play a role in the formation of the oxide nanofeatures, as described herein. In some embodiments, the titanium is present in a range from about 0.1 weight percent to about 2 weight percent, and yttrium from about 0.1 weight percent to about 3 weight percent of the alloy. In addition, the alloy may include one or more of vanadium, molybdenum, manganese, tungsten, niobium, silicon or tantalum.

[0023] The first population of particulate phases may be the above-described nanofeatures, providing enhanced tensile and creep properties to the alloy. The nanofeatures of the first population have a median size less than about 20 nanometers (nm). In some embodiments, the particulate phases of the first population have a median size less than about 15 nm. In certain embodiments, the median size of the particulate phases is less than about 10 nm. In some embodiments, the first population of particulate phases may include a complex oxide. A "complex oxide" as used herein is an oxide phase that includes more than one non-oxygen elements. The complex oxide may be a single oxide phase having more than one non-oxygen elements such as, for example, ABO (where A, B signify non-oxygen elements); or may be a mixture of multiple simple oxide phases (having one nonoxygen element) such as, for example A<sub>x</sub>B<sub>y</sub>O<sub>z</sub>, where x, y, z denote the relative molar ratios of the elements in the mixture. The examples included here do not account for charge balance, and hence will include the oxides of elements of different valencies and deviations from stoichiometry.

[0024] In one embodiment, an oxide material may be added to the alloy matrix, and processed to precipitate nanofeatures of the first population. At least a part of the added oxide phase may be dissolved in the alloy structure and precipitated as the nanofeatures. In one embodiment, the precipitated oxide in the NFA may include transition metals (for example, titanium and yttrium) present in the starting materials and the metallic element(s) of the initial oxide addition.

**[0025]** In one embodiment, the particulate phases of the first population include at least two elements from the group of yttrium, titanium, aluminum, zirconium, molybdenum, silicon, hafnium, magnesium, tungsten, and tantalum. The particulate phases may include a combination

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of two or more simple oxides; a combination of one or more simple oxide and one or more complex oxides; or a combination of multiple different complex oxides. In a particular embodiment, the particulate phases of the first population include a complex oxide with a single phase including more than one non-oxygen element, such as for example, a yttrium titanium oxide; a yttrium titanium oxide; a magnesium titanium oxide; a naluminum titanium oxide; a magnesium titanium oxide; a magnesium zirconium oxide; zirconium hafnium oxide; a yttrium zirconium oxide; a yttrium magnesium oxide; a yttrium zirconium titanium oxide; or a yttrium aluminum titanium oxide.

**[0026]** It should be noted here that the use of the plural term "phases" in this context does not necessitate that multiple phase compositions are present within a population; rather, "phases" is used to denote the presence of a plurality of particles in the matrix, which may or may not be of homogeneous composition.

[0027] In some embodiments, the article 10 (FIGS. 1 and 2) further includes a second population of particulate phases within the alloy matrix. The addition of the second particulate phases may enhance the tensile and creep properties of the NFA, while maintaining a desirable level of ductility. The second population of particulate phases may have a different particle size distribution than that of the first population of the particulate phases. The second population of the particulate phases may have a median particulate size in a range from about 25 nm to about 10 microns. In one embodiment, the second population of particulate phases has a median size in a range from about 50 nm to about 3 microns.

[0028] The second population of the particulate phases may be distributed uniformly or non-uniformly within the article 10. In one embodiment, the second population of the particulate phases is disposed macroscopically non-uniformly within the alloy matrix. For example, as discussed with respect to the first population of particulate phases in previous embodiments, a concentration of the second particulate phases in each intermediate region is between the concentrations of the particulate phases in adjacent regions (FIG. 2). The concentrations of the particulate phases may increase or decrease from the first region 18 towards the second region 20. The concentrations of the second population of particulate phases in each region of the article may independently be within a range from about 1 volume percent to about 15 volume percent, and more particularly, from about 1 volume percent to about 6 volume percent of the alloy. In a particular embodiment, the concentration the population of particulate phases (including both first population and second population) in each region of the article is in a range from about 2 volume percent to about 6 volume percent in the alloy.

**[0029]** In some embodiments, the second population may include an oxide, a boride, a carbide, a nitride, or a combination thereof. An oxide may be added to the alloy during processing to further strengthen the alloy. In one

embodiment, the concentration of total oxygen in the alloy is in a range from about 0.1 weight percent to about 0.6 weight percent of the alloy. In some embodiments, a precipitated particulate phase of the second population is an intermetallic phase. Non-limiting examples of the intermetallic phase may include a Laves phase, a Mu phase, a Z-phase, and a Ni<sub>3</sub>M structure. Various features and methods of forming an alloy having a precipitated first population of particulate phases and an added second population of particulate phases are described in details in previously filed US patent applications serial nos. 13/931108 and 14/074768.

**[0030]** Referring to FIGS 1 and 2 again, the article 10 may be a turbomachinery component, in some embodiments. In other embodiments, the article 10 may also be applicable for any other applications involving operation at a high temperature, such as a fastener, a pipe etc, as well as a low temperature, such as pipes and disks for transporting oils and gases. In one embodiment, the article 10 is a turbine wheel. In another embodiment, the article 10 is a turbine spacer.

[0031] As discussed previously, critical mechanical properties change from the bore to the rim of a turbine wheel. For example, the bore is limited by burst strength, and hence would require a higher ultimate tensile strength, and the rim is limited by a material's creep life. Generally, increasing the concentration of the oxide nanofeatures results in improved tensile properties as required for the wheel's bore and improved creep properties for the wheel's rim. However, the concentration of the oxide nanofeatures is limited to a nominal amount because of a reduction in the ductility of the material, which is a larger concern at the bore than the rim.

[0032] Some embodiments of the present invention provide a turbomachinery component having macroscopically non-uniform dispersion of a first population of the particulate phases that includes an oxide phase, to provide required mechanical properties in particular locations or regions, for example at a bore and a rim of the turbomachinery component. FIG. 3 illustrates a top-down cross-section of a turbomachinery component 30 having a radially symmetrical body, for example a wheel or a spacer. The center of the radially symmetric component 30 is located at 31. The component 30 includes a nanostructured ferritic alloy (NFA) as described herein. In the illustrated embodiment, the turbomachinery component 30 includes an inner surface 32 (bore) proximate to a center 31 of the radially symmetrical body of the component 30, and an outer surface 36 (rim) distal to the center 31 of the component 30. The inner surface 32 of the component 30 defines a hole concentric with the radially symmetrical body. In one embodiment, a first concentration of the first particulate phases in the alloy at the inner surface 32 is less than a second concentration of the first particulate phases at the outer surface 36 of the wheel. In one embodiment, the wheel 30 includes a nanostructured ferritic alloy having a graded concentration of the first particulate phases from the inner surface 32 to the

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outer surface 36.

[0033] In some embodiments as illustrated in FIG. 4, the turbomachinery component 30 has a first region 38 extending from the inner surface 32 to a predetermined surface 34, and a second region 40 extending from the outer surface 36 to the predetermined surface 34. In one embodiment, the first region 38 and the second region 40 include the same composition of the NFA matrix and the concentration of the first particulate phases in the alloy varies. A first concentration of the first particulate phases in the first region 38 is less than the second concentration of the first particulate phases in the second region 40 of the component 30.

[0034] In some embodiments, the first concentration of the first particulate phases in the first region 38 is in a range from about 0.1 volume percent to about 2 volume percent of the alloy, and the second concentration of the first particulate phases in the second region 40 is in a range from about 0.7 volume percent to about 3 volume percent of the alloy. In some embodiments, the component 30 may have a number of intermediate regions disposed between the first region 38 and the second region 40, as discussed in previous embodiments. In certain embodiments, the component 30 may include a graded nanostructured ferritic alloy i.e. a nanostructured ferritic alloy having a gradually increasing concentration of the first particulate phases from the inner surface 32 to the outer surface 36 (FIG. 3).

[0035] By tailoring the concentration of the first particulate phases (that includes an oxide phase) in the alloy matrix, desired mechanical properties in specific locations of a component can be achieved. For example, a wheel may have a low concentration of an oxide phase near the bore region to provide good ultimate tensile strength and ductility to resist burst, and a high concentration of the oxide phase near the rim region to enhance creep resistance. Typically, these location specific properties can be achieved by using multiple alloys. However, use of these multiple dissimilar chemistry alloys results in inter-diffusion at the joining surface. This inter-diffusion may adversely affect mechanical properties during the service of the component, and thus reduce service life. Use of a consistent alloy matrix throughout the wheel with varying concentration of an oxide phase enables location specific properties to be achieved while maintaining the same matrix to eliminate diffusion issues and property changes with time.

**[0036]** Some embodiments provide a method of forming an article. The method includes joining a first composition and a second composition to form an article. The first composition and the second composition may be joined through one or more than one intermediate composition disposed between them. In one embodiment, a number of compositions may be joined by joining one composition with an adjacent composition. The first composition may have a first oxygen concentration and the second composition may have a second oxygen concentration that is different from the first oxygen concentration.

The resulting article includes a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the article. The first population of particulate phases includes an oxide phase. In certain embodiments, the resulting material includes a NFA.

**[0037]** Oxygen concentration, as used herein, refers to a total oxygen concentration of a composition, which may include dissolved oxygen and any other oxygen that is present in the form of an oxide or in other phases present in the NFA.

[0038] The method of forming a composition of NFA may include forming an alloy powder and consolidating the powder. The alloy powder may be formed by any of the methods known in the art. A process of forming the alloy powder may start from melting starting materials such as, for example, iron and chromium to form an initial melt. A vacuum induction melting process may be conveniently used to melt the starting material. The melted material may be atomized to form the alloy powder that can be milled along with an added oxide material to form a milled alloy powder. In one embodiment, the oxide material includes yttria, zirconia, hafnia, alumina, silica, magnesia, or a combination thereof. Usually, the milled alloy powder may be processed by consolidating at a temperature to precipitate a desired concentration of the first population of the particulate phases having an oxide phase with a desired size. Suitable processing techniques may include isothermal forging, hot isostatic pressing (HIP), extrusion, or a combination thereof. In one embodiment, the processing of the milled alloy powder includes hot isostatic pressing (HIP). At least some of the added oxide is dissolved into the alloy matrix during powder attrition, and precipitates in the formation of the aforementioned nanofeatures when the powder is raised to a temperature during the consolidation process. In any given instance of this method, the amount of added oxide that dissolves can be less than a majority, or substantially all of the added oxide, depending on processing parameters and materials selected. In one embodiment, the first particulate phases of complex oxides may precipitate during the consolidation step. In one embodiment, a second population of particulate phases may be established by adding and mixing an oxide to the milled alloy powder as described in patent applications serial nos. 13/931108 and 14/074768.

[0039] An article, for example the turbomachinery component 30 (FIG. 4) may be manufactured using several techniques. The first region 38 includes the first composition, and the second region 40 includes the second composition. The first composition and the second composition may be formed by the process as discussed above. The formation of the first composition includes milling an alloy powder in presence of a first amount of an oxide, and the formation of the second composition includes milling the alloy powder in presence of a second amount of the oxide. The alloy powders are milled until the oxide is at least partially dissolved into the alloy powder. In any given instance of this method, the amount of

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added oxide that dissolves can be less than the majority, or a majority, or substantially all of the added oxide, depending on processing parameters and materials selected.

[0040] In some embodiments, the first composition and the second composition are present in milled alloy powder form. Referring to FIG. 5, the method includes steps of disposing the first composition in a first region 52 of a container 50 (for example, HIP can), and disposing a second composition in a second region 54 of the container 50. The container 50 is cylindrical about an axis 60. The first region 52 of the container 50 proximate to the axis 60, is defined by a first surface 56 that may correspond to the predetermined surface 34 of the component 30 of FIG. 4. Further, a portion of the first region 52 of the container 50 may correspond to the first region 38 of the component 30. A second surface 58 of the container 50 may correspond to the second surface 36 (FIG.4), i.e. the second region 54 of the container 50 may correspond to the second region 40 of the component 30 (FIG. 4). The two alloy powders may be separated by a metallic sheet (for example, baffle) at the time of disposing the compositions in the container 50. The method further includes simultaneously consolidating the milled alloy powders of the first composition and the second composition, and thereby joining the two consolidated compositions to form a solid feedstock (defined below) having a first portion and a second portion corresponding to the first and second regions 52 and 54 of the container 50. The metallic sheet can be removed from the container before the consolidation step to allow the two compositions to join during the HIP process. In certain embodiments, the two alloy powders are consolidated by HIP followed by forging or extrusion. The consolidation process may be performed at a temperature to precipitate a first concentration and a second concentration of an oxide phase including titanium and yttrium in the first region 52 and the second region 54 of the container, respectively. In certain embodiments, the first concentration of the oxide phase in the first region 52 is less than the second concentration of the oxide phase in the second region 54.

[0041] The container 50 used to consolidate the NFA alloy, may not have a bore hole as shown in FIGS. 3 and 4 defined by the inner surface 32 of the radially symmetrical body of the component 30. The bore hole can be machined in a first portion of the resulting solid feedstock after completion of the processing of the NFA. As used herein, the first portion of the solid feedstock corresponds to the first composition that forms the inner surface 32 of the first region 38 of the component 30 after the bore hole is machined.

[0042] In some embodiments, the first composition and the second composition are present in form of solid feed-stock. Solid feedstock refers to a solid continuous structure that does not include a powder form. The milled alloy powders of first composition and the second composition are separately consolidated in desired shapes to form

solid feedstocks. For example, referring to FIG. 5, a first (i.e., inner) feedstock corresponding to the first region 52 including the first composition and a second feedstock corresponding to the second region 54 including the second composition are manufactured beforehand, and then joined. As discussed, a bore hole can be machined in the first feedstock including the first composition. In these embodiments, joining may be performed by welding, coextruding, solid state joining, diffusion bonding, shrink fitting, or a combination thereof.

[0043] In some embodiments, at least one of the first composition or the second composition is in form of solid feedstock, and the other composition is in powder form. In one example, the first composition may be a solid feedstock that can be placed in the first region 52 of the container 50, and the second composition may be a powder that can be disposed in the second region 54 (i.e. around the solid feedstock of the first composition) of the container 50. In another example, the second composition may be a solid feedstock of having a hollow space substantially in the middle, which can be placed in the second region 54 of the container 50. The first composition may be a powder that can be disposed in the first region 52 (i.e., the hollow space of the solid feedstock). In these embodiments, the method further includes consolidating the powder of the second composition and thereby bonding the second composition to the first composition. In some embodiments, the first and the second compositions are processed by HIP followed by forging. In some embodiments, the first composition and the second compositions are processed by HIP and extrusion. Examples of other suitable bonding techniques include co-extrusion, and spray techniques such as cold spray, thermal spray, and plasma spray.

**[0044]** 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 true scope of the invention.

**[0045]** Various aspects and embodiments of the present invention are defined by the following numbered clauses:

## 1. An article, comprising:

a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix, the particulate phases comprising an oxide phase.

- 2. The article of clause 1, wherein the matrix comprises nickel, iron, chromium, aluminum, cobalt, titanium, or a combination thereof.
- 3. The article of clause 1 or 2, wherein the matrix comprises iron and chromium.

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- 4. The article of any preceding clause, wherein the oxide phase comprises aluminum, yttrium, magnesium, molybdenum, zirconium, silicon, titanium, hafnium, tungsten, tantalum, or a combination thereof.
- 5. The article of any preceding clause, wherein the oxide phase comprises titanium and yttrium.
- 6. The article of any preceding clause, wherein the first population of particulate phases has a median size less than about 20 nm.
- 7. The article of any preceding clause, wherein the first population of particulate phases has a median size less than about 10 nanometers.
- 8. The article of any preceding clause, further comprising a second population of particulate phases disposed within the matrix, wherein the second population of particulate phases has a different size distribution from the size distribution of the first population of particulate phases.
- 9. The article of clause 8, wherein the second population of particulate phases is distributed macroscopically non-uniformly within the matrix.
- 10. The article of clause 8 or 9, wherein the second population of particulate phases comprises an intermetallic compound.
- 11. The article of any of clauses 8 to 10, wherein the second population of particulate phases comprises an oxide, a boride, a carbide, a nitride, or combinations thereof.
- 12. The article of any of clauses 8 to 11, wherein the second population of particulate phases has a median size in a range from about 25 nm to about 10 microns.
- 13. The article of any preceding clause, wherein a first concentration of the first population of the particulate phases in a first region of the article is not equal to a second concentration of the first population of the particulate phases in a second region of the article, and wherein each of the first concentration and second concentration is independently within a range from about 0.1 volume percent to about 5 volume percent.
- 14. The article of clause 13, wherein at least one intermediate region is disposed between the first region and the second region, and wherein the concentration of the first population of the particulate phases in the at least one intermediate region has a value that is between the first concentration and the second concentration.

- 15. The article of clause 13 or 14, wherein the article is a turbomachinery component, a fastener or a pipe.
- 16. The article of clause 15, wherein the article is a wheel or a spacer.
- 17. The article of clause 16, wherein a first region comprises an inner surface of the wheel or spacer, and a second region comprises an outer surface of the wheel or spacer, and wherein a first concentration of the first population of the particulate phases at the inner surface is less than a second concentration of the first population of the particulate phases at the outer surface.
- 18. The article of clause 17, wherein the first concentration is in a range from about 0.1 volume percent to about 2 volume percent, and the second concentration is in a range from about 0.7 volume percent to about 3 volume percent.
- 19. A turbomachinery component, comprising:

a radially symmetrical body comprising an inner surface proximate to a center of the body and an outer surface distal to the center of the body; wherein the body comprises

a material comprising

a metal matrix, the matrix comprising iron and chromium;

a first population of particulates having a median size less than about 20 nanometers, the particulate phases comprising an oxide phase, the oxide phase comprising titanium and yttrium, wherein a concentration of the first population of the particulate phases at the inner surface is less than a concentration of the first population of the particulate phases at the outer surface, and wherein the concentration of the particulate phases at the inner surface is in a range from about 0.1 volume percent to about 2 volume percent, and the concentration of the particulate phases at the outer surface is in a range from about 0.7 volume percent to about 3 volume percent.

# 20. A method comprising:

joining a first composition comprising a first oxygen concentration to a second composition having a second oxygen concentration, the second oxygen concentration different from the first oxygen concentration, to form a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix, the particulate phases comprising an oxide phase.

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- 21. The method of clause 20, further comprising milling an alloy powder comprising iron and chromium in the presence of a first amount of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming the first composition.
- 22. The method of clause 20 or 21, further comprising milling an alloy powder comprising iron and chromium in the presence of a second amount of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming the second composition.
- 23. The method of any of clauses 20 to 22, wherein the first composition, the second composition, or both the first composition and the second composition, are powder, and wherein joining further comprises consolidating the powder.
- 24. The method of clause 23, wherein both the first composition and the second composition are powder.
- 25. The method of clause 24, further comprising:

disposing powder comprising the first composition in a first region of a container; disposing powder comprising the second composition in a second region of the container; and consolidating the powders and thereby joining the first and second compositions.

- 26. The method of clause 20, further comprising heating the first composition, the second composition, or the material to form the first population of particulate phases.
- 27. The method of clause 20, further comprising establishing a second population of particulate phases within the matrix, the second population of particulate phases having a median size in a range from about 25 nm to about 10 microns.
- 28. The method of clause 20, wherein the first composition and the second composition are solid feed-stock, and wherein joining comprises co-extruding, welding, solid-state joining, diffusion bonding, shrink fitting, or a combination thereof.
- 29. The method of clause 23, wherein the first composition is a solid feedstock and the second composition is a powder, and wherein joining comprises consolidating the powder and bonding the first composition to the second composition.
- 30. A method, comprising:

milling a first powder comprising iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming a first composition having a first oxygen concentration;

milling a second powder comprising iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming a second composition having a second oxygen concentration that is greater than the first oxygen concentration;

disposing powder comprising the first composition in a first region of a container;

disposing powder comprising the second composition in a second region of the container; and consolidating the powders and thereby joining the first and second compositions at a temperature to precipitate an oxide phase comprising titanium and yttrium within a matrix comprising iron and chromium;

wherein the first region of the container and the second region of the container respectively correspond to an inner surface and an outer surface of a radially symmetrical body of a turbomachinery component.

#### Claims

1. An article, comprising:

a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix, the particulate phases comprising an oxide phase.

- The article of claim 1, wherein the matrix comprises nickel, iron, chromium, aluminum, cobalt, titanium, or a combination thereof.
- 3. The article of claim 1 or claim 2, wherein the matrix comprises iron and chromium.
  - 4. The article of any preceding claim, wherein the oxide phase comprises aluminum, yttrium, magnesium, molybdenum, zirconium, silicon, titanium, hafnium, tungsten, tantalum, or a combination thereof.
  - **5.** The article of any preceding claim, wherein the oxide phase comprises titanium and yttrium.
- 50 **6.** The article of any preceding claim, wherein the first population of particulate phases has a median size less than about 20 nm.
  - 7. The article of any preceding claim, further comprising a second population of particulate phases disposed within the matrix, wherein the second population of particulate phases has a different size distribution from the size distribution of the first population of

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particulate phases.

- **8.** The article of claim 7, wherein the second population of particulate phases is distributed macroscopically non-uniformly within the matrix.
- **9.** The article of claim 7 or claim 8, wherein the second population of particulate phases comprises an intermetallic compound.
- 10. The article of any one of claims 7 to 9, wherein the second population of particulate phases comprises an oxide, a boride, a carbide, a nitride, or combinations thereof.
- 11. The article of any one of claims 7 to 10, wherein the second population of particulate phases has a median size in a range from about 25 nm to about 10 microns.
- 12. The article of any preceding claim, wherein a first concentration of the first population of the particulate phases in a first region of the article is not equal to a second concentration of the first population of the particulate phases in a second region of the article, and wherein each of the first concentration and second concentration is independently within a range from about 0.1 volume percent to about 5 volume percent.

# **13.** A turbomachinery component, comprising:

a radially symmetrical body comprising an inner surface proximate to a center of the body and an outer surface distal to the center of the body; wherein the body comprises

a material comprising

a metal matrix, the matrix comprising iron and chromium;

a first population of particulates having a median size less than about 20 nanometers,

the particulate phases comprising an oxide phase, the oxide phase comprising titanium and yttrium, wherein a concentration of the first population of the particulate phases at the inner surface is less than a concentration of the first population of the particulate phases at the outer surface, and wherein the concentration of the particulate phases at the inner surface is in a range from about 0.1 volume percent to about 2 volume percent, and the concentration of the particulate phases at the outer surface is in a range from about 0.7 volume percent to about 3 volume percent.

### **14.** A method comprising:

joining a first composition comprising a first ox-

ygen concentration to a second composition having a second oxygen concentration, the second oxygen concentration different from the first oxygen concentration, to form a material comprising a metal matrix and a first population of particulate phases disposed macroscopically non-uniformly within the matrix, the particulate phases comprising an oxide phase.

#### 10 **15.** A method, comprising:

milling a first powder comprising iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming a first composition having a first oxygen concentration;

milling a second powder comprising iron and chromium in the presence of an oxide until the oxide is at least partially dissolved into the alloy powder, thus forming a second composition having a second oxygen concentration that is greater than the first oxygen concentration; disposing powder comprising the first composition in a first region of a container;

disposing powder comprising the second composition in a second region of the container; and consolidating the powders and thereby joining the first and second compositions at a temperature to precipitate an oxide phase comprising titanium and yttrium within a matrix comprising iron and chromium;

wherein the first region of the container and the second region of the container respectively correspond to an inner surface and an outer surface of a radially symmetrical body of a turbomachinery component.

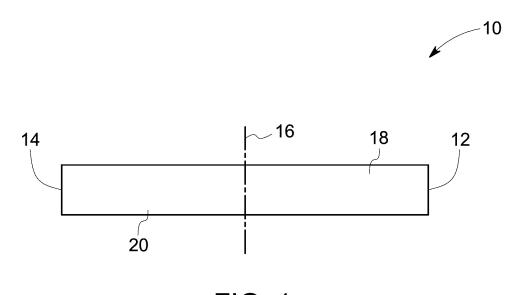


FIG. 1

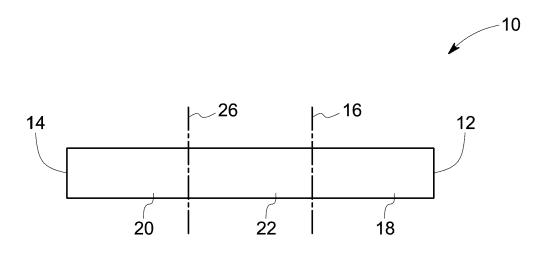


FIG. 2

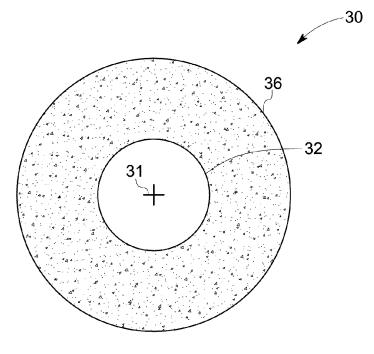


FIG. 3

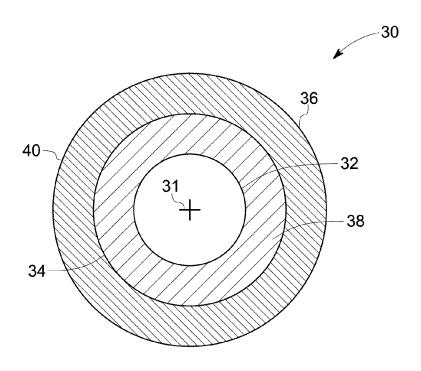


FIG. 4

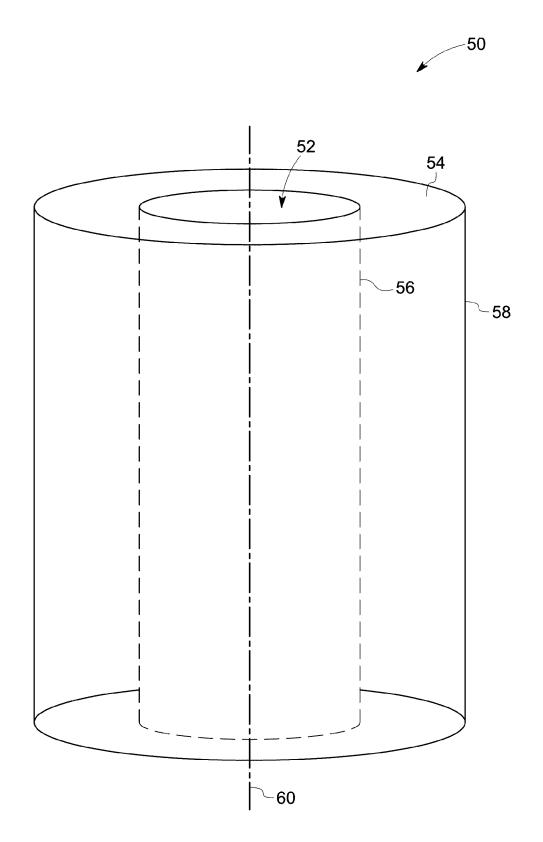


FIG. 5

# EP 2 886 672 A2

#### REFERENCES CITED IN THE DESCRIPTION

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# Patent documents cited in the description

- US 931108 A [0029]
- US 14074768 A [0029]

- WO 13931108 A [0038]
- WO 14074768 A [0038]