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(54) **Alloys for high temperature applications, articles made therefrom, and method for repair of articles**

(57) An alloy for use in high temperature applications is presented. The alloy comprises, in atom percent, at least about 50% rhodium (Rh); at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof; from about 5% to about 24% ruthenium (Ru); and from about 1% to about 40% chromium (Cr); wherein the alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in the alloy, respectively. Articles comprising the alloy and methods employing the alloy for repairing articles are also presented.

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Description

[0001] The present invention relates to materials designed to withstand high temperatures. More particularly, this invention relates to heat-resistant alloys for high-temperature applications, such as, for instance, gas turbine engine components of aircraft engines and power generation equipment. The present invention further relates to methods for repairing articles for high temperature applications.

[0002] There is a continuing demand in many industries, notably in the aircraft engine and power generation industries where efficiency directly relates to operating temperature, for alloys that exhibit sufficient levels of strength and oxidation resistance at increasingly higher temperatures. Gas turbine airfoils on such components as vanes and blades are usually made of materials known in the art as "superalloys." The term "superalloy" is usually intended to embrace iron-, cobalt-, or nickel-based alloys, which include one or more additional elements to enhance high temperature performance, including such non-limiting examples as aluminum, tungsten, molybdenum, titanium, and iron. The term "based" as used in, for example, "nickel-based superalloy" is widely accepted in the art to mean that the element upon which the alloy is "based" is the single largest elemental component by atom fraction in the alloy composition. Generally recognized to have service capabilities limited to a temperature of about 1200°C, conventional superalloys used in gas turbine airfoils often operate at the upper limits of their practical service temperature range. In typical jet engines, for example, bulk average airfoil temperatures range from about 900°C to about 1000°C, while airfoil leading and trailing edge and tip temperatures can reach about 1150°C or more. At such elevated temperatures, the oxidation process consumes conventional superalloy parts, forming a weak, brittle metal oxide that is prone to chip or spall away from the part.

[0003] Erosion and oxidation of material at the edges of airfoils lead to degradation of turbine efficiency. As airfoils are worn away, gaps between components become excessively wide, allowing gas to leak through the turbine stages without the flow of the gas being converted into mechanical energy. When efficiency drops below specified levels, the turbine must be removed from service for overhaul and refurbishment. A significant portion of this refurbishment process is directed at the repair of the airfoil leading and trailing edges and tips. For example, damaged material is removed and then new material built onto the blade by any of several methods, such as, for example, welding with filler material, welding or brazing new sections onto the existing blade, or by plasma spraying or laser deposition of metal powders onto the blade. The performance of alloys commonly used for repair is comparable or inferior to that of the material of the original component, depending upon the microstructure of the repaired material, its defect density due to processing, and its chemistry. Furthermore, in current practice, the original edge material is made of the same material as the rest of the original blade, often a superalloy based on nickel or cobalt. Because this material was selected to balance the design requirements of the entire blade, it is generally not optimized to meet the special local requirements demanded by conditions at the airfoil leading or trailing edges. However, maximum temperatures, such as those present at airfoil tips and edges, are expected in future applications to be over about 1300°C, at which point many conventional superalloys begin to melt. Clearly, new materials for repair and manufacture must be developed to improve the performance of repaired components and to exploit efficiency enhancements available to new components designed to operate at higher turbine operating temperatures.

[0004] These and other needs are addressed by embodiments of the present invention. One embodiment is an alloy comprising, in atom percent, at least about 50% rhodium (Rh); at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof; from about 5% to about 24% ruthenium (Ru); and from about 1% to about 40% chromium (Cr); wherein the alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in the alloy, respectively.

[0005] Another embodiment is an article for use in a high temperature, oxidative environment, comprising the alloy of the present invention.

[0006] A third embodiment is a method for repairing an article. The method comprises providing an article, providing a repair material comprising the alloy of the present invention, and joining the repair material to the article.

[0007] The invention will now be described in greater detail, by way of example, with reference to the drawing, the single figure of which is an isometric view of an airfoil as typically found on a gas turbine engine component.

[0008] The description herein employs examples taken from the gas turbine industry, particularly the portions of the gas turbine industry concerned with the design, manufacture, operation, and repair of aircraft engines and power generation turbines. However, the scope of the invention is not limited to only these specific industries, as the embodiments of the present invention are applicable to many and various applications that require materials resistant to high temperature and aggressive environments. Unless otherwise noted, the temperature range of interest where statements and comparisons are made concerning material properties is from about 1000°C to about 1300°C. The term "high temperature" as used herein refers to temperatures above about 1000°C.

[0009] The alloy of the present invention balances several competing material requirements, including, for example, cost, strength, ductility, and oxidation resistance. In accordance with one embodiment of the present invention, the alloy comprises, in atom percent, at least about 50% rhodium (Rh), at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof, from about 5% to about 24% ruthenium (Ru), and from about 1% to about 40% chromium (Cr). The alloy comprises less than about 50% by volume of an A3-structured phase, which is a solid solution containing, among other elements, Ru and Cr, and is commonly referred to in the art as "epsilon phase," or ε. The presence of this phase strengthens the alloy at the cost of some ductility. The remainder of the alloy comprises a comparatively ductile A1-structured, or face-centered cubic (FCC) phase. In order to achieve a desirable balance of properties, the composition of the alloy is maintained such that a quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in the alloy, respectively. By adding Pd, Cr, and Ru in the above proportions to Rh, the present inventors have discovered a material having suitable high temperature strength (due to solution strengthening obtained from the alloying elements, and in some cases further strengthening due to the presence of the A3-structured phase) with sufficient ductility (due to the substantial proportion of the A1-structured phase) to be formed into useful shapes. Moreover, the cost of the alloy is reduced by adding these alloying elements to the Rh without reducing the oxidation resistance of the material below required levels. Those skilled in the art will appreciate that Pd is less expensive and less dense than Pt, and so in many applications where weight and cost are important considerations, optimal compositions often minimize the use of Pt in favor of Pd. However, Pt may be used in place of some or all of the Pd addition where very high environmental resistance is desired above all other characteristics.

[0010] The mix of the above properties and others such as modulus of elasticity can be controlled by varying the relative proportions of constituent elements. For example, Cr additions tend to lower the alloy density while increasing the thermal expansion coefficient, and Ru additions tend to increase strength and modulus. Moreover, maintaining the Cr and Ru in accordance with the expression described above controls the amount of A3-structured phase in the alloy, allowing further control over the strength and ductility of the material. In certain embodiments, the alloy comprises, in atom percent, from about 7% to about 20% ruthenium, and from about 1% to about 25% chromium. In particular embodiments, the alloy comprises, in atom percent, from about 8% to about 20% ruthenium, and from about 1% to about 10% chromium. Maintaining alloy composition within these ranges tends to minimize the amount of A3-structured phase, thereby maximizing the ductility, and therefore the formability, of the alloy.

[0011] Alloys set forth herein as embodiments of the present invention are suitable for production using any of the various known methods of metal production and forming. Conventional casting, powder metallurgical processing, directional solidification, and single-crystal solidification are non-limiting examples of methods suitable for forming ingots of these alloys. Thermal and thermo-mechanical processing techniques common in the art for the formation of other alloys, including, for instance, forging and heat treating, are suitable for use in manufacturing and strengthening the alloys of the present invention.

[0012] Another embodiment is an article for use in a high temperature, oxidative environment. The article comprises the alloy described above. The article may be one that has been repaired, or it may be a newly manufactured article. In some embodiments, the article comprises a component of a gas turbine engine, such as, for example, a turbine blade, vane, or a combustor component. Referring to Figure 1, a vane or a blade comprises an airfoil 10, which comprises multiple component sections, including a blade tip 11 (in the case where the component is a blade), a leading edge 12, and a trailing edge 13. The alloy of the present invention may be suitably disposed anywhere on the component, including, in certain embodiments, at one or more of the above component sections. In certain embodiments, the article comprises a coating disposed on a substrate, and the coating comprises the alloy. Having only particular sections (i.e., those sections known to experience the most aggressive stress-temperature combinations) of the airfoil comprise the alloy of the present invention minimizes certain drawbacks of alloys comprising significant amounts of platinum group metals such as, for example, ruthenium, rhodium, and palladium, including their high cost and high density in comparison to conventional airfoil materials. These drawbacks have a reduced effect on the overall component because the comparatively expensive and dense alloy (relative to conventional superalloys) comprises only a fraction of the overall surface area of the component. The properties of the component are thus "tailored" to the expected localized environments, reducing the need for compromise during the design process and increasing the expected operating lifetimes for new and repaired components.

[0013] A further embodiment of the present invention is a method for repairing an article. In this method, an article is provided. The article, in certain embodiments, comprises a component of a gas turbine engine, including, for example, a blade, a vane, or a combustion component. A repair material is provided, and this repair material comprises the alloy described above for previous embodiments of the present invention. This repair material is joined to the article. In some embodiments, joining is accomplished, at least in part, by disposing a coating comprising the repair material onto the article being repaired. Suitable methods for disposing the coating include, for example, thermal spraying, plasma spraying, HVOF spraying, and laser deposition. In other embodiments, the repair material is joined to the substrate by one or more conventional joining processes, including, for example, welding, brazing, or diffusion bonding. Regardless of whether the repair material is in the form of a coating or a solid section, it may be disposed at any section of the article deemed to require the performance characteristics of the repair material. These sections include, for example, the leading and trailing edges of airfoils, and blade tips.

[0014] For the sake of good order, various aspects of the invention are set out in the following clauses:-

1. An alloy comprising, in atom percent:

   at least about 50% rhodium (Rh);
   at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
   from about 5% to about 24% ruthenium (Ru); and
   from about 1% to about 40% chromium (Cr);

   wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively.

2. The alloy of clause 1, comprising in atom percent
   from about 7% to about 20% ruthenium, and
   from about 1% to about 25% chromium.

3. The alloy of clause 1, comprising in atom percent
   from about 8% to about 20% ruthenium, and
   from about 1% to about 10% chromium.

4. An article for use in a high temperature, oxidative environment, said article comprising:

   an alloy comprising, in atom percent,
   at least about 50% rhodium (Rh);
   at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
   from about 5% to about 24% ruthenium (Ru); and
   from about 1% to about 40% chromium (Cr);

   wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively.

5. The article of clause 4, wherein said article comprises a coating disposed on a substrate, and wherein said coating comprises said alloy.

6. The article of clause 4, wherein said article comprises a component of a gas turbine assembly.

7. The article of clause 6, wherein said component comprises at least one of a turbine blade, a turbine vane, and a combustor component.

8. The article of clause 7, wherein said alloy is disposed at at least one component section selected from the group consisting of a leading edge, a trailing edge, and a blade tip.

9. The article of clause 4, wherein said alloy comprises
   from about 7% to about 20% ruthenium, and
   from about 1% to about 25% chromium.

10. The article of clause 4, wherein said alloy comprises
   from about 8% to about 20% ruthenium, and
   from about 1% to about 10% chromium.

11. The article of clause 4, wherein said article comprises a repaired article.

12. A gas turbine engine component comprising:

   an alloy comprising, in atom percent,
   at least about 50% rhodium (Rh);
   at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
   from about 7% to about 20% ruthenium (Ru); and
   from about 1% to about 25% chromium (Cr);

   wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively; wherein said turbine engine component comprises one of a blade and a vane and said alloy is disposed in at least one section of said component selected from the group consisting of a leading edge, a trailing edge, and a blade tip.

13. A method for repairing an article, said method comprising:

   providing an article;

providing a repair material, said repair material comprising, in atom percent,
at least about 50% rhodium (Rh),
at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof,
from about 5% to about 24% ruthenium (Ru), and
from about 1% to about 40% chromium (Cr),

wherein said repair material comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said repair material, respectively; and
joining said repair material to said article.

14. The method of clause 13, wherein said repair material comprises, in atom percent,
from about 7% to about 20% ruthenium, and
from about 1% to about 25% chromium.

15. The method of clause 13, wherein said repair material comprises, in atom percent,
from about 8% to about 20% ruthenium, and
from about 1% to about 10% chromium.

16. The method of clause 13, wherein joining comprises disposing a coating onto said article, said coating comprising said repair material.

17. The method of clause 16, wherein disposing said coating comprises disposing said coating by at least one process selected from the group consisting of thermal spraying, plasma spraying, HVOF spraying, and laser deposition.

18. The method of clause 13, wherein joining comprises at least one of welding, brazing, and diffusion bonding.

19. The method of clause 13, wherein said article comprises a component of a gas turbine engine selected from the group consisting of a blade, a vane, and a combustion component.

20. The method of clause 19, wherein joining comprises disposing said repair material at at least one component section selected from the group consisting of a leading edge, a trailing edge, and a blade tip.

21. A method for repairing a gas turbine engine component, said method comprising:

providing at least one gas turbine engine component selected from the group consisting of a blade, a vane, and a combustion component;
providing a repair material, said repair material comprising, in atom percent,
at least about 50% rhodium (Rh),
at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof,
from about 7% to about 20% ruthenium (Ru), and
from about 1% to about 25% chromium (Cr),

wherein said repair material comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said repair material, respectively; and
joining said repair material to said component by disposing said repair material at at least one component section selected from the group consisting of a leading edge, a trailing edge, and a blade tip.

Claims

1. An alloy comprising, in atom percent:

at least about 50% rhodium (Rh);
at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
from about 5% to about 24% ruthenium (Ru); and
from about 1% to about 40% chromium (Cr);

wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively.

2. The alloy of claim 1, comprising in atom percent
from about 7% to about 20% ruthenium, and
from about 1 % to about 25% chromium.

3. The alloy of claim 1, comprising in atom percent
from about 8% to about 20% ruthenium, and
from about 1% to about 10% chromium.

4. An article for use in a high temperature, oxidative environment, said article comprising:

an alloy comprising, in atom percent,
at least about 50% rhodium (Rh);

at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
from about 5% to about 24% ruthenium (Ru); and
from about 1% to about 40% chromium (Cr);

wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively.

5. The article of claim 4, wherein said article comprises a coating disposed on a substrate, and wherein said coating comprises said alloy.

6. The article of claim 4, wherein said article comprises a component of a gas turbine assembly.

7. The article of claim 6, wherein said component comprises at least one of a turbine blade, a turbine vane, and a combustor component.

8. The article of claim 7, wherein said alloy is disposed at at least one component section selected from the group consisting of a leading edge (12), a trailing edge (13), and a blade tip (11).

9. The article of claim 4, wherein said alloy comprises
from about 7% to about 20% ruthenium, and
from about 1% to about 25% chromium.

10. The article of claim 4, wherein said alloy comprises
from about 8% to about 20% ruthenium, and
from about 1% to about 10% chromium.

11. The article of claim 4, wherein said article comprises a repaired article.

12. A gas turbine engine component comprising:

an alloy comprising, in atom percent,
at least about 50% rhodium (Rh);
at least about 5% of a metal selected from the group consisting of platinum (Pt), palladium (Pd), and combinations thereof;
from about 7% to about 20% ruthenium (Ru); and
from about 1% to about 25% chromium (Cr);

wherein said alloy comprises less than about 50% by volume of an A3-structured phase, and wherein the quantity defined by the expression ([Cr] + 2[Ru]) is in the range from about 25% to about 50%, where [Ru] and [Cr] are the atom percentages of ruthenium and chromium in said alloy, respectively; wherein said turbine engine component comprises one of a blade and a vane and said alloy is disposed in at least one section of said component selected from the group consisting of a leading edge (12), a trailing edge (13), and a blade tip (11).

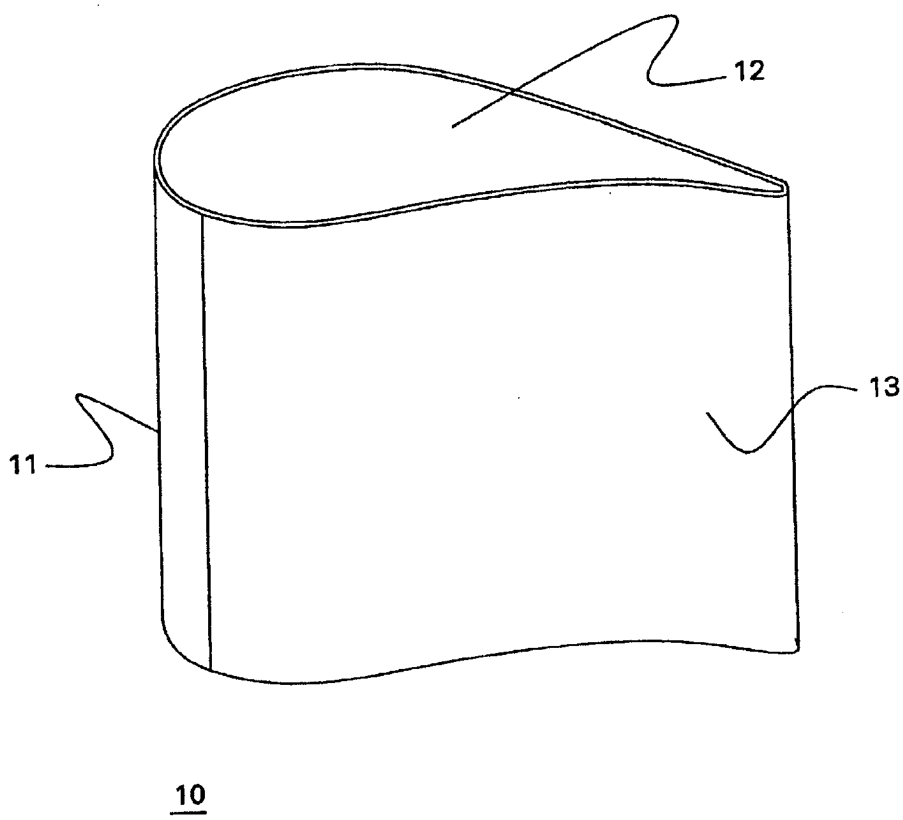

FIG.1

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EUROPEAN SEARCH REPORT

Application Number
EP 04 25 4572

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 6 582 534 B2 (M.R.JACKSON ET AL) 24 June 2003 (2003-06-24) * claims 1,11 * -----	1,4,12	C22C5/04
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	24 November 2004	Gregg, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 04 25 4572

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24-11-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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