(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 647 609 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
19.04.2006 Bulletin 2006/16

(21) Application number: **05256349.1**

(22) Date of filing: **13.10.2005**

(51) Int Cl.:
C22F 1/00 $^{(2006.01)}$ *C22F 1/10* $^{(2006.01)}$
C23C 8/16 $^{(2006.01)}$ *C22F 1/02* $^{(2006.01)}$
C21D 1/76 $^{(2006.01)}$ *C22C 19/05* $^{(2006.01)}$

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(30) Priority: **13.10.2004 JP 2004298835**

(71) Applicant: **SUMITOMO METAL INDUSTRIES, LTD.**
Osaka-shi,
Osaka 541-0041 (JP)

(72) Inventors:
- **Anada, Hiroyuki**
  Chuo-ku
  Osaka-shi
  Osaka 541-0041 (JP)
- **Kinomura, Shoji**
  Chuo-ku
  Osaka-shi
  Osaka 541-0041 (JP)
- **Hirohata, Noriaki**
  Chuo-ku
  Osaka-shi
  Osaka 541-0041 (JP)
- **Kanzaki, Manabu**
  Chuo-ku
  Osaka-shi
  Osaka 541-0041 (JP)
- **Kitamura, Kazuyuki**
  Chuo-ku
  Osaka-shi
  Osaka 541-0041 (JP)

(74) Representative: **Simons, Amanda Louise**
J.A. Kemp & Co.,
14 South Square,
Gray's Inn
London WC1R 5JJ (GB)

(54) A method of producing a NI based alloy

(57) A Ni-based alloy is subjected to heat treatment in an atmosphere (a) consisting of carbon dioxide gas and optionally up to 5 vol % of one or more oxidizing gases or (b) consisting of 0.0001 Vol.% or more carbon dioxide gas, 99.9999 vol. % or less of one or more non-oxidizing gases and optionally up to 5 vol % of one or more oxidizing gases in order to form an oxide film composed of chromium oxide on the surface of the alloy. The atmosphere desirably contains 5 vol.% or less oxygen gas. Especially, the atmosphere desirably consists of carbon dioxide gas and hydrogen gas.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention relates to a method of producing a Ni-based alloy, which elutes little Ni even when used in a high-temperature water environment for a long period, and particularly relates to a method of producing the Ni-based alloy suitable for use in a member for a nuclear power plant.

Background Art

[0002] A Ni-based alloy is used for various kinds of members due to its superior mechanical properties. Particularly, for the member in a nuclear reactor, which is exposed to high-temperature water, the Ni-based alloy superior in corrosion resistance is used. For instance, for a steam generator of a pressurized water reactor (PWR), a 60%Ni-30%Cr-10%Fe alloy is used.

[0003] 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. A Ni-based alloy is superior in corrosion resistance and has a low corrosion rate. However, when used for a long period, a very small amount of Ni elutes from the alloy.

[0004] Eluted Ni is carried to a reactor core part along with circulating furnace water and is irradiated with neutrons in the proximity of the fuel. Then, the irradiated Ni with neutrons is converted to radioactive Co through a nuclear reaction. Radioactive Co has a very long half-life, 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, the countermeasures have been taken until now 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] The Patent Document 1 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 400 to 750°C, and forming an oxide film mainly containing chromium oxide on the surface of it.

[0007] The Patent Document 2 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] The Patent Document 3 discloses a method of producing 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.

[0009] The Patent Document 4 discloses a method for forming a chromium enriched layer on an alloy workpiece containing Ni and Cr by exposing the work-piece with a gaseous mixture consisting of water vapor and at least one of non-oxidizing gases.

Patent Document 1: JP S64-55366A
Patent Document 2: JP H08-29571A
Patent Document 3: JP 2002-121630A
Patent Document 4: JP 2002-322553A

Disclosure of the Invention

Subject to be Solved by the Invention

[0010] The film formed by the method disclosed in the Patent Document 1 has such insufficient thickness that it tends to be damaged during service for a long period, and may lose the effect of preventing the elution.

[0011] The method disclosed in the Patent Document 2 has such a problem that oxidized Ni is easily taken into a film and the Ni elutes during use.

[0012] Methods for forming an oxide film by controlling the amount of water vapor (a dew point) such as the methods disclosed in the Patent Documents 3 and 4 have difficulty in forming the oxide film consistent from the inlet side to the outlet side of water vapor. This is for the following reason.

[0013] In the case of continuous treatment for forming an oxide film in a long tube, for instance, 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 (H_2O) has the higher diffusibility than other oxidizing gases such as CO_2 have, hence it is hard to form the oxide film consistent from the inlet side to outlet side on the tube by the oxidation treatment in a water vapor atmosphere.

[0014] The present invention was accomplished for the purpose of solving these problems, and is directed at providing a method of producing a Ni-based alloy having a uniform oxide film comprising chromium oxide inexpensively formed on the surface.

Method to Solve the Subject

[0015] The present invention is summarized into the method of producing a Ni-based alloy described in the following items (1) to (14).

(1) A method of producing a Ni based alloy having an oxide film comprising chromium oxide on its surface, characterized by subjecting the alloy to a heat treatment in an atmosphere (a) consisting of carbon dioxide gas and optionally up to 5 vol % of one or more oxidizing gases or (b) consisting of 0.0001 Vol.% or more carbon dioxide gas, 99.9999 vol.% or less of one or more non-oxidizing gases and optionally up to 5 vol % of one or more oxidizing gases.

(2) A method of producing a Ni based alloy according to (1), characterized in that the atmosphere consists of carbon dioxide gas, at least one of hydrogen gas and one or more rare gases and optionally up to 5 vol % of one or more oxidizing gases.

(3) A method of producing a Ni based alloy according to (1),
characterized in that the atmosphere consists of carbon dioxide gas and hydrogen gas and optionally up to 5 vol % of one or more oxidizing gases.

(4) A method of producing a Ni based alloy according to any one of (1) to (3), characterized in that the atmosphere contains 5 vol.% or less oxygen gas.

(5) A method of producing a Ni based alloy according to any one of (1) to (4), characterized in that the atmosphere contains 50 vol.% or less carbon dioxide gas.

(6) A method of producing a Ni based alloy according to any one of (1) to (4), characterized in that the atmosphere contains 10 vol.% or less carbon dioxide gas.

(7) A method of producing a Ni based alloy according to any one of (1) to (6), characterized in that the temperature of the heat treatment ranges from 500°C to 1,250°C.

(8) A method of producing a Ni based alloy according to any one of (1) to (7), characterized in that the period of the heat treatment ranges from 10 seconds to 35 hours

(9) A method of producing a Ni based alloy according to any one of (1) to (8), characterized in that the Ni based alloy consists of, by mass %, C:0.15% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr:10.0-40.0%, Fe:15.0% or less, Ti:0.5% or less, Cu:0.50% or less, Al:2.00% or less, and the balance Ni and impurities.

(10) A method of producing a Ni based alloy according to any one of (1) to (8), wherein the Ni based alloy consists of, by mass %, C:0.15% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr: 14.0-17.0%, Fe:6.0-10.0%, Ti:0.5% or less, Cu:0.50% or less, Al:2.00% or less, and the balance Ni and impurities.

(11) A method of producing a Ni based alloy according to any one of (1) to (8), characterized in that the Ni based alloy consists of, by mass %, C:0.06% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr:27.0-31.0%, Fe:7.0-11.0%, Ti:0.5% or less, Cu:0.50% or less, Al:2.00% or less, and the balance Ni and impurities.

(12) A method of producing a Ni based alloy according to any one of (9) to (11), characterized in that the Ni based alloy contains, by mass %, Nb and/or Ta: 3.15-4.15% each element alone or in total in lieu of part of Ni.

(13) A method of producing a Ni based alloy according to any one of (9) to (12), characterized in that the Ni based alloy contains, by mass %, Mo: 8-10% in lieu of part of Ni.

(14) A method of producing a Ni based alloy according to any one of (1) to (13), characterized in that the Ni based alloy is preferably used for a material of a member for a nuclear power plant.

[0016] 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 $MnCr_2O_4$, 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 layer formed as the upper layer (the outside layer) and/or the lower layer (the inside layer) of the chromium oxide layer.

Advantageous Effect of the Invention

[0017] The method of producing Ni based alloy according to the present invention can form chromium oxide on the surface of a Ni-based alloy inexpensively and uniformly. Therefore, 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.

Best Mode for Carrying Out the Invention

1. Atmosphere for heat treatment

[0018] In a method of producing a Ni-based alloy according to the present invention, a Ni-based alloy is subjected to a heat treatment in the atmosphere consisting of carbon dioxide gas or the atmosphere consisting of 0.0001 vol.% or more carbon dioxide gas and 99.9999 vol.% or less non-oxidizing gas in order to form an oxide film composed of chromium oxide on the surface of the alloy. In other words, the present invention is characterized by a heating atmosphere containing carbon dioxides of 0.0001 vol.% or more for forming an oxide film comprising chromium oxide on the surface of the Ni-based alloy through the oxidative effect. When the atmosphere contains less than 0.0001 vol.% carbon dioxide, the oxide film comprising chromium oxide may be insufficiently formed. There is no particular upper limit on the concentration of carbon dioxide contained in an atmosphere for heat treatment and it could be 100 vol.%. However, from the viewpoint of manufacturing cost reduction, it is preferable that non-oxidizing gas, to be described in later paragraphs, is added in an atmosphere for heat treatment in order to set the concentration of carbon dioxide to be 50 vol.% or less, and more preferably 10 vol.% or less.

[0019] 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. More specifically, in an atmosphere comprising carbon dioxides, as shown in the following reaction formula, CO_2 adsorbs to a Ni-based alloy, and then a Ni-based alloy directly takes O (oxygen) therein from CO_2 to form chromium oxide.

$$CO_2\text{+Metal} \rightarrow CO + \text{Metal-O}$$

[0020] As described above, though the Patent Documents 3 and 4 disclose a method for forming an oxide film by heating a Ni alloy under a water vapor atmosphere, the method has difficulty in forming an oxide film consistent from the inlet side to the outlet side of water vapor.

[0021] 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. A merit of using carbon dioxide gas includes that it can produce a desired oxidation atmosphere more inexpensively than a method of controlling the concentration of water with a conventional dew point controller.

[0022] An atmosphere for heat treatment may contain 99. 9999 vol. % or less non-oxidizing gases, that do not promote Cr oxide, in addition to carbon dioxide gas. Such gases involve hydrogen gas, rare gas (Group 18 gases, e.g. Ar, He and so on), carbon monoxide gas, nitrogen gas and hydrocarbon gas. Among these gases, carbon monoxide gas, nitrogen gas and hydrocarbon gas may cause carburisation or nitriding when they are contained in an atmosphere for heat treatment. Therefore, it is preferable to use at least either or both of hydrogen gas and rare gas. By adjusting the concentration of the non-oxidizing gas, the concentration of the carbon dioxide gas can be appropriately controlled.

[0023] An atmosphere for heat treatment may contain 5 vol.% or less of one or more oxidizing gases (e.g. oxygen) that cause the oxidation of a Ni-based alloy in addition to carbon dioxide gas, or carbon dioxide gas and non-oxidizing gas. However, from the viewpoint of safety, it is preferable to avoid an atmosphere for heat treatment wherein both hydrogen gas and oxygen gas are contained so that these gases do not react with each other to cause an explosion.

[0024] 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 a manufacturing cost. Therefore, it is most preferable to perform heat treatment under the atmosphere of the mixed gas consisting of carbon dioxides and hydrogen gas.

2. Heating temperature and heating time

[0025] Heating temperature: 500 to 1,250°C

[0026] A heating temperature has only to be in a range for producing the appropriate thickness and composition of an oxide film on a surface of the alloy being heated, and imparting the appropriate strength to the alloy itself. When the heating temperature is lower than 500°C, the oxidation of chromium can be insufficient, but when exceeding 1,250°C, the strength of the Ni-based alloy may not be ensured. Consequently, the heating temperature is preferably in a range of 500 to 1,250°C.

Heating time: 10 seconds to 35 hours

[0027] A heating time has only to be set into a range capable of giving an alloy the appropriate thickness and composition of an oxide film. More specifically, the alloy is preferably heated for 10 seconds or longer in order to form the oxide film mainly containing chromium oxide, but the oxide film does not grow any more by heating for longer than 35 hours. Consequently, the heating time is preferably in a range of 10 seconds to 35 hours.

[0028] The higher is the heating temperature, the shorter is the heating time. Accordingly, when a heating temperature is set in a range from 1, 000 to 1,200°C for instance, a heating time may be in a range of 10 seconds to 60 minutes.

[0029] 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.

3. Ni-based alloy to be treated

[0030] An example of the Ni-based alloy used in a producing 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 and impurities. Reasons for limiting each element are as follows. In addition, "%" on content means "mass%" in the following discussion.

C: 0.15% or less

[0031] C content exceeding 0.15% 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. 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.

Si: 1.00% or less

[0032] Si is used as a deoxidizing material in refining process and remains as an impurity in an alloy. The content needs to be limited to 1.00% or less. When Si content exceeds 0.50%, the cleanliness factor of the alloy can be decreased. Accordingly, Si content is preferably limited to 0.50% or less.

Mn: 2.0% or less

[0033] Mn content exceeding 2.0% lowers the corrosion resistance of an alloy. Accordingly, the content is preferably controlled to 2.0% or less. Mn has a lower free energy of formation for the oxide than Cr, hence, Mn is precipitated as $MnCr_2O_4$ by heating. In addition, 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 because Mn has comparatively high rate of diffusion. If $MnCr_2O_4$ layer exists, it protects a Cr_2O_3 layer in a use 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 Mn content is more than 0.1%. Consequently, desirable Mn content is 0.1 to 2.0%, and further desirably is 0.1 to 1.0%.

P: 0.030% or less

[0034] 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.

S: 0.030% or less

[0035] 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.

Cr: 10.0 to 40.0%

[0036] 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, Cr content exceeding 40.0% may deteriorate the corrosion resistance of the alloy, because Ni content becomes relatively low. Accordingly, Cr content is preferably 10.0 to 40.0%. In particular, when Cr content is 14.0% to 17.0%, the alloy has superior corrosion resistance in a chloride-containing environment, and when Cr content is 27.0% to 31.0%, the corrosion resistance not only in a chloride-containing environment, but also in high-temperature pure water and an alkaline environment becomes superior.

Fe: 15.0% or less

[0037] When Fe content is more than 15.0%, it may impair the corrosion resistance of the Ni-based alloy, and therefore Fe content should be set at 15.0% or less. In addition, Fe is an element that 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. The content of Fe can be decided in terms of the balance between Ni and Cr. When Cr content is 14.0 to 17.0%, preferable Fe content is 6.0 to 10.0%, and when Cr content is 27.0 to 31.0%, preferable Fe content is 7.0 to 11.0%.

Ti: 0.5% or less

[0038] Ti content exceeding 0.5% may reduce cleanliness of an alloy. Accordingly, 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.

Cu: 0.50% or less

[0039] 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.

Al: 2.00% or less

[0040] Al is used as a deoxidizing material in refining process 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.

[0041] The above-described Ni-based alloy has only to include the above-described elements and the balance Ni and impurities, however one or more elements among Nb, Ta and Mo may be added in appropriate amount in order to improve characteristics such as corrosion resistance and strength.

Nb and/or Ta: 3.15-4.15% each element alone or in total

[0042] Nb and Ta are effective for improving the strength of the alloy, because they easily form carbides. In addition, they have an effect of fixing C in the alloy, hence they inhibit a shortage of Cr in grain boundaries and improve the corrosion resistance of grain boundaries. Accordingly, one or both of these elements are desired to be contained. The effect becomes remarkable, when the content of either element is 3.15% or more in the case of the alloy containing either one, or when the total content of these is 3.15% or more in the case of the alloy containing both. 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 either element in the case of the alloy containing either one, or the total content of these in the case of the alloy containing both, is preferably controlled to 4.15% or less. Consequently, the content of one element or both elements of Nb and Ta is desirably controlled to 3.15 to 4.15%.

Mo: 8-10%

[0043] 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. Accordingly, the content of Mo, when added, is desirably controlled to 8 to 10%.

[0044] The above described Ni-based alloys are typically two kinds described below.

(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 and impurities.

(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 and impurities.

[0045] 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.

[0046] The alloy (b) includes 27.0 to 31.0% Cr and about 60% Ni, therefore, 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.

Embodiments

[0047] 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 with the use of an alloy-A shown in Table 1, and a tube was manufactured into the dimension with a diameter of 20 mm, a wall thickness of 1.5 mm and a length of 10 m with the use of alloys B to G shown in Table 1. Then, the tubes were continuously heat-treated under the conditions shown in table 2.

[0048] 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. 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 tout is the oxide film thickness in the downstream side. The evaluation results are shown in Table 2 as "○" when dispersions are 1.00 or under, or as "X" when dispersions are over 1.00.

Table 1

Alloy	Chemical Composition (mass %)					the balance Ni and impurities					
	C	Si	Mn	P	S	Cr	Fe	Ti	Cu	Al	Others
A	0.019	0.32	0.31	0.011	0.001	29.8	9.1	0.21	0.01	0.15	
B	0.022	0.33	0.28	0.012	0.001	16.2	8.9	0.23	0.18	0.13	
C	0.019	0.38	0.27	0.012	0.001	20.5	4.7	0.24	0.05	0.15	Nb:3.5
D	0.020	0.40	0.23	0.015	0.001	20.7	4.5	0.22	0.03	0.18	Ta3.7
E	0.018	0.37	0.25	0.013	0.001	20.6	4.7	0.22	0.03	0.19	Nb:3.3 Ta:0.3
F	0.019	0.38	0.26	0.011	0.001	20.8	4.6	0.26	0.07	0.13	Mo:8.5
G	0.020	0.33	0.29	0.013	0.001	20.6	4.9	0.21	0.09	0.11	Nb:3.3 Ta:0.3 Mo: 8.7

Table 2

No.		Alloy	Gas Content in the atmosphere of the Heat Treatment (Vol.%)						Heating temp. (℃)	Heating time	evaluation
			Oxidizing Gas			Non-oxidizing Gas					
			CO_2	O_2	H_2O	H_2	Ar	He			
Example of the Present Invention	1	A	0.3000	—	—	99.7000	—	—	1100	300s	○
	2	A	0.1500	—	—	99.8500	—	—	1100	300s	○
	3	A	0.1000	—	—	99.9000	—	—	1100	300s	○
	4	A	100.0000	—	—	—	—	—	1100	300s	○
	5	A	98.9000	—	—	1.1000	—	—	1100	300s	○
	6	A	50.0000	—	—	50.0000	—	—	1100	300s	○
	7	A	10.0000	—	—	90.0000	—	—	1100	300s	○
	8	A	0.1000	—	—	—	99.9000	—	1100	300s	○
	9	A	0.1000	—	—	—	—	99.9000	1100	300s	○
	10	A	0.1000	—	—	98.8000	1.1000	—	1100	300s	○
	11	A	0.1000	—	—	97.7000	1.1000	1.1000	1100	300s	○
	12	A	0.1000	—	—	99.9000	—	—	650	15h	○
	13	A	98.9000	1.1000	—	—	—	—	1100	300s	○
	14	A	49.9500	0.0500	—	—	50.0000	—	1100	300s	○
	15	B	100.0000	—	—	—	—	—	1100	300s	○
	16	B	0.1000	—	—	99.9000	—	—	1100	300s	○
	17	B	0.1000	—	—	—	99.9000	—	1100	300s	○
	18	B	0.1000	—	—	98.8000	1.1000	—	1100	300s	○
	19	B	0.1000	—	—	99.9000	—	—	650	15h	○
	20	B	98.8000	1.1000	—	0.1000	—	—	1100	300s	○
	21	B	49.9500	0.0500	—	0.1000	49.9000	—	1100	300s	○
	22	C	0.1000	—	—	99.9000	—	—	1100	300s	○
	23	D	0.1000	—	—	99.9000	—	—	1100	300s	○
	24	E	0.1000	—	—	99.9000	—	—	1100	300s	○
	25	F	0.1000	—	—	99.9000	—	—	1100	300s	○
	26	G	0.1000	—	—	99.9000	—	—	1100	300s	○
Comparative Example	27	A	—	—	0.8610	99.1390	—	—	1100	300s	×
	28	A	—	—	0.8610	99.1390	—	—	1100	300s	×
	29	A	—	—	0.8610	98.0390	1.1000	—	1100	300s	×

"s" means "seconds" and "h" means "hours" in the section of the heating time.

[0049] As shown in Table 2, oxide films formed in the conditions shown in No. 1 and 2 with the use of CO_2 as an oxidizing gas, showed as small dispersions as 0.05 and 0.17, whereas the oxide film formed in a condition shown in No. 27 with the use of H_2O showed the dispersion of 3.00, which was quite large compared to the case with the use of CO_2. Other examples treated by the producing method of the present invention showed the dispersions evaluated as O, whereas examples treated by a comparative method using H_2O showed large dispersions.

Industrial Applicability

[0050] The method according to the present invention can inexpensively form uniform chromium oxide on the surface of a Ni-based alloy, Therefore, 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.

Claims

1. A method of producing a Ni based alloy having an oxide film comprising chromium oxide on its surface, **characterized by** subjecting the alloy to a heat treatment in an atmosphere (a) consisting of carbon dioxide gas and optionally up to 5 vol % of one or more oxidizing gases or (b) consisting of 0.0001 Vol.% or more carbon dioxide gas, 99.9999 vol.% or less of one or more non-oxidizing gases and optionally up to 5 vol % of one or more oxidizing gases.

2. A method according to claim 1, **characterized in that** the atmosphere consists of carbon dioxide gas, at least one of hydrogen gas and one or more rare gases and optionally up to 5 vol % of one or more oxidizing gases.

3. A method according to claim 1, **characterized in that** the atmosphere consists of carbon dioxide gas and hydrogen gas and optionally up to 5 vol % of one or more oxidizing gases.

4. A method according to any one of claims 1 to 3,
characterized in that the atmosphere contains 5 vol.% or less oxygen gas.

5. A method according to any one of claims 1 to 4,
characterized in that the atmosphere contains 50 vol.% or less carbon dioxide gas.

6. A method according to any one of claims 1 to 4,
characterized in that the atmosphere contains 10 vol.% or less carbon dioxide gas.

7. A method according to any one of claims 1 to 6,
characterized in that heat treatment is carried out at a temperature in the range of from 500°C to 1,250°C.

8. A method according to any one of claims 1 to 7,
characterized in that heat treatment is carried out for a period of from 10 seconds to 35 hours.

9. A method according to any one of claims 1 to 8, **characterized in that** the Ni based alloy consists of, by mass %, C:0.15% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr:10.0 to 40.0%, Fe: 15.0% or less, Ti:0.5% or less, Cu:0.50% or less, Al:2.00% or less, and optionally one or more of Nb, Ta and Mo the balance being Ni and impurities.

10. A method according to any one of claims 1 to 8, wherein the Ni based alloy consists of, by mass %, C:0.15% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr:14.0 to 17.0%, Fe: 6. 0 to 10.0%, Ti: 0.5% or less, Cu:0.50% or less, Al:2.00% or less, and optionally one or more of Nb, Ta and Mo the balance being Ni and impurities.

11. A method according to any one of claims 1 to 8,
characterized in that the Ni based alloy consists of, by mass %, C:0.06% or less, Si:1.00% or less, Mn:2.0% or less, P:0.030% or less, S:0.030% or less, Cr: 27.0 to 31.0%, Fe: 7 . 0 to 11.0%, Ti:0.5% or less, Cu:0.50% or less, Al:2.00% or less, and optionally one or more of Nb, Ta and Mo the balance being Ni and impurities.

12. A method according to any one of claims 9 to 11,
characterized in that the Ni based alloy contains a total of 3.15 to 4.15% by mass Nb and/or Ta.

13. A method according to any one of claims 9 to 12,
characterized in that the Ni based alloy contains 8 to 10% by mass Mo.

14. A method according to any one of claims 1 to 13,
characterized in that the Ni based alloy is used in the production of an element of a nuclear power plant.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 25 6349

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	GB 2 159 542 A (* MAN MASCHINENFABRIK AUGSBURG NURNBERG AG) 4 December 1985 (1985-12-04) * page 1, line 26 - line 33 * * page 1, column 51 - column 108 *	1,14	C22F1/00 C22F1/10 C23C8/16 C22F1/02 C21D1/76 C22C19/05
Y	* page 2, line 68 - line 120 * * page 4, line 119 - page 5, line 26 * -----	2-6	
Y	PATENT ABSTRACTS OF JAPAN vol. 015, no. 167 (C-0827), 26 April 1991 (1991-04-26) -& JP 03 036255 A (HITACHI LTD), 15 February 1991 (1991-02-15) * abstract * * page 333; claims 1-8 * -----	2-6	
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 05, 31 May 1999 (1999-05-31) -& JP 11 029822 A (HITACHI LTD), 2 February 1999 (1999-02-02) * abstract * * paragraphs [0003], [0006], [0012], [0013], [0018]; table 1 * -----	1,2	TECHNICAL FIELDS SEARCHED (IPC) C22F C23C C21D C22C
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 14, 31 December 1998 (1998-12-31) -& JP 10 237651 A (MATSUSHITA ELECTRIC IND CO LTD), 8 September 1998 (1998-09-08) * abstract * -----	1,4-6	
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 293 (C-615), 6 July 1989 (1989-07-06) -& JP 01 087753 A (TOSHIBA CORP; others: 01), 31 March 1989 (1989-03-31) * abstract * ----- -/--	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	2 December 2005	Lilimpakis, E

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

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 25 6349

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 423 (C-638), 20 September 1989 (1989-09-20) -& JP 01 159362 A (SUMITOMO METAL IND LTD), 22 June 1989 (1989-06-22) * abstract * -----	1,2	
P,A	EP 1 475 451 A (SUMITOMO METAL INDUSTRIES, LTD) 10 November 2004 (2004-11-10) * paragraph [0056]; claims 1-4; table 1 * -----	1,9-14	
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 566 (P-1629), 14 October 1993 (1993-10-14) -& JP 05 164886 A (TOSHIBA CORP), 29 June 1993 (1993-06-29) * abstract * * paragraph [0014] * -----	1,7-10	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	2 December 2005	Lilimpakis, E

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

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 25 6349

02-12-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2159542 A	04-12-1985	DE 3419638 A1	28-11-1985
		SE 8502590 A	26-11-1985
JP 03036255 A	15-02-1991	JP 2708555 B2	04-02-1998
JP 11029822 A	02-02-1999	NONE	
JP 10237651 A	08-09-1998	JP 3446520 B2	16-09-2003
JP 01087753 A	31-03-1989	NONE	
JP 01159362 A	22-06-1989	NONE	
EP 1475451 A	10-11-2004	AU 2003207059 A1	04-09-2003
		WO 03069011 A1	21-08-2003
		JP 2003239060 A	27-08-2003
		US 2004103963 A1	03-06-2004
JP 05164886 A	29-06-1993	JP 2535114 B2	18-09-1996

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82