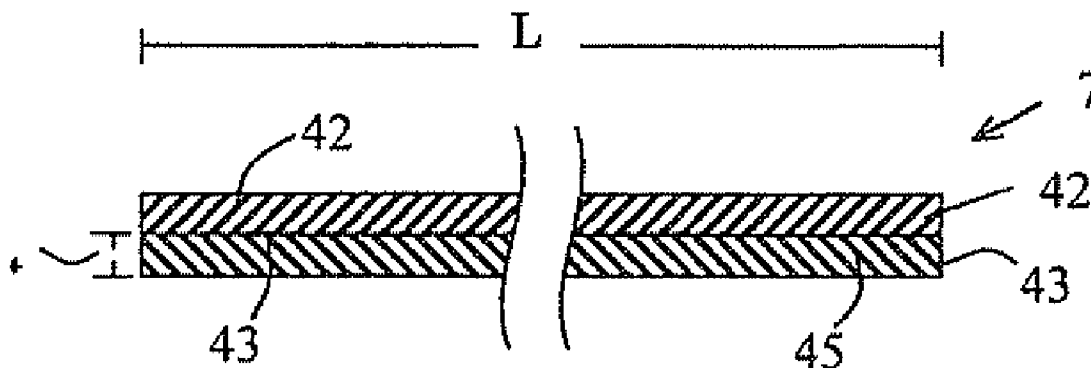




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(19) **United States**(12) **Patent Application Publication****Anada et al.**(10) **Pub. No.: US 2010/0032061 A1**(43) **Pub. Date: Feb. 11, 2010**(54) **METHOD FOR MANUFACTURING A
NI-BASED ALLOY ARTICLE AND PRODUCT
THEREFROM**(76) Inventors: **Hiroyuki Anada**, Nishinomiya-shi
(JP); **Shoji Kinomura**,
Takarazuka-shi (JP); **Noriaki
Hirohata**, Osaka (JP); **Manabu
Kanzaki**, Amagasaki-shi (JP);
Kazuyuki Kitamura, Kobe-shi (JP)Correspondence Address:
CLARK & BRODY
1090 VERMONT AVENUE, NW, SUITE 250
WASHINGTON, DC 20005 (US)(21) Appl. No.: **12/538,385**(22) Filed: **Aug. 10, 2009****Related U.S. Application Data**(63) Continuation-in-part of application No. 11/055,198,
filed on Feb. 4, 2005, now abandoned.**Publication Classification**(51) **Int. Cl.**
C23C 8/10 (2006.01)(52) **U.S. Cl.** **148/281; 148/282; 148/286**(57) **ABSTRACT**

A method for manufacturing a Ni-based alloy article which elutes little Ni even when used in a high-temperature water environment for a long period comprises heating the Ni-based alloy in a carbon dioxide-containing atmosphere for a set period of time at an elevated temperature to form an oxide film comprising chromium oxide on a surface thereof. Using carbon dioxide as an oxidizing gas produces an oxide film of generally uniform thickness along a length of the article being treated so that resistance to nickel elution is more uniform over the entire article.



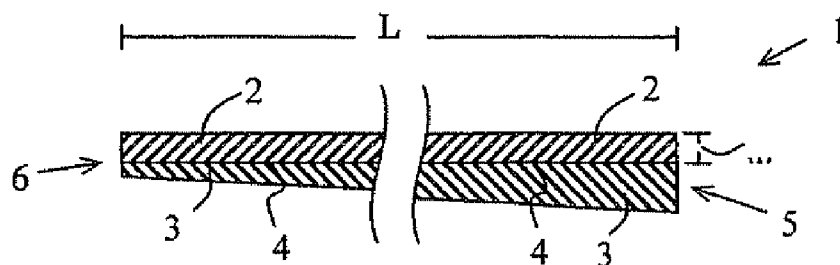


Fig.1
Prior Art

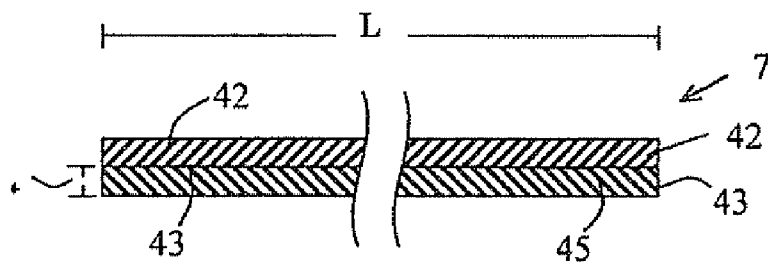


Fig.3

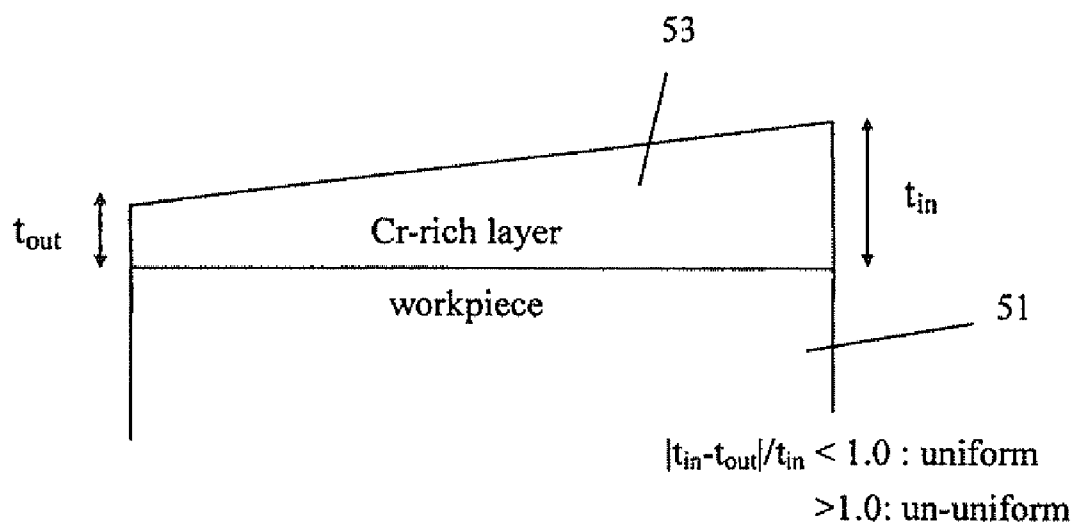


Fig.4

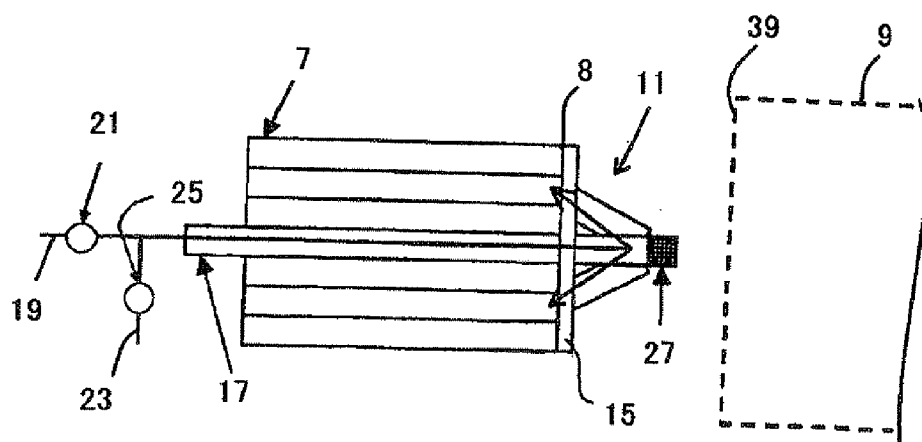


Fig.2A

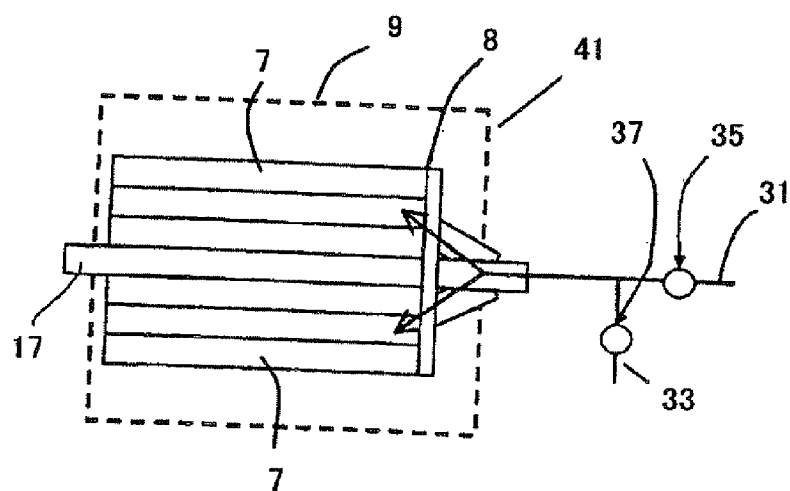


Fig.2B

METHOD FOR MANUFACTURING A NI-BASED ALLOY ARTICLE AND PRODUCT THEREFROM

[0001] This application is a continuation-in-part application of application Ser. No. 11/055,198 filed on Feb. 4, 2005 and which is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to a method for manufacturing a Ni-based alloy which elutes little Ni even when used in a high-temperature water environment for a long period, and particularly to a method for manufacturing the Ni-based alloy suitable for use in a member for a nuclear power plant.

BACKGROUND ART

[0003] It is well known that Ni-based alloys are useful for various kinds of members due to their superior mechanical properties and corrosion resistance. This is particularly so for members such as steam generator tubes used in a nuclear reactor, which are exposed to high-temperature water. For instance, for steam generator components of a pressurized water reactor (PWR), a 60% Ni-30% Cr-10% Fe alloy is used.

[0004] These members are used in the environment of high-temperature water on the order of 300° C. in a nuclear reactor for several years to several tens of years. Although a Ni-based alloy is superior in corrosion resistance and has a low corrosion rate, when used for a long period, a very small amount of Ni can elute from the base metal alloy. This eluted Ni can then be carried to the core of a reactor along with circulating furnace water and irradiated with neutrons in the proximity of the fuel. Then, the irradiated Ni with neutrons is converted to Co through a nuclear reaction. Co has a very long half-value period, and incessantly emits radioactive rays for a long term. Therefore, as the elution amount of Ni increases, the exposed dose of an operator conducting a periodic inspection increases.

[0005] The reduction of the exposed dose is a very important subject for using a light water reactor for a long period. Accordingly, countermeasures have been taken in order to prevent Ni from eluting from a Ni-based alloy, through improving the corrosion resistance of materials and controlling the water quality of the nuclear reactor water.

[0006] One method has been to form an oxide film on the Ni-based alloy tubes. Japanese Patent Laid-Open No. 64-55366 discloses a method for improving uniform corrosion resistance of a heat exchanger tube made of a Ni-based alloy, by annealing it in an atmosphere having the degree of vacuum of 10^{-2} to 10^{-4} Torr at a temperature between 400 and 750° C., and forming an oxide film mainly containing chromium oxide.

[0007] In another method, Japanese Patent Laid-Open No. 8-29571 discloses a method of manufacturing a member for a nuclear power plant by solution-treating a Ni-based precipitation-strengthened alloy, and then heat-treating it in an oxidizing atmosphere of air with 10^{-3} Torr to ambient pressure, while combining the treatment with at least one part of aging treatment and oxide film-forming treatment.

[0008] Two other approaches to form oxide films to resist nickel elution involve the control of the dew point and addition of water vapor during heat treating. In Japanese Patent

Laid-Open No. 2002-121630, a method is disclosed for manufacturing a Ni-based alloy product through heat-treating a Ni-based alloy product in an atmosphere of hydrogen or a mixed gas of hydrogen with argon, having a dew point of -60 to +20° C. In Japanese Patent Laid-Open No. 2002-322553, a method is taught for forming a chromium enriched layer on an alloy workpiece containing Ni and Cr by contacting the workpiece with a gaseous mixture consisting of water vapor and at least one non-oxidizing gas.

[0009] These prior art solutions are not without their shortcomings. For example, the film formed by the method disclosed in Japanese Patent Laid-Open No. 64-55366 has such insufficient thickness such that it tends to be damaged during service for a long period, thus losing the effect of preventing the elution.

[0010] The method disclosed in Japanese Patent Laid-Open No. 8-29571 has such a problem that oxidized Ni is easily taken into a film and the Ni elutes in service.

[0011] The method for forming an oxide film by controlling the amount of water vapor (a dew point) such as the method disclosed in Japanese Patent Laid-Open Nos. 2002-121630 and 8-29571, has difficulty in forming the oxide film consistent from the inlet side of the tube where the treating gas is first introduced to the outlet side where the treating gas exits. In this regard, FIG. 1 shows a cross sectional schematic of a part of such a Ni-based alloy tube **1** having a wall **2** of thickness "w", a length "L", and an oxide film **3** on an inner wall surface **4**. The end **5** of the tube is the end that receives the oxidizing gas first, thus the greater thickness. The opposite end **6** where the gas exits the tube after treatment has a considerably smaller thickness. This smaller thickness zone at the end **6** of the tube creates more opportunity for nickel elution. The reason for this difficulty in the case of continuous treatment for forming an oxide film in a long tube is that the growth rate of the oxide film is limited not only by oxygen potential but also by the diffusibility of an oxidizing gas to the surface of a material to be treated through a concentration boundary layer. Here, the concentration boundary layer means a boundary layer having a concentration gradient of a gas, from the surface of the material to a portion apart from the surface (for instance, the vicinity of the medial axis inside of the tube). The diffusibility is affected by physical properties such as diffusion coefficient and coefficient of kinematic viscosity of a gas, and oxidation treatment conditions such as the concentration and flow rate of the gas. Water vapor (H₂O) has the high diffusibility so that when a long tube is oxidized in a water vapor atmosphere, a long tube hardly has the oxide film consistent from the inlet side of the tube first receiving the treating gas to the outlet side where the treating gas exits.

[0012] As such, there is a need to improve the manner in which protective oxide films are formed on these types of Ni-based alloys, and particularly alloy tubes. The present invention responds to this need by developing a method for forming the oxide film whereby the film has a generally uniform thickness along the length of the article being treated so that elution of nickel during power plant operation is inhibited.

SUMMARY OF THE INVENTION

[0013] The present invention was accomplished for the purpose of solving the problems noted above, and is directed at providing a method for manufacturing a Ni-based alloy having uniform chromium oxide inexpensively formed on the surface.

[0014] The method according to the present invention can form chromium oxide on the surface of a Ni-based alloy so inexpensively and uniformly that the manufactured Ni-based alloy elutes very little Ni even when used in high-temperature water such as in a nuclear power plant for a long time. Accordingly, the Ni-based alloy is most suitable for a member for a nuclear power plant, such as steam generator tubing, and a spacer spring, a coil spring, a finger spring, a channel fastener and a nozzle stub for a lid used in high-temperature water.

[0015] The invention is an improvement over prior art methods of forming oxide films on a surface of a nickel based chromium containing alloy article by subjecting the alloy to an oxidizing treatment at an elevated temperature for a period of time, the oxidizing treatment including the use of an oxidizing gas. According to the invention, an effective amount of carbon dioxide as the oxidizing gas is employed to form the oxide film. The thus-produced oxide film has a generally uniform thickness along a length of the alloy article being treated.

[0016] The oxidizing gas can be entirely carbon dioxide or a mixture of carbon dioxide and one or more of hydrogen, oxygen and an inert gas. More specifically, the concentration of the oxidizing gas can range between 0.009% and 99.9999% by volume of carbon dioxide with the balance being one or more of hydrogen, oxygen and the inert gas. Preferably, the oxidizing gas is a mixture of hydrogen and carbon dioxide, with the carbon dioxide volume percentage ranging between 0.009% and 1.0% by volume with the balance being essentially hydrogen, and even more preferably between 0.009% and 0.50% by volume with the balance being essentially hydrogen.

[0017] The nickel-based chromium containing article is preferably heated to an elevated temperature ranging between 500° and 1,200° C., with a more preferred range being between 1,000 and 1,200° C. The period of time for heating can range between 10 seconds and 35 hours, with a preferred range being between 1 and 10 minutes, and even more preferably 3-5 minutes. The higher the heating temperature, the shorter is the heating time. Accordingly, when a heating-temperature is set in a range of 1,000 to 1,200° C., for instance, a heating time may be in a range of 10 seconds to 60 minutes.

[0018] While virtually any nickel-based chromium containing alloy is believed to be adapted for formation of the oxide film on a given article, and preferred alloy composition comprises, by mass %: 0.15% or less C; 1.00% or less Si; 2.0% or less Mn; 0.030% or less P; 0.030% or less S; 10.0-40.0% Cr; 15.0% or less Fe; 0.5% or less Ti; 0.50% or less Cu; 2.00% or less Al; and the balance Ni with unavoidable impurities.

[0019] While the article can be made of any shape, it is preferred that the article be in tube form, with the inner surface of the tube being treated with the oxidizing gas by its introduction into one end of the tube and removal from the opposite end, thus forming the oxide film with a generally uniform thickness from one end to the opposite end. A measurement of the uniformity of the oxide film can be seen when comparing the change in thickness over the length of a tube being treated. With the alloy article tube having a thickness of the oxide film t_{in} as measured at the opposite end (the end to last receive the oxidizing gas), and a thickness of oxide film t_{out} as measured at the one end (the end to first receive the oxidizing gas), the relationship $|t_{in}-t_{out}|/t_{in}<1.0$ should be satisfied. Measurements using this formula that are equal to or

exceeding 1.0 means that a significant difference in thickness of the oxide film is present. $|t_{in}-t_{out}|/t_{in}$ is preferably 0.5 or less, and further preferably 0.1 or less is present.

[0020] The invention also includes the product of the inventive process. By practicing the invention, a nickel-based chromium containing alloy article such as a tube is made that has an inner surface coated with an oxide film comprising chromium oxide. When the article is a tube, one end of the tube has an oxide film thickness of t_{in} and an opposite end of the tube has an oxide film thickness of t_{out} , and wherein the oxide film thicknesses satisfy the equation $t_{in}-t_{out}/t_{in}<1.0$. The alloy tube can be made of a nickel-based chromium containing alloy suitable for use as a steam generation tube in a nuclear power plant. More particularly, the nickel-based chromium containing alloy comprises, by mass %: 0.15% or less C; 1.00% or less Si; 2.0% or less Mn; 0.030% or less P; 0.030% or less S; 10.0-40.0% Cr; 15.0% or less Fe; 0.5% or less Ti; 0.50% or less Cu; 2.00% or less Al; and the balance Ni with unavoidable impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Reference is now made to the drawings of the invention wherein:

[0022] FIG. 1 is a cross sectional schematic of a prior art Ni-based alloy tube;

[0023] FIGS. 2A and 2B are cross sectional schematics showing the manner of treating Ni-based alloy tubes for oxide film formation according to the invention;

[0024] FIG. 3 is a cross sectional schematic drawing showing an alloy article having a uniform oxide film along its length; and

[0025] FIG. 4 shows a coated workpiece and the formula evidencing variation in oxide film thickness over the length of the workpiece.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0026] The present invention brings a significant improvement to the field of creating oxide films on nickel-based chromium containing alloys and articles, and especially alloy tubes intended for use in steam generation systems. By practicing the invention, the thus-formed oxide film is created in a more uniform manner along the length of the article being treated. Thus, the benefits of the oxide film, especially resistance to elution of nickel, are realized across the length of the article being treated. Moreover, the manufacturing process is improved because the oxidizing gas as carbon dioxide is non-toxic, nonflammable, and inexpensive to use.

[0027] Here, "oxide film comprising chromium oxides" means an oxide film mainly containing Cr_2O_3 , but may contain oxides other than Cr_2O_3 , such as oxides of $MnCr_2O_4$, TiO_2 , Al_2O_3 and SiO_2 . In addition, so far as the Ni-based alloy has the oxide film comprising chromium oxides on the surface, the alloy may have other oxides layers formed on the upper layer (the outside layer) and/or the lower layer (the inside layer) of the chromium oxide layer.

[0028] As is known in the art, these Ni-based alloy tubes are made using a number of steps, including casting, forming the cast product as an ingot into a seamless tube or pipe by hot working, including forging and/or extrusion. After hot working the ingot into pipe or tube form, additional steps including cold working, e.g., drawing and/or pilgering are conducted. The cold worked tube is then subjected to annealing and other

thermal treatments to form the finished product. These methods and apparatus are clearly disclosed in the cited prior art discussed above, and a more detailed description of the various stages of manufacture are not deemed necessary for understanding of the invention. Also, and while tubes are exemplified herein, any shaped article and its associated manufacturing process is deemed within the scope of the invention.

[0029] Unlike the prior art processes above that employ water vapor as the oxidizing agent, the present invention uses carbon dioxide in effective amounts for oxide film formation. The present invention in terms of treatment is also believed to be adaptable for any shapes of nickel-based chromium containing articles that require an oxide film for corrosion and other types of protection, wherein the articles are subjected to heat treating under an oxidizing gas as the carbon dioxide for a set period of time to form the desired oxide film. A preferred article to form the oxide film is seamless tubes and a preferred stage for treatment is annealing following cold working. The inventive method can form chromium oxide on the surface of a Ni-based alloy article so inexpensively and uniformly that the manufactured Ni-based alloy article elutes very little nickel even when used in high-temperature water such as in a nuclear power plant for a long time. Accordingly, the Ni-based alloy is most suitable for a member for a nuclear power plant, such as steam generator tubing, and a spacer spring, a coil spring, a finger spring, a channel fastener and a nozzle stub for a lid used in high-temperature water.

[0030] The invention in its broadest sense involves the heat treatment of a nickel-based chromium-containing alloy article to form an oxide film on a surface thereof. The heat treatment involves the steps of heating the article to within a temperature range of 500 to 1200° C. for a period of time in a controlled atmosphere containing an effective amount of carbon dioxide as an oxidizing agent so as to produce an oxide film containing chromium oxides on the surface of the article being treated. Preferably, the heat treatment is the annealing step in the manufacture of Ni-based alloy seamless tubes, one that is typically done in a hydrogen atmosphere. The atmosphere, the heat treatment temperature and time, and the type of alloys to be used are discussed below by their respective headings.

Atmosphere for Heat Treatment

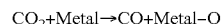
[0031] The controlled atmosphere that the Ni-based alloy article is subjected to is an oxidizing atmosphere. Unlike the prior art methods that use water or control of the dew point to form the oxide film, the present invention employs an oxidizing atmosphere that contains an effective amount of carbon dioxide. The effective amount of carbon dioxide is considered to be an amount, when present with the article being treated, that forms an oxide film containing chromium oxides on the article surface. The use of the effective amount of carbon dioxide also produces the oxide film in a thickness that is generally uniform along the length of the article being treated.

[0032] The effective amount of carbon dioxide can be combined with one or more other gases to make up the heat treating atmosphere, or it can constitute virtually the entire atmosphere aside from impurities. For example, the oxidizing gas can be 100% carbon dioxide or a mixture of carbon dioxide and one or more of hydrogen, an inert gas, e.g., argon or helium, or oxygen as a supplemental oxidizer. More specifically, the Ni-based alloy article can be heated in the atmosphere of carbon dioxide or in the atmosphere of a mixed gas

that would contain carbon dioxide in a range of 0.009% to 99.9999% by volume with the balance being one or more of hydrogen, an inert gas, and 5 vol. % or less oxygen gas. Here, in the case of adding oxygen gas, a countermeasure has to be considered for safety in order not to react hydrogen with oxygen and cause explosion.

[0033] As noted above, heating the alloy article in such an atmosphere results in creation of an oxide film comprising chromium oxide formed on the surface. When the atmosphere contains less than 0.009 vol. % carbon dioxide, the oxide film comprising chromium oxide may be insufficiently formed. Since the atmosphere can be all carbon dioxide, there is no upper limit to the carbon dioxide amount.

[0034] Carbon dioxide gas in a high-temperature atmosphere has an effect of forming an oxide film comprising chromium oxide on the surface of a Ni-based alloy article. Specifically, in an atmosphere comprising carbon dioxides, as shown in the following reaction formula, CO₂ adsorbs to a Ni-based alloy, and then a Ni-based alloy directly takes O (oxygen) therein from CO₂ to form chromium oxide.



[0035] As described above, the prior art discloses a method for forming an oxide film by heating a Ni-based alloy under a water vapor atmosphere, wherein the atmosphere enters a tube from one end and exits the tube from its other end. However, this method has difficulty in forming an oxide film consistent from the inlet side to the outlet side of water vapor, or along the length of the article being treated.

[0036] However, because the diffusibility of carbon dioxide is lower than that of water vapor, the thickness of a formed oxide film is hardly affected by oxidation conditions such as the concentration and flow rate of a supplied gas. As a result of this, oxidation treatment in the carbon dioxide atmosphere can form a more consistent oxide film on the surface of an alloy than that in a conventional atmosphere of water vapor. Another merit of using carbon dioxides includes producing a desired oxidation atmosphere more inexpensively than a method of controlling the concentration of water with a conventional dew point generator.

[0037] As stated above, care must be taken if the atmosphere is to contain hydrogen and oxygen for the obvious explosion potential. Consequently, a preferable atmosphere for heat treatment is a mixed gas atmosphere comprising carbon dioxide with the balance hydrogen gas and/or a rare/inert gas. Then, there is no need to consider the reaction of hydrogen and oxygen for the mixed gas, and furthermore, by adjusting the concentration of the mixed gas, the concentration of the carbon dioxide contributing to the oxidation of a Ni-based alloy can be appropriately controlled and the composition and the thickness of an oxide film can be appropriately controlled. Particularly, hydrogen gas is industrially often used as an atmospheric gas for heat treatment, so that the use of it for diluting carbon dioxides can reduce manufacturing costs. Accordingly, it is most preferable for heat-treating the Ni-based alloy under an atmosphere of a mixed gas comprising carbon dioxide with the balance hydrogen gas. In the preferred atmosphere of the heat treatment, the concentration of the carbon dioxide is preferably 50 vol. % or less, and most preferably is 10 vol. % or less. Even more preferred levels include carbon dioxide levels of 1.0 vol. % or less, with a target of even less carbon dioxide, less than 0.5 vol. %.

[0038] Referring now to FIGS. 2A and 2B, an exemplary arrangement is disclosed showing how a Ni-based alloy tube

is heat treated with carbon dioxide as the oxidizing gas to form the oxide film. A number of alloys tubes 7 are bundled together for entry into a heat treating furnace 9. A manifold 11 is provided that has a number of openings (not shown) in the plate 15, with each opening aligning with an open and leading end 8 of each tube 7. The manifold 11 also has a supply pipe 17 which connects to a source of oxidizing gas, in this case, hydrogen via hydrogen gas supply line 19 and controller 21, and carbon dioxide gas via supply line 23 and controller 25. The manifold 11 is also equipped with a plug 27 that seals another manifold opening, and its use is explained below.

[0039] In operation, the tubes 7 are fed into the annealing furnace 9 with the oxidizing gas as a controlled mix of hydrogen and carbon dioxide flowing into the leading ends 8 of the tubes 7 first entering the furnace. The furnace is also supplied with hydrogen gas to shield the outside of the tubes 7 from oxidation, as is practiced in the prior art. Referring to FIG. 2B, as the manifold 11 attached to the leading ends 8 of the tubes 7 exits the furnace 9, and the plug 27 is removed, and hydrogen and carbon dioxide is supplied by connecting the carbon dioxide supply line 31 and its controller 35, and the hydrogen supply line 33 and its controller 37 to the manifold as it emerges from the furnace 9. Since the furnace is typically too long to accommodate the supply pipe 17, the source of the oxidizing gas is switched from the entrance end of the furnace 39 to the exit end 41.

[0040] FIG. 3 shows a typical tube after heat treatment with carbon dioxide as the oxidizing gas. The tube 7 has a wall 42 with an inner surface 43, the inner surface 43 having an oxide film 45. The thickness "t" of the film is generally uniform along the length of the tube 7, a vast improvement over the uneven thickness of the prior art films as shown in FIG. 1.

Heat Treatment Temperature and Heat Treatment Time

[0041] Heating Temperature

[0042] The alloy article should be subjected to an elevated temperature so as to produce the appropriate thickness and composition of an oxide film on a surface of the article being heated, and impart the appropriate strength to the article itself. It is preferred that this range be between 500 and 1,200° C. When the heating temperature is lower than 500° C., the oxidation of chromium can be insufficient, but when exceeding 1,200° C., the strength of the Ni-based alloy may not be ensured. A more preferred range is 1,000 to 1,200° C., with a target of around 1,100° C.

[0043] Heating Time

[0044] The alloy article should be subjected to the elevated temperature for a time sufficient to give the alloy article the appropriate thickness and composition of an oxide film. Specifically, the alloy is preferably heated for 10 seconds or longer in order to form the oxide film mainly containing chromium oxide, but if the alloy is heated for 35 hours or longer, the oxide film does not grow any more. Consequently, the heating time is preferably in a range of 10 seconds to 35 hours, with a more preferred range of 1-10 minutes and even more preferred range of 3-5 minutes.

[0045] The higher the heating temperature, the shorter is the heating time. Accordingly, when a heating temperature is set in a range of 1,000 to 1,200° C. for instance, a heating time may be in a range of 10 seconds to 60 minutes.

[0046] As described above, by appropriately adjusting the conditions of a heating temperature, a heating time and a gas concentration, the thickness and composition of an oxide film can be adjusted as would be known to those of skill in the art.

For example, to increase the thickness of the oxide film, one would increase the carbon dioxide concentration of the gas, if it is a mixture of carbon dioxide and one or more other gases.

Ni-Based Alloy to be Treated

[0047] It is believed that any nickel-based alloy that contains chromium is adaptable for the formation of a protective oxide film using carbon dioxide as the oxidizing gas under conditions of elevated temperature and sufficient time. An example of the Ni-based alloy used in the manufacturing method of the present invention comprises, by mass %: 0.15% or less C; 1.00% or less Si; 2.0% or less Mn; 0.030% or less P; 0.030% or less S; 10.0-40.0% Cr; 15.0% or less Fe; 0.5% or less Ti; 0.50% or less Cu; 2.00% or less Al; and the balance Ni with impurities. Reasons for limiting each element will be now described below. In addition, "%" on content means "mass %" in the following discussion.

[0048] C: 0.15% or less

[0049] More than 0.15% C contained in the alloy may cause the lowering of stress corrosion cracking resistance. Accordingly, when C is added, the content is preferably controlled to 0.15% or less, and further preferably to 0.06% or less. On the other hand, C has an effect of increasing the strength of grain boundaries in an alloy. In order to acquire the effect, the content of C is preferably 0.01% or more.

[0050] Si: 1.00% or less

[0051] Si is used as a deoxidizing material in nickel manufacture and remains as an impurity in an alloy. Thus, the content needs to be limited to 1.00% or less. When the Si content exceeds 0.50%, the cleanliness factor of the alloy can be decreased, so that the Si content is preferably limited to 0.50% or less.

[0052] Mn: 2.0% or less

[0053] Because Mn exceeding 2.0% lowers the corrosion resistance of an alloy, the content is preferably controlled to 2.0% or less. Mn has a lower free energy of formation for the oxide than Cr, so that Mn is precipitated as $MnCr_2O_4$ by heating. In addition, Mn has such a comparatively high rate of diffusion that Cr_2O_3 normally forms in the vicinity of a base metal by heating with precedence, and $MnCr_2O_4$ forms as an upper layer on the outside of it. If $MnCr_2O_4$ layer exists, it protects a Cr_2O_3 layer in a service environment, and even when the Cr_2O_3 layer is disrupted by some reason, $MnCr_2O_4$ promotes the restoration of the Cr_2O_3 layer. Such an effect becomes remarkable when 0.1% or more Mn is contained. Consequently, desirable Mn content is 0.1 to 2.0%, and further desirably is 0.1 to 1.0%.

[0054] P: 0.030% or less

[0055] P is an element existing as an impurity in an alloy. P content exceeding 0.030% may exert an adverse effect on corrosion resistance. Accordingly, P content is preferably limited to 0.030% or less.

[0056] S: 0.030% or less

[0057] S is an element existing as an impurity in the alloy. When the content exceeds 0.030%, S may exert adverse effect on corrosion resistance. Accordingly, S content is preferably limited to 0.030% or less.

[0058] Cr: 10.0 to 40.0%

[0059] Cr is a necessary element for forming an oxide film comprising chromium oxide. In order to form such an oxide film on the surface of the alloy, the content is preferably 10.0% or more. However, when the content exceeds 40.0%,

Ni content becomes relatively low, so that the corrosion resistance of the alloy may be lowered. Accordingly, Cr content is preferably 10.0 to 40.0%.

[0060] Fe: 15.0% or less

[0061] When Fe content is more than 15.0%, it may impair the corrosion resistance of the Ni-based alloy, so that Fe shall be 15.0% or less. In addition, Fe is an element which is dissolved in Ni and is usable as a substitute for a part of expensive Ni, so that 4.0% or more Fe is desirably contained.

[0062] Ti: 0.5% or less

[0063] A Ti content exceeding 0.5% may reduce cleanliness of an alloy, so that the content is desirably controlled to be 0.5% or less, and further desirably to 0.4% or less. However, from the viewpoint of improving the workability of the alloy and inhibiting grain growth in welding, 0.1% or more Ti is preferably contained.

[0064] Cu: 0.50% or less

[0065] Cu is an element existing as an impurity in the alloy. If the content exceeds 0.50%, the corrosion resistance of the alloy can be lowered. Accordingly, Cu content is desirably limited to 0.50% or less.

[0066] Al: 2.00% or less

[0067] Al is used as a deoxidizing material in nickel manufacture and remains as an impurity in an alloy. Remaining Al forms an oxide-based inclusion in the alloy, reduces the cleanliness of the alloy, and may exert an adverse effect on the corrosion resistance and mechanical properties of the alloy. Accordingly, Al content is desirably limited to 2.00% or less.

[0068] The above described Ni-based alloy has only to include the above described elements and the balance Ni with impurities, but Nb, Ta and Mo may be appropriately added in order to improve characteristics such as corrosion resistance and strength.

[0069] Nb and Ta: 3.15-4.15% element or in total

[0070] Nb and Ta form carbides so easily that they are effective for improving the strength of the alloy. In addition, they have an effect of fixing C in the alloy, so that they inhibit a shortage of Cr in grain boundaries and improve the corrosion resistance of grain boundaries. Accordingly, one or both of these elements had better be contained. The above described effect becomes remarkable, when either one element is 3.15% or more for the alloy containing the one element, or when the total content is 3.15% or more for the alloy containing both elements. However, the excessive content of Nb and/or Ta may impair hot workability and cold workability, and may increase susceptibility to heating embrittlement. Accordingly, the content of one element for the alloy which contains the one element, or the total content of the elements for the alloy which contains both elements, is preferably controlled to 4.15% or less. After all, the content of one element or both elements of Nb and Ta is desirably controlled to 3.15 to 4.15%.

[0071] Mo: 8-10%

[0072] Mo is effective in improving pitting corrosion resistance, so that it may be contained as needed. The above described effect becomes remarkable when the content is 8% or more, but when it exceeds 10%, intermetallic compounds precipitate and may lower corrosion resistance. After all, the content of Mo, when added, is desirably controlled to 8 to 10% in the case.

[0073] The above described Ni-based alloys are typically two kinds described below.

[0074] (a) A Ni-based alloy comprising 0.15% or less C, 1.00% or less Si, 2.0% or less Mn, 0.030% or less P, 0.030% or less S, 14.0-17.0% Cr, 6.0-10.0% Fe, 0.5% or less Ti, 0.50% or less Cu, 2.00% or less Al, and the balance Ni with impurities.

[0075] (b) A Ni-based alloy comprising 0.06% or less C, 1.00% or less Si, 2.0% or less Mn, 0.030% or less P, 0.030% or less S, 27.0-31.0% Cr, 7.0-11.0% Fe, 0.5% or less Ti, 0.50% or less Cu, 2.00% or less Al, and the balance Ni with impurities.

[0076] The alloy (a) includes Cr of 14.0 to 17.0% and Ni of about 75% and has superior corrosion resistance in a chloride-containing environment. In the alloy, Fe content is desirably controlled to 6.0 to 10.0%, from the viewpoint of a balance between the contents of Ni and Cr.

[0077] The alloy (b) includes 27.0 to 31.0% Cr and about 60% Ni, so that it has superior corrosion resistance not only in a chloride-containing environment, but also in high-temperature pure water and an alkaline environment. In this alloy as well, Fe content is desirably controlled to 7.0-11.0% from the viewpoint of a balance between the contents of Ni and Cr.

Comparative Investigation

[0078] In order to demonstrate the improvements in oxide film thickness uniformity when practicing the invention, an alloy tube was subjected to different oxidizing atmospheres and evaluated for oxide film thickness. A Ni-based alloy having the following composition in mass % was employed as part of the testing: C: 0.019, Si: 0.32, Mn: 0.31, P: 0.011, S: 0.001, Cr: 29.80, Fe: 9.1, Ti: 0.21, Cu 0.014, Al: 0.15, with the balance nickel and unavoidable impurities. A tube was manufactured into the dimension with a diameter of 20 mm, a wall thickness of 1.5 mm and a length of 20 m. Then, the tube was continuously heat-treated in a heating furnace.

[0079] During continuous heat treatment, three different gas compositions were used, one with 0.300 vol. % carbon dioxide with the balance hydrogen (condition No. 1), one with 0.150 vol. % carbon dioxide with the balance hydrogen (condition No. 2), and one with 0.8610 vol. % H₂O with the balance hydrogen (condition No. 3). The tubes were heated in a furnace having a temperature of 1,100° C. for 300 seconds with the gas being passed through the tube to form an oxide film on the inner surface of the tube. The film compositions of both ends cut out from the tube after heat treatment were examined with EDX (Energy Dispersive X-ray micro-analyzer), and the result proved that an oxide film comprising chromium oxide was formed on any tube.

[0080] The thickness of an oxide film is measured by observing the cross section with a scanning electron microscope (SEM; Scanning Electron Microscope), and the dispersion of the thickness was evaluated as $|t_{in} - t_{out}|/t_{in}$, where t_{in} is the oxide film thickness in the upstream side of a gas flow and t_{out} is the oxide film thickness in the downstream side. To relate the testwork to a continuous operation, t_{in} would represent the trailing end of the tubes passing through the furnace that are the last area to see the oxidizing gas whereas t_{out} is the end of the tube that first sees the oxidizing gas. FIG. 4 is a representation of the thickness analysis with showing the workpiece 51 and oxide film 53 as a chromium-rich layer on its surface, with a non-uniform thickness as would be found in the prior art.

[0081] Oxide films formed in the conditions for the shown in Nos. 1 and 2 with the use of CO₂ as an oxidizing gas, showed dispersions as 0.05 and 0.17, whereas the oxide film formed in condition No. 3 with the use of H₂O, showed the dispersion of 3.00, which was quite large compared to the case with the use of CO₂. What this means is that the oxide film formed with H₂O as the oxidizing gas showed a large variation in thickness from one end of the tube to the other end. In contrast, the difference between the thicknesses on the opposite ends of the tube treated according to the invention showed hardly any difference, thus indicating a generally uniform thickness along the length of the tube.

[0082] Additional experiments were conducted using other levels of CO₂. Table 1 shows the composition of the Ni-based alloy being tested, with the temperature, time, and analysis method.

TABLE 1

Ni-based alloy composition	C: 0.019, Si: 0.32, Mn: 0.31, P: 0.011, S: 0.001, Cr: 29.80, Fe: 9.1, Ti: 0.21, Cu: 0.014, Al: 0.15, with the balance nickel and inevitable impurities ¹
Temperature	1100° C.
Time	300 seconds
Analysis Method	EDX, SEM

¹This composition coincides with the composition used in the CO₂ film formation testing described above.

[0083] Table 2 shows the results of the investigation of forming the chromium oxide film using different gas compositions.

TABLE 2

Test No.	CO ₂ Flow L/min	H ₂ Flow L/min	CO ₂ Vol. %	Tube specifications				
				Dispers. as Dispers.	Dispers. 20 mm	Diameter (mm)	Wall Thickness (mm)	Length (meters)
W-1	0.04	12	0.332	0.08		19	1	4
W-2	0.04	3	1.316	0.08		19	1	4
W-3	0.2	33.3	0.597		0.67	19	1	20
W-4	0.01	33.3	0.030		<0.01	19	1	20
W-5	0.003	33.3	0.009		<0.01	19	1	20

It is evident from Table 2 that a gas composition consisting of hydrogen and carbon dioxide forms an oxide film for a wide range of CO₂ vol. % when CO₂ is combined with hydrogen. This range extends as low as 0.009 vol. % CO₂ with the balance hydrogen. This result would also be expected when the remaining gas would be other gases such as an inert gas, a gas having 5 vol. % or less of oxygen, or one or more of these gases in combination, with hydrogen.

INDUSTRIAL APPLICABILITY

[0084] The method according to the present invention can inexpensively form uniform chromium oxide on the surface of a Ni-based alloy, so that it can manufacture a Ni-based alloy which elutes extremely little Ni even when used in a high-temperature water environment such as in a nuclear power plant, for a long time. Accordingly, the Ni-based alloy is most suitable for members of a nuclear power plant, such as steam generator tubing, and a spacer spring, a coil spring, a finger spring, a channel fastener and a nozzle stub for a lid used in high-temperature water.

[0085] As such, an invention has been disclosed in terms of preferred embodiments thereof which fulfills each and every one of the objects of the present invention as set forth above and provides a new and improved method of manufacturing Ni-based alloy articles, and a product therefrom.

[0086] Of course, various changes, modifications and alterations from the teachings of the present invention may be contemplated by those skilled in the art without departing from the intended spirit and scope thereof. It is intended that the present invention only be limited by the terms of the appended claims.

We claim:

1. A method of forming an oxide film comprising chromium oxide on a surface of a nickel-based chromium containing alloy article, the oxide film formed by carbon dioxide in contact with the surface, the method including subjecting the alloy to an oxidizing treatment at an elevated temperature for a period of time, the oxidizing treatment including the use of an oxidizing gas, wherein an effective amount of the carbon dioxide is provided as the oxidizing gas to form the oxide film, the oxide film having a generally uniform thickness along a length of the alloy article being treated, wherein the nickel-based chromium containing alloy comprises, by mass %: 0.15% or less C; 1.00% or less Si; 2.0% or less Mn; 0.030% or less P; 0.030% or less S; 10.0-40.0% Cr; 4.0-15.0% Fe; 0.5% or less Ti; 0.50% or less Cu; 2.00% or less Al; and the balance Ni with unavoidable impurities, wherein the oxidizing gas consisting of a mixture of the effective amount of carbon dioxide gas with one or more of hydrogen, 5 vol. %

or less oxygen, and an inert gas, wherein the concentration of the oxidizing gas ranges between 0.009 and 99.9999% by volume of carbon dioxide.

2. The method of claim 1, wherein the oxidizing gas comprises a mixture of hydrogen and carbon dioxide.

3. The method of claim 1, wherein the concentration of the carbon dioxide is between 0.009% and 1.0% by volume.

4. The method of claim 1, wherein a remainder of the oxidizing gas is hydrogen.

5. The method of claim 1, wherein the elevated temperature ranges between 500° C. and 1,250° C.

6. The method of claim 1, wherein the period of time ranges between 10 seconds and 35 hours.

7. The method of claim 1, wherein the alloy article is a tube, the surface is an inner surface of the tube, and the oxidizing gas is introduced into one end of the tube and removed from an opposite end.

8. The method of claim 7, wherein the alloy article tube has a thickness of the oxide film t_{in} as measured at the opposite end, and a thickness of oxide film t_{out} as measured at the one end, and $|t_{in}-t_{out}|/t_{in}<1.0$.

9. The method of claim **1**, wherein the alloy article is made of a nickel-based chromium containing alloy suitable for a member for a nuclear power plant.

10. The method of claim **9**, wherein the member for nuclear power plant is a steam generator tube.

11. The method of claim **1**, wherein the effective amount of carbon dioxide as the oxidizing gas is provided in a controlled manner.

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