



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
31.08.2016 Bulletin 2016/35

(51) Int Cl.:
C22C 38/44 ^(2006.01) **C21D 6/00** ^(2006.01)
C22C 38/52 ^(2006.01)

(21) Application number: **16156815.9**

(22) Date of filing: **23.02.2016**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(71) Applicant: **General Electric Company**
Schenectady, NY 12345 (US)

(72) Inventor: **MAJKA, Theodore Francis**
Greenville, SC South Carolina 29615 (US)

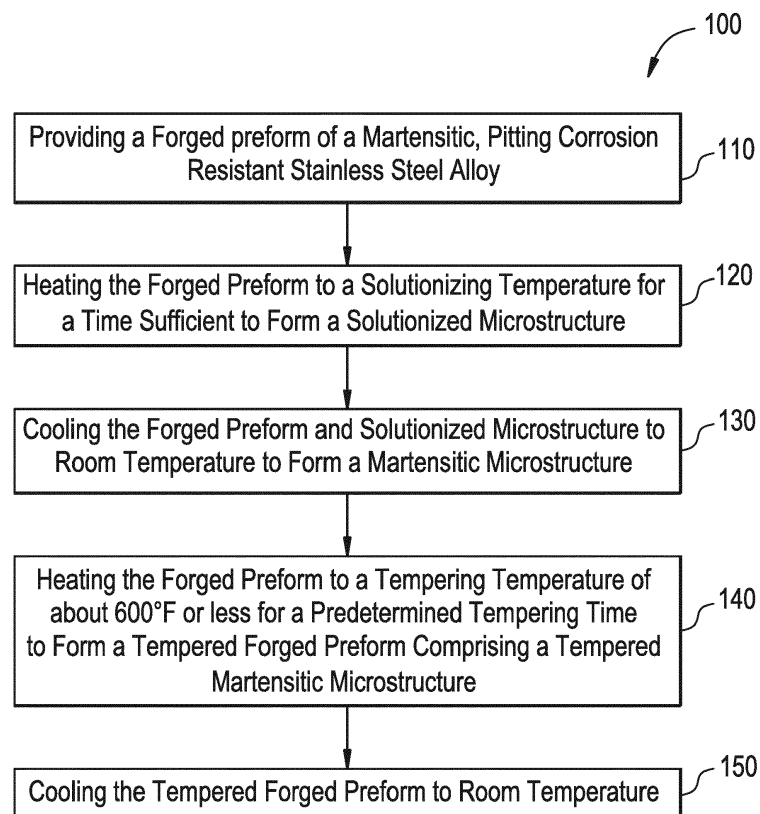
(74) Representative: **Pöpper, Evamaria et al**
General Electric Technology GmbH
GE Corporate Intellectual Property
Brown Boveri Strasse 7
5400 Baden (CH)

(30) Priority: **26.02.2015 US 201514632159**

(54) **CORROSION PITTING RESISTANT MARTENSITIC STAINLESS STEEL**

(57) A forged, martensitic, stainless steel alloy is disclosed. The alloy comprises, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance

iron and incidental impurities. The forged, martensitic, stainless steel alloys are highly resistant to pitting corrosion and provide a combination of tensile strength, ductility, and fracture toughness suitable for use as turbine compressor airfoils.



Description**BACKGROUND OF THE INVENTION**

[0001] The subject matter disclosed herein generally relates to corrosion resistant stainless steels. More particularly, it relates to corrosion pitting resistant, martensitic, stainless steels, including those suitable for turbine rotating components.

[0002] The metal alloys used for rotating components of a gas turbine, particularly the front stage compressor airfoils, including rotating and stationary blades, must have a combination of high strength, toughness, fatigue resistance and other physical and mechanical properties in order to provide the required operational properties of these machines. In addition, the alloys used must also have sufficient resistance to various forms of corrosion and corrosion mechanisms, particularly pitting corrosion, due to the extreme environments in which turbines are operated, including exposure to various ionic reactant species, such as various species that include chlorides, sulfates, nitrides and other corrosive species. Corrosion can also diminish the other necessary physical and mechanical properties, such as the high cycle fatigue strength, by initiation of surface cracks that propagate under the cyclic thermal and stresses associated with operation of the turbine.

[0003] At present, there are no high-strength steels available that sufficiently resist corrosion pitting to survive harsh marine/industrial environments, such as coastal industrial power plants, for more than 2-3 years. Even alloys that are known to have many advantageous corrosion resistance properties, including resistance to intergranular attack, such as 450 and 450+ stainless steel, are still susceptible to corrosion pitting mechanisms. While these martensitic stainless steels have provided a combination of corrosion resistance, mechanical strength and fracture toughness properties sufficient to make them suitable for use in rotating steam and gas turbine components, these alloys are still known to be susceptible to corrosion pitting phenomena. For example, stainless steel airfoils, such as those used in the front stage compressors of industrial gas turbines, have shown susceptibility to corrosion pitting on the surfaces, particularly the leading edge surface, of the airfoil. Without being limited by theory, corrosion pitting is believed to be associated with various electrochemical reaction processes enabled by airborne deposits, especially corrosive species present in the deposits, and moisture from intake air on the airfoil surfaces. Electrochemically-induced corrosion pitting phenomena occurring at the airfoil surfaces can in turn result in cracking of the airfoils due to the cyclic thermal and operating stresses experienced by these components. High levels of moisture can result from various sources, including use in high moisture environments, such as facilities located near oceans or other bodies of water, as well as on-line water washing, fogging, evaporative cooling, or various combinations thereof, to enhance compressor efficiency. Corrosive contaminants usually result from the environments in which the turbines are operating because they are frequently placed in highly corrosive environments, such as those near chemical or petrochemical plants, where various chemical species may be found in the intake air, or those at or near ocean coastlines or other saltwater environments where various sea salts may be present in the intake air, or combinations of the above, or in other applications where the inlet air contains corrosive chemical species.

[0004] In view of the above, stainless steel alloys suitable for use as turbine airfoils, particularly industrial gas turbine airfoils, in the operating environments described and having improved resistance to corrosion pitting are very desirable.

BRIEF DESCRIPTION OF THE INVENTION

[0005] According to one aspect of the invention, a forged, corrosion pitting resistant, martensitic, stainless steel alloy is disclosed. The alloy comprises, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities.

[0006] According to another aspect of the invention, a method of making a forged, martensitic, pitting corrosion resistant, stainless steel alloy is disclosed. The method includes providing a forged preform of martensitic, pitting corrosion resistant stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities. The method also includes heating the forged preform to a solutionizing temperature for a time sufficient to form a solutionized microstructure. The method further includes cooling the forged preform and solutionized microstructure to room temperature to form a martensitic microstructure. Yet further, the method includes heating the forged preform to a tempering temperature of about 600°F for a tempering time sufficient to form a tempered forged preform comprising a tempered martensitic microstructure. Still further, the method includes cooling the tempered forged preform to room temperature.

[0007] These and other advantages and features will become more apparent from the following description taken in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWING

[0008] The subject matter, which is regarded as the invention, is particularly pointed out and distinctly claimed in the claims at the conclusion of the specification. The foregoing and other features, and advantages of the invention are apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

The Figure is a flow chart of an embodiment of a method of making the martensitic stainless alloys disclosed herein.

[0009] The detailed description explains embodiments of the invention, together with advantages and features, by way of example with reference to the drawings.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Corrosion pitting as described above is presently observed in service on front stage compressor airfoils. The corrosion pitting resistant, martensitic, stainless steel alloys described herein provide an iron-based, pitting corrosion resistant material that is a significant enhancement for many heavy marine and industrial applications that are susceptible to corrosion pitting phenomena as described above, including front stage turbine compressor airfoils, in regards to service reliability, reduction of maintenance concerns and costs, and avoidance of unplanned downtime due to airfoil failures. The stainless steel alloys described herein specifically have greater resistance to corrosion pitting than GTD-450 and GTD-450+ stainless steels. Due to the significant operational costs associated with downtime of an industrial gas turbine, including the cost of purchased power to replace the output of the turbine, as well as the maintenance cost of dismantling the turbine to effect repair or replacement of the airfoils and the repair or replacement costs of the airfoils themselves, the enhancements in pitting corrosion resistance of the alloys and methods of making them have significant commercial value. An additional benefit of the corrosion pitting resistant iron-base alloys and methods of making them is that they do not require the addition of separate coatings for pitting corrosion protection. The stainless steel alloys described herein are particularly configured and well suited for forging, particularly the forging of turbine airfoil articles

[0011] In an exemplary embodiment, a forged, martensitic, stainless steel alloy includes, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities. More particularly, the forged, martensitic, stainless steel alloy includes, by weight: about 13.5 to about 14.5 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 6.5 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.30 percent carbon; and the balance iron and incidental impurities. Even more particularly, the forged, martensitic, stainless steel alloy includes, by weight: about 14 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 molybdenum, about 1.0 to about 3.0 percent nickel, about 0.025 carbon; and the balance iron and incidental impurities. The stainless steel alloy composition is selected and configured to provide a martensitic microstructure by heat treatment as described herein. The stainless steel alloy composition is selected and configured to provide a martensitic stainless steel alloy with a minimum tensile strength of about 150 ksi, a molybdenum content of greater than 6%, and a pitting resistance equivalent number, or PREN, of greater than about 31.8. The stainless steel alloys disclosed herein achieve these corrosion and strength properties by a combination of compositional chemistry and heat treatment. For example, the stainless steel alloys disclosed herein exhibit exceptional resistance to corrosion pitting and may be heat treated to provide high strength and fracture toughness suitable for application as early stage turbine compressor airfoils (e.g. stages 1 through stage 5), including both blades and vanes, for industrial gas turbines. In another aspect, the stainless steel alloys described herein obtain strength primarily from the development of a martensitic microstructure and solid solution strengthening in conjunction with the martensitic reaction, while also developing a predetermined amount of retained austenite and substantially no delta ferrite, which in an embodiment also includes no delta ferrite.

[0012] The pitting resistance equivalent number provides a guideline for comparing the pitting corrosion resistance of stainless steel alloys based on alloy chemistry. The higher the PREN the more resistance to pitting corrosion, but there are practical limits to how much the value can be increased before the ability to successfully heat treat the alloy is compromised. The PREN may be calculated using equation 1 below.

$$\text{PREN} = (\% \text{Cr}) + 3.3(\% \text{Mo}) + 16(\% \text{N}) \quad (1)$$

[0013] The martensitic stainless steel alloys described herein have a PREN greater than about 31.8, and more particularly greater than about 33.3. In one embodiment, the PREN ranged from greater than about 31.8 to about 42.4, and more particularly about 33.3 to about 36.0.

[0014] The stainless steel alloys disclosed herein may be described as iron-based alloys comprising five alloy constituents, including Cr, Mo, Co, Ni, and C. All other elements are impurities incidental to the manufacture of stainless steel, and may include, in weight percent, Mn (0.25 max.), Al (0.03 max.), V (0.10 max.), Si (0.25 max.), S (0.005 max.), or P (0.02 max.), for example, and are kept below the maximum prescribed levels described herein to ensure the consistency of properties and microstructure from lot to lot. When balanced within the stated ranges the disclosed stainless steel alloys provide a martensitic microstructure with the desired strength and fracture toughness levels along with corrosion pitting resistance.

[0015] As noted, Cr is a required constituent and will be present in an amount sufficient to form a passive film of chromium oxide on the alloy surface. In one embodiment, Cr is present in an amount of at least about 11.5 weight percent. In another embodiment, Cr is present in an amount of about 12 to about 16 weight percent, and more particularly about 13.5 to about 14.5 weight percent, and even more particularly about 14 weight percent.

[0016] As indicated by equation 1, Mo has a larger effect than Cr on the corrosion pitting resistance of stainless steel. In one embodiment, Mo is present in an amount of about 6.0 to about 8.0 weight percent, and more particularly about 6.0 to about 6.5 weight percent, and even more particularly about 6 weight percent. At least about 6 weight percent is required to ensure sufficient resistance to pitting in marine, chloride environments. Studies have shown that Mo enhances the repassivation capability of stainless steel. Conventional high Mo content stainless steels are typically either ferritic grades or austenitic grades with high Ni levels. Martensitic high Mo content stainless steels grades that have been investigated have generally focused on exploiting the ultra-high strength capabilities present in high-temperature tempered materials and have been designed and heat treated at high tempering temperatures, such as 1,100°F, for use at elevated operating temperatures. However, in these materials corrosion resistance and toughness is sacrificed at the high tempering temperatures due to the precipitation and formation of Mo-rich and Cr-rich intermetallic phases, which deplete the matrix of the corrosion resisting elements Mo and Cr. At high tempering temperatures a secondary hardening effect also occurs due to formation of these intermetallic compounds. The intermetallic phases include the laves phase (Fe_2Mo), Fe_7Mo_6 , FeMo , the sigma phase (Fe-Cr-Mo), and a complex BCC chi phase (Fe-Cr-Mo). Cobalt does not participate in the phases associated with these precipitation reactions. These intermetallic phases also drastically decrease the toughness of the alloy. Thus, martensitic stainless alloys of this invention are tempered at low tempering temperatures as described herein to avoid the precipitation of these intermetallic phases. The tempered alloys are suitable for use in relatively lower temperature applications where corrosion resistance with moderate strength and good toughness are important. The martensitic stainless alloys of this invention balance high Mo additions with the low-tempering temperature region of the hardness vs tempering temperature curve to avoid the formation of intermetallic phases and keep Mo and Cr in solution to maintain a high level as toughness. In one embodiment, the microstructure of the martensitic stainless steel alloys of this invention contains substantially no laves phase, which in an embodiment also includes no laves phase. In another embodiment, the microstructure of the martensitic stainless steel alloys of this invention contains substantially no chi phase, which in an embodiment also includes no chi phase. In yet another embodiment, the microstructure of the martensitic stainless steel alloys of this invention contains substantially no delta ferrite phase, which in an embodiment also includes no delta ferrite phase. In still another embodiment, the microstructure of the martensitic stainless steel alloys of this invention contains substantially no laves phase, chi phase and delta ferrite phase, which in an embodiment also includes no laves phase, chi phase and delta ferrite phase.

[0017] As will also be understood from equation 1, N has a large effect on the PREN, and may optionally be included in the claimed stainless steel materials. However, N is difficult to add in significant amounts in vacuum melted materials. In addition, N can also combine with Cr in the alloy microstructure to form chromium nitrides, which can embrittle and sensitize the stainless steel materials by local depletion of chromium within the alloy microstructure, particularly at the alloy surface, where contact with corrosive species is possible, as described herein. Thus, where present, N will generally be present in amount of 0.02 weight percent or less, and more particularly about 0.001 to about 0.02 weight percent.

[0018] The development of a martensitic microstructure from the martensite transformation requires a high temperature austenitic microstructure. Thus, the composition of the claimed stainless steel alloys will have a high temperature microstructure that includes austenite. Since both Cr and Mo are ferrite stabilizers, consequently, an austenite former is required to balance the phase diagram and develop a high temperature austenite phase to facilitate a martensitic heat treatment and provide the martensitic microstructure, while also developing a predetermined amount of retained austenite and substantially no delta ferrite, which in an embodiment also includes no delta ferrite. Co was selected to stabilize austenite. In one embodiment, Co is present in an amount of about 16.0 to about 20.0 weight percent, and more particularly about 16.5 to about 20.0 weight percent, and even more particularly about 16.5 to about 18.0 weight percent. As an austenite stabilizer, cobalt provides a sufficiently large austenite phase field for temperature and/or time latitude in the heat treatment process. In addition, the effect of Co on the martensite start, M_s , temperature is not as pronounced as that of Ni, providing for the use of standard quench and temper heat treatment protocols.

[0019] Ni is a required constituent and will be present in an amount sufficient to stabilize austenite. Ni is an austenite stabilizer and increases the amount of retained austenite in these alloys. Thus, the amount of Ni should be controlled to provide a predetermined amount of a retained austenite phase in the alloy microstructure. In one embodiment the

predetermined amount of the retained austenite phase comprises at least about 15 percent by volume of the alloy microstructure. In another embodiment, the predetermined amount of retained austenite phase comprises about 15 percent to about 25 percent by volume of the alloy microstructure. In one embodiment, the amount of Ni comprises about 1.0 to about 3.0 weight percent, and more particularly, about 1.0 to about 2.0, and yet more particularly about 1.0 to about 1.5 weight percent. The predetermined amount of retained austenite improves the fracture toughness of the claimed alloys. Ni significantly depresses the M_s temperature and the quantities disclosed herein provide a M_s temperature that is compatible with the heat treatment temperatures and times disclosed herein to provide the desired martensitic structure while also promoting an increased amount of retained austenite. Ni in the amounts described herein also increases the Charpy V-notch toughness of the martensitic stainless steel alloys described herein.

[0020] As noted, C is a required constituent and will be present in an amount sufficient to provide a predetermined hardness and/or a predetermined tensile strength. The amount of C is also selected to avoid the formation of coarse $M_{23}C_6$ carbides. These carbides preferentially nucleate at grain boundaries and cause reduced toughness. Chromium carbides also deplete the matrix surrounding the carbide of chromium, leading to a reduction of corrosion resistance. In one embodiment, C is present in an amount less than about 0.05 weight percent. In another embodiment, C is present in an amount of about 0.020 to about 0.40 weight percent, and more particularly about 0.20 to about 0.30 weight percent, and even more particularly about 0.025 weight percent. In one embodiment, the predetermined hardness is about 30 to about 42 HRC, and the predetermined ultimate tensile strength (UTS) is about 150 to about 200 ksi. The amount of C may be used together with a low temperature tempering heat treatment, as described herein, to provide a predetermined strength and a predetermined fracture toughness that are sufficient for use as turbine airfoil components, including turbine compressor vanes and blades, and more particularly turbine compressor vanes and blades suitable for use in the first through fifth stages of an industrial gas turbine compressor.

[0021] Referring to the Figure, according to another aspect, a method 100 of making a forged, martensitic, pitting corrosion resistant, stainless steel alloy is disclosed. The method 100 includes providing 110 a forged preform of a martensitic, pitting corrosion resistant stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities. The stainless steel alloys can be provided in any suitable manner, including being processed by substantially conventional methods. For example, the alloy may be produced by electric furnace melting with argon oxygen decarburization (AOD) ladle refinement, followed by electro-slag remelting (ESR) of the ingots. Other similar melting practices may also be used. A suitable forming operation, such as various forging methods, may then be employed to produce bar stocks and forging preforms that have a precursor shape of the desired article, including the various articles described herein, such as, for example, turbine compressor airfoils.

[0022] The method 100 also includes heating 120 the forged preform to a solutionizing temperature for a time sufficient to form a solutionized microstructure. In one embodiment, the solutionizing temperature comprises about 2,000 to about 2,100°F and the solutionizing time comprises about 1 to about 3 hours.

[0023] The method further includes cooling 130 the forged preform and solutionized microstructure to room temperature to form a martensitic microstructure. Any suitable method of cooling may be employed that provides a cooling rate sufficient to promote a martensitic transformation of the alloy microstructure. In one embodiment, cooling comprises water, polymer, oil, gas, or air quenching.

[0024] The method also includes heating 140 the forged preform to a tempering temperature of about 600°F or less for a predetermined tempering time sufficient to form a tempered forged preform comprising a tempered martensitic microstructure. Any suitable heating method and tempering time may be employed. In one embodiment, the predetermined tempering time is about 3 to about 6 hours. In one embodiment, the wherein the tempered forged preform comprises a turbine compressor airfoil preform. Still further, the method includes cooling 150 the tempered forged preform to room temperature. Low tempering temperatures, 600°F or less, are utilized to avoid the formation of the precipitates described herein, particularly the embrittling chi and laves phases. It has been shown that when more than 3.5% Mo is present in a 12% Cr steel there is a high-temperature aging reaction based on the precipitation of the laves phase. High Mo contents can also result in the high temperature formation of the intermetallic chi phase which gives rise to brittleness and low tensile ductility. The formation of these compounds result in a dramatic loss in impact resistance. Consequently, the focus will be on solid solution strengthening (from both substitutional elements and interstitial carbon) and low-temperature tempering at a temperature of 600°F or lower. The low temperature tempering also establishes a predetermined maximum operating temperature of these alloys that is less than the tempering temperature, preferably at least about 50 to about 100°F lower than the tempering temperature to avoid subsequent tempering of the martensite and changes to the alloy microstructure. It is desirable to keep as much Cr and Mo as possible in solution to provide corrosion resistance and not have the elements bound in intermetallic compounds or carbides.

[0025] In addition to resistance to pitting corrosion, the martensitic stainless steel alloys disclosed herein have a combination of strength, ductility, and fracture toughness that makes them suitable for use to form various turbine airfoil and other components. In one embodiment, the martensitic stainless steel alloys exhibited better pitting corrosion re-

sistance than GTD-450 and GTD-450+ after salt fog exposure for 500 hours in accordance with ASTM G85, and in another embodiment exhibited substantially no pitting corrosion after 500 hours of exposure in accordance with ASTM G85, which may also be described in an embodiment as no pitting corrosion in conjunction with this salt fog exposure. In another embodiment, the martensitic stainless steels alloys disclosed herein exhibited substantially no pitting corrosion after 1,000 hours of salt fog exposure in accordance with ASTM B117, which may also be described in an embodiment as no pitting corrosion in conjunction with this salt fog exposure. In one embodiment, the martensitic stainless steels alloys have an ultimate tensile strength of about 150 ksi or more, and more particularly about 150 to about 200 ksi. In another embodiment, the martensitic stainless steels alloys have an elongation of at least about 14 percent, and more particularly an elongation of about 14 to about 24 percent. In yet another embodiment, the martensitic stainless steels alloys have a tensile reduction in area of at least about 41 percent, and more particularly about 41 to about 49 percent. In yet another embodiment, the martensitic stainless steels alloys have a Charpy V-notch toughness of about 85 to about 95 J.

[0026] The alloys disclosed herein may be used to form turbine airfoil components, including those used for compressor airfoil components of industrial gas turbines. A typical compressor airfoil in the form of a turbine compressor blade is well known. A compressor blade has a leading edge, a trailing edge, a tip edge and a blade root, such as a dovetailed root that is adapted for detachable attachment to a compressor disk. The span of a blade extends from the tip edge to the blade root. The surface of the blade comprehended within the span constitutes the airfoil surface of the turbine airfoil. The airfoil surface is that portion of the turbine compressor airfoil that is exposed to the flow path of air from the turbine inlet through the compressor section of the turbine into the combustion chamber and other portions of the turbine. While the alloys disclosed herein are particularly useful for use in turbine compressor airfoils in the form of turbine compressor blades and vanes, they are broadly applicable to all manner of turbine compressor airfoils used in a wide variety of components. These include turbine airfoils associated with turbine compressor vanes and nozzles, shrouds, liners and other turbine compressor airfoils, i.e., turbine components having airfoil surfaces such as diaphragm components, seal components, valve stems, nozzle boxes, nozzle plates, or the like. Also, while these alloys are useful for gas turbine compressor blades and vanes, they can potentially also be used for the turbine components of industrial steam turbines, including compressor blades and vanes, steam turbine buckets and other steam turbine airfoil components, oil and gas machinery components, as well as other applications requiring high tensile strength, fracture toughness and resistance to pitting corrosion so long as the operating temperature range of the components is compatible with the predetermined maximum operating temperature of the alloys as described herein.

[0027] 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 items. 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). Furthermore, unless otherwise limited all ranges disclosed herein are inclusive and combinable (e.g., ranges of "up to about 25 weight percent (wt. %), more particularly about 5 wt. % to about 20 wt. % and even more particularly about 10 wt. % to about 15 wt. %" are inclusive of the endpoints and all intermediate values of the ranges, e.g., "about 5 wt. % to about 25 wt. %, about 5 wt. % to about 15 wt. %", etc.). The use of "about" in conjunction with a listing of constituents of an alloy composition is applied to all of the listed constituents, and in conjunction with a range to both endpoints of the range. Finally, unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. 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). Reference throughout the specification to "one embodiment", "another embodiment", "an embodiment", and so forth, means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and may or may not be present in other embodiments.

[0028] It is to be understood that the use of "comprising" in conjunction with the alloy compositions described herein specifically discloses and includes the embodiments wherein the alloy compositions "consist essentially of" the named components (i.e., contain the named components and no other components that significantly adversely affect the basic and novel features disclosed), and embodiments wherein the alloy compositions "consist of" the named components (i.e., contain only the named components except for contaminants which are naturally and inevitably present in each of the named components).

[0029] While the invention has been described in detail in connection with only a limited number of embodiments, it should be readily understood that the invention is not limited to such disclosed embodiments. Rather, the invention can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but which are commensurate with the spirit and scope of the invention. Additionally, while various embodiments of the invention have been described, it is to be understood that aspects of the invention may include only some of the described embodiments. Accordingly, the invention is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

[0030] Various aspects and embodiments of the present invention are defined by the following numbered clauses:

EP 3 061 841 A1

1. A forged, martensitic, stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities.

2. The alloy of clause 1, wherein the alloy comprises about 16.5 to about 20.0 percent cobalt.

3. The alloy of any preceding clause, wherein the alloy has a microstructure that contains substantially no laves phase.

4. The alloy of any preceding clause, wherein the alloy has a microstructure that comprises substantially no chi phase.

5. The alloy of any preceding clause, wherein the alloy has a microstructure that comprises substantially no delta ferrite phase.

6. The alloy of any preceding clause, wherein the alloy has a microstructure that comprises substantially no laves phase, chi phase and delta ferrite phase.

7. The alloy of any preceding clause, wherein the alloy has a microstructure that comprises a retained austenite phase.

8. The alloy of any preceding clause, wherein the retained austenite phase comprises at least about 15 percent by volume of the microstructure.

9. The alloy of any preceding clause, wherein the retained austenite phase comprises about 15 percent to about 25 percent by volume of the microstructure.

10. The alloy of any preceding clause, wherein the alloy is configured to provide a tensile elongation of at least about 14 percent.

11. The alloy of any preceding clause, wherein the elongation is about 14 to about 24 percent.

12. The alloy of any preceding clause, wherein the alloy is configured to provide a tensile reduction in area of at least about 41 percent.

13. The alloy of any preceding clause, wherein the reduction in area is about 41 to about 49 percent.

14. The alloy of any preceding clause, wherein the alloy has a pitting resistance equivalence number of about 31.8 or more.

15. The alloy of any preceding clause, wherein the alloy has an ultimate tensile strength of about 150 ksi or more.

16. The alloy of any preceding clause, wherein the alloy comprises a turbine compressor airfoil.

17. A method of making a forged, martensitic, stainless steel alloy, comprising:

providing a forged preform of martensitic, pitting corrosion resistant stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities;

heating the forged preform to a solutionizing temperature for a time sufficient to form a solutionized microstructure;

cooling the forged preform and solutionized microstructure to room temperature to form a martensitic microstructure;

heating the forged preform to a tempering temperature of about 600°F for a tempering time sufficient to form a tempered forged preform comprising a tempered martensitic microstructure; and

cooling the tempered forged preform to room temperature.

18. The method of any preceding clause, wherein the solutionizing temperature comprises about 2,000 to about 2,100°F and the time comprises about 1 to about 3 hours.

19. The method of any preceding clause, wherein the tempering time is about 3 to about 6 hours.

20. The method of any preceding clause, wherein the tempered forged preform comprises a turbine airfoil preform.

Claims

1. A forged, martensitic, stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities.

2. The alloy of claim 1, wherein the alloy has a microstructure that contains substantially no laves phase.

3. The alloy of claim 1 or 2, wherein the alloy has a microstructure that comprises substantially no chi phase.

4. The alloy of claim 1, 2 or 3, wherein the alloy has a microstructure that comprises substantially no delta ferrite phase.

5. The alloy of claim 1, wherein the alloy has a microstructure that comprises substantially no laves phase, chi phase and delta ferrite phase.

6. The alloy of any preceding claim, wherein the alloy has a microstructure that comprises a retained austenite phase.

7. The alloy of any preceding claim, wherein the alloy has a pitting resistance equivalence number of about 31.8 or more.

8. The alloy of any preceding claim, wherein the alloy comprises a turbine compressor airfoil.

9. A method (100) of making a forged, martensitic, stainless steel alloy, comprising:

providing(110) a forged preform of martensitic, pitting corrosion resistant stainless steel alloy comprising, by weight: about 12.0 to about 16.0 percent chromium; greater than 16.0 to about 20.0 percent cobalt, about 6.0 to about 8.0 percent molybdenum, about 1.0 to about 3.0 percent nickel, about 0.020 to about 0.040 percent carbon; and the balance iron and incidental impurities;

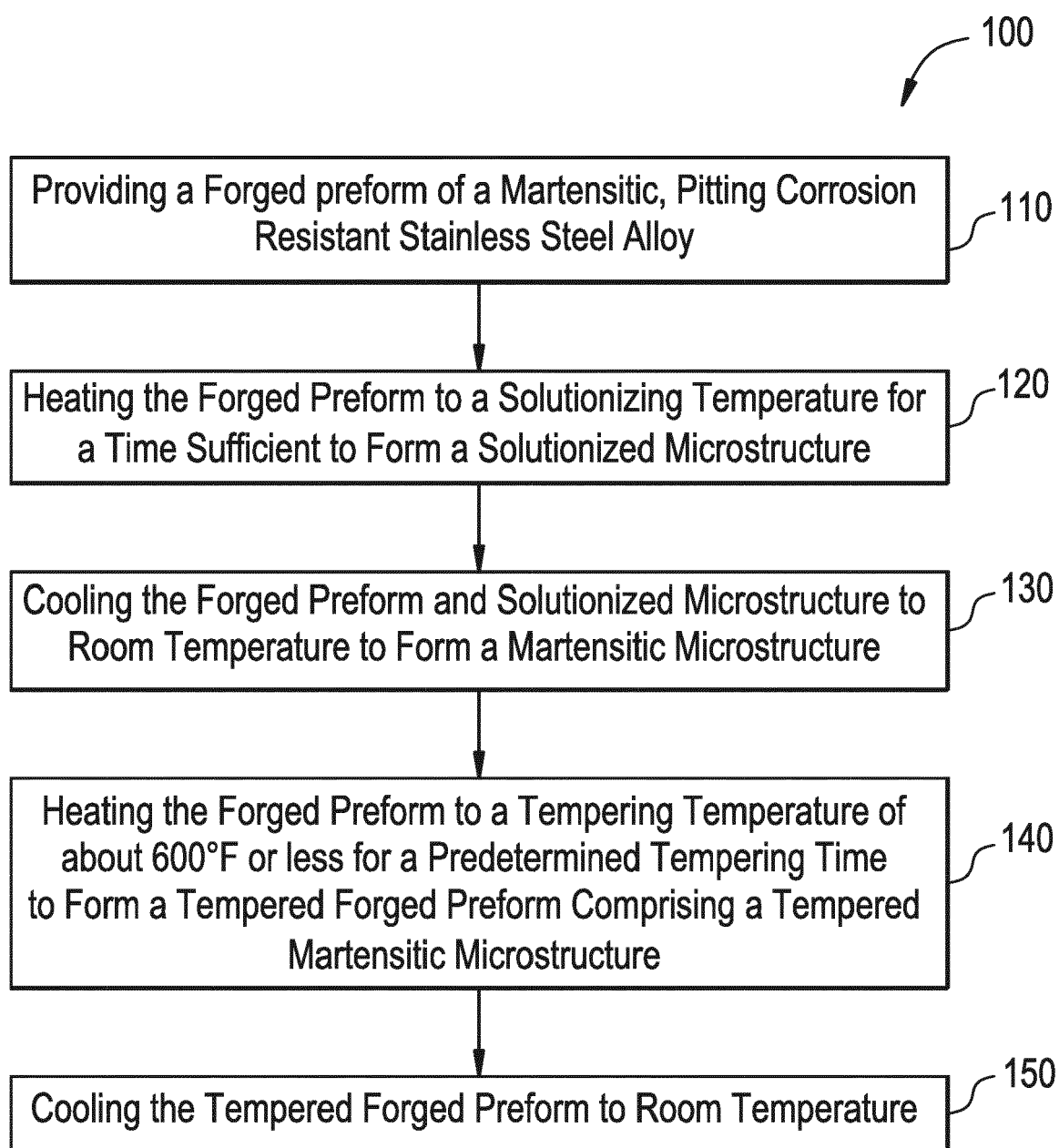
heating (120) the forged preform to a solutionizing temperature for a time sufficient to form a solutionized microstructure;

cooling (130) the forged preform and solutionized microstructure to room temperature to form a martensitic microstructure;

heating (140) the forged preform to a tempering temperature of about 600°F for a tempering time sufficient to form a tempered forged preform comprising a tempered martensitic microstructure; and

cooling (150) the tempered forged preform to room temperature.

10. The method of claim 9, wherein the tempering time is about 3 to about 6 hours.





EUROPEAN SEARCH REPORT

Application Number
EP 16 15 6815

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2009/081068 A1 (GARRISON JR WARREN M [US]) 26 March 2009 (2009-03-26) * paragraphs [0016], [0040] - [0044], [0049], [0054] *	1-10	INV. C22C38/44 C21D6/00 C22C38/52
X	US 2008/277030 A1 (COOPER CLARK V [US] ET AL) 13 November 2008 (2008-11-13) * paragraphs [0009], [0026], [0027], [0029], [0044] * * claims 1,6,13 *	1-10	
X	US 2008/128052 A1 (BENN RAYMOND C [US] ET AL) 5 June 2008 (2008-06-05) * paragraphs [0013], [0016], [0017], [0022], [0023] * * claims 1,4,7 *	1-10	
A	E. ANGELINI ET AL: "Microstructural evolution and localized corrosion resistance of an aged superduplex stainless steel", CORROSION SCIENCE., vol. 46, no. 6, 14 November 2003 (2003-11-14), pages 1351-1367, XP055271606, GB ISSN: 0010-938X, DOI: 10.1016/j.corsci.2003.09.024 * page 1352, line 34 - line 44 *	9	TECHNICAL FIELDS SEARCHED (IPC) C22C C21D F02F
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 May 2016	Examiner Martinavicius, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 16 15 6815

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-05-2016

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009081068 A1	26-03-2009	US 2009081068 A1	26-03-2009
		US 2012000579 A1	05-01-2012
-----		-----	
US 2008277030 A1	13-11-2008	CA 2592420 A1	06-07-2006
		EP 1831408 A2	12-09-2007
		JP 4919968 B2	18-04-2012
		JP 2008525639 A	17-07-2008
		KR 20070095935 A	01-10-2007
		US 2008277030 A1	13-11-2008
		WO 2006071502 A2	06-07-2006
-----		-----	
US 2008128052 A1	05-06-2008	CA 2591093 A1	15-06-2006
		EP 1846585 A2	24-10-2007
		JP 2008523250 A	03-07-2008
		KR 20070086625 A	27-08-2007
		US 2008128052 A1	05-06-2008
		WO 2006063315 A2	15-06-2006
-----		-----	