



(11) **EP 3 524 705 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
14.08.2019 Bulletin 2019/33

(51) Int Cl.:
C22C 38/00 (2006.01) **C22C 30/02** (2006.01)
C22C 38/58 (2006.01)

(21) Application number: **17858416.5**

(86) International application number:
PCT/JP2017/036059

(22) Date of filing: **04.10.2017**

(87) International publication number:
WO 2018/066579 (12.04.2018 Gazette 2018/15)

(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

(72) Inventors:
• **OKADA, Hirokazu**
Tokyo 100-8071 (JP)
• **HAMAGUCHI, Tomoaki**
Tokyo 100-8071 (JP)
• **KURIHARA, Shinnosuke**
Tokyo 100-8071 (JP)

(30) Priority: **05.10.2016 JP 2016197458**

(74) Representative: **J A Kemp**
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(71) Applicant: **Nippon Steel & Sumitomo Metal
Corporation**
Tokyo 100-8071 (JP)

(54) **NiCrFe ALLOY**

(57) A NiCrFe alloy having excellent creep strength and stress relaxation cracking resistance is provided. The NiCrFe alloy according to the present invention has a chemical composition consisting of, in mass%, C: 0.03 to 0.15%, Si: not more than 1.00%, Mn: not more than 2.00%, P: not more than 0.040%, S: not more than 0.0050%, Cr: 18.0 to 25.0%, Ni: 25.0 to 40.0%, Ti: 0.10 to 1.60%, Al: 0.05 to 1.00%, N: not more than 0.020%, O: not more than 0.008%, and rare earth metal (REM): 0.001 to 0.100%, with the balance being Fe and impurities, the chemical composition satisfying Formulae (1) to (3):

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

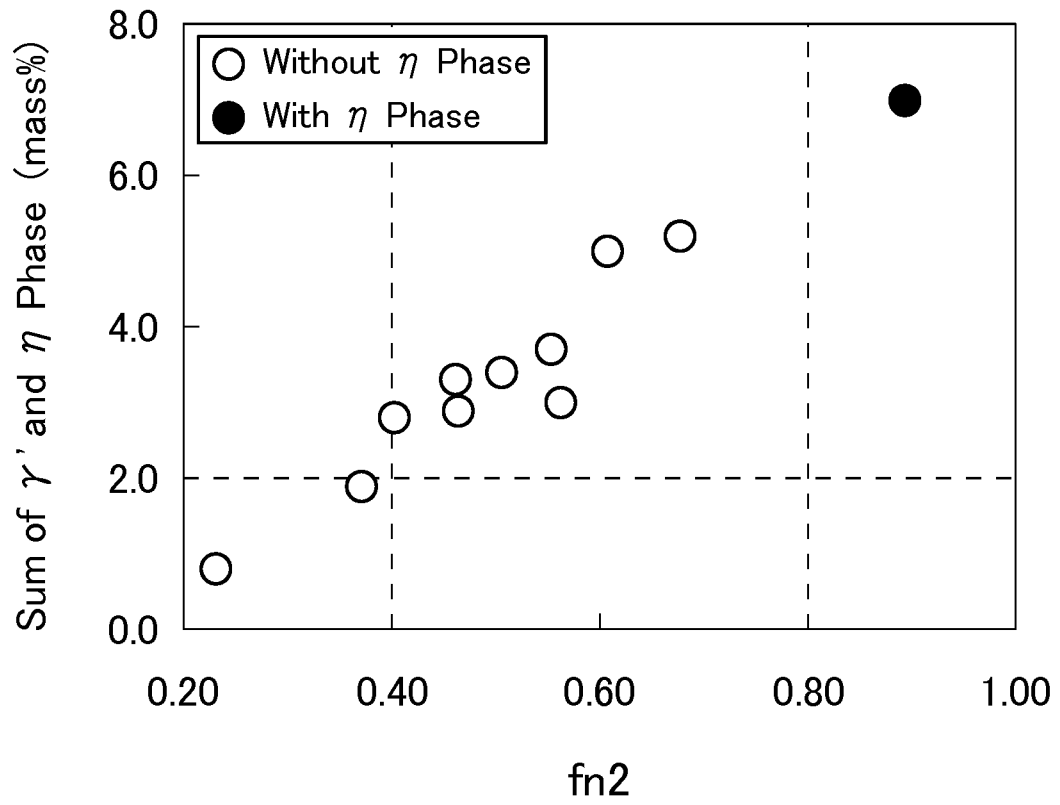
$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in the formulae is substituted by the content (mass%) of the corresponding element, and A(REM) in Formula (3) is substituted by the atomic weight of each rare earth metal.

EP 3 524 705 A1

FIG. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to an austenitic heat resistant alloy, and more specifically a NiCrFe alloy.

BACKGROUND ART

[0002] Conventionally, facilities such as thermal power generation boilers and chemical plants are operated in high temperature environments (such as 400 to 800°C) and, in addition, they are brought into contact with process fluids including sulfides and/or chlorides. Therefore, materials to be used in such facilities require their creep strength and corrosion resistance at high temperatures.

[0003] Examples of the material for use in such facilities include 18-8 stainless steel such as SUS304H, SUS316H, SUS321H, and SUS347H, and NiCrFe alloys represented by Alloy 800H, which is specified as NCF800H by the JIS standard.

[0004] A NiCrFe alloy excels in corrosion resistance and high temperature strength compared to an 18-8 stainless steel. Further, a NiCrFe alloy excels in economic efficiency compared to a Ni-base alloy represented by Alloy617. Therefore, NiCrFe alloys are widely used in regions of severe use environments.

[0005] NiCrFe alloys used in such severe use environments are proposed in Japanese Patent Application Publication No. 2013-227644 (Patent Literature 1), Japanese Patent Application Publication No. 06-264169 (Patent Literature 2), Japanese Patent Application Publication No. 2002-256398 (Patent Literature 3), and Japanese Patent Application Publication No. 08-13104 (Patent Literature 4).

[0006] An austenitic heat resistant alloy disclosed in Patent Literature 1 consists of, in mass%, C: less than 0.02%, Si: not more than 2%, Mn: not more than 2%, Cr: not less than 20% and less than 28%, Ni: more than 35% and not more than 50%, W: 2.0 to 7.0%, Mo: less than 2.5% (including 0%), Nb: less than 2.5% (including 0%), Ti: less than 3.0% (including 0%), Al: not more than 0.3%, P: not more than 0.04%, S: not more than 0.01%, and N: not more than 0.05%, with the balance being Fe and impurities, wherein $f1 = (1/2)W + Mo$ is 1.0 to 5.0, $f2 = (1/2)W + Mo + Nb + 2Ti$ is 2.0 to 8.0, and $f3 = Nb + 2Ti$ is 0.5 to 5.0.

[0007] A heat resistant and corrosion resistant alloy disclosed in Patent Literature 2 consists of, in weight%, 55 to 65% of Nickel, 19 to 25% of Chromium, 1 to 4.5% of Aluminum, 0.045 to 0.3% of Yttrium, 0.15 to 1% of Titan, 0.005 to 0.5% of Carbon, 0.1 to 1.5% of Silicon, not more than 1% of Manganese, a total of 0.005% of at least one element selected from the group consisting of Magnesium, Calcium, and Cerium, a total of less than 0.5% of Magnesium and Calcium, less than 1% of Cerium, 0.0001 to 0.1% of Boron, not more than 0.5% of Zirconium, 0.0001 to 0.2% of Nitrogen, and not more than 10% of Cobalt, with the balance being Fe and accompanying impurities.

[0008] An austenitic alloy disclosed in Patent Literature 3 contains, in mass%, C: 0.01 to 0.1%, Mn: 0.05 to 2%, Cr: 19 to 26%, and Ni: 10 to 35%, with the Si content satisfying a formula of $0.01 < Si < (Cr + 0.15 \times Ni - 18)/10$.

[0009] A heat resistant alloy disclosed in Patent Literature 4 consists of, in weight%, C: 0.02 to 0.15%, Si: 0.70 to 3.00%, Mn: not more than 0.50%, Ni: 30.0 to 40.0%, Cr: 18.0 to 25.0%, Al: 0.50 to 2.00%, and Ti: 0.10 to 1.00%, with the balance being Fe and inevitable impurities.

CITATION LIST

PATENT LITERATURE

[0010]

Patent Literature 1: Japanese Patent Application Publication No. 2013-227644

Patent Literature 2: Japanese Patent Application Publication No. 06-264169

Patent Literature 3: Japanese Patent Application Publication No. 2002-256398

Patent Literature 4: Japanese Patent Application Publication No. 08-13104

NON PATENT LITERATURE

[0011] Non Patent Literature 1: Hans van Wortel: "Control of Relaxation Cracking in Austenitic High Temperature Components", CORROSION2007 (2007), NACE, Paper No.07423

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0012] The austenitic heat resistant alloy disclosed in Patent Literature 1 controls the formation of Laves phase by specifying the contents of W, Mo, Nb, and Ti, thereby improving creep strength and toughness. The heat resistant and corrosion resistant alloy disclosed in Patent Literature 2 improves high-temperature oxidation resistance by causing γ' to be precipitated during creep. The austenitic alloy disclosed in Patent Literature 3 improves carburizing properties by suppressing exfoliation of the oxide film dominantly composed of Cr_2O_3 and formed on the material surface. The heat resistant alloy disclosed in Patent Literature 4 contains a specific amount of Cr, a reduced amount of Mn, and a fixed amount of Si, thereby making it possible to obtain excellent oxidation resistance even in a case in which the Ni content is reduced.

[0013] On the other hand, Non Patent Literature 1 discloses that a NiCrFe alloy has a high susceptibility to stress relaxation cracking. This means that a NiCrFe alloy requires stress relief heat treatment, after working, for a bent part and welded part, in which residual stress is present. Therefore, a NiCrFe alloy requires not only excellent creep strength but also excellent stress relaxation cracking resistance.

[0014] An objective of the present invention is to provide a NiCrFe alloy which excels in creep strength and stress relaxation cracking resistance.

SOLUTION TO PROBLEM

[0015] A NiCrFe alloy according to the present invention has a chemical composition consisting of, in mass%, C: 0.03 to 0.15%, Si: not more than 1.00%, Mn: not more than 2.00%, P: not more than 0.040%, S: not more than 0.0050%, Cr: 18.0 to 25.0%, Ni: 25.0 to 40.0%, Ti: 0.10 to 1.60%, Al: 0.05 to 1.00%, N: not more than 0.020%, O: not more than 0.008%, rare earth metal (REM): 0.001 to 0.100%, B: 0 to 0.010%, Ca: 0 to 0.010%, Mg: 0 to 0.010%, V: 0 to 0.5%, Nb: 0 to 1.0%, Ta: 0 to 1.0%, Hf: 0 to 1.0%, Mo: 0 to 1.0%, W: 0 to 2.0%, Co: 0 to 3.0%, and Cu: 0 to 3.0%, with the balance being Fe and impurities, the chemical composition satisfying Formulae (1) to (3):

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in the above described formulae is substituted by the content (mass%) of the corresponding element. A(REM) in Formula (3) is substituted by the atomic weight of each rare earth metal.

ADVANTAGEOUS EFFECT OF INVENTION

[0016] A NiCrFe alloy according to the present invention excels in creep strength and stress relaxation cracking resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0017] FIG. 1 is a diagram to show a relation between fn_2 of each Reference mark of Examples, and a sum (mass%) of γ' and η phase after aging treatment.

DESCRIPTION OF EMBODIMENTS

[0018] The present inventors have conducted detailed study on the creep strength and the stress relaxation cracking resistance of NiCrFe alloys. As a result, the present inventors have obtained the following findings.

(A) To obtain excellent creep strength, the precipitation amount of γ' (intermetallic compound: $\text{Ni}_3(\text{Ti}, \text{Al})$), which precipitates during creep under a high-temperature environment, may be increased. If γ' precipitates sufficiently

during creep under a high-temperature environment, the creep strength of the alloy is increased by precipitation hardening. However, if γ' precipitates excessively, deformability within an austenite grain deteriorates, thus causing stress concentration in grain boundary surfaces. As a result, the stress relaxation cracking resistance of the alloy deteriorates. Therefore, to achieve excellent creep strength and excellent stress relaxation cracking resistance at the same time, it is necessary to adjust the amount of γ' which precipitates during creep under a high temperature environment. To obtain an appropriate amount of γ' precipitation, the contents of Ti and Al, which constitute γ' , may be adjusted.

Specifically, the chemical composition of NiCrFe alloy satisfies Formula (1) to maintain stress relaxation cracking resistance while ensuring creep strength:

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

where, each symbol of element in Formula (1) is substituted by the content (mass%) of the corresponding element. Now define fn1 as $\text{fn1} = \text{Ti} + 48\text{Al}/27$. fn1 is an index to indicate the amount of γ' that precipitates during creep. fn1 is a total content of Al and Ti, the content of Al being converted into the amount of Ti. When fn1 is less than 0.50, a sufficient precipitation amount of γ' will not be obtained. For that reason, the NiCrFe alloy cannot obtain excellent creep strength. On the other hand, when fn1 is more than 2.20, the stress relaxation cracking resistance of the NiCrFe alloy will deteriorate due to a large amount of precipitation of γ' .

(B) The γ' that has precipitated during creep under a hot-temperature environment may change in its form over time. Specifically, while fine γ' precipitates in an early stage of creep, the γ' may change to a coarse and acicular η phase (Ni_3Ti) during creep under a high-temperature environment over time. Formation of η phase will decrease the creep strength of the NiCrFe alloy.

Then, the present inventors have investigated in detail on a case in which γ' phase changes to η phase under a high-temperature environment. As a result, they supposed that the Ti content with respect to the total content of Al and Ti, the content of Al being converted into the amount of Ti is related to the change from γ' phase to η phase. Accordingly, the present inventors have investigated in detail on the Ti content with respect to the total content of Al and Ti, the content of Al being converted into the amount of Ti, and the microstructure during creep.

Now define fn2 as $\text{fn2} = \text{Ti}/(\text{Ti} + 48\text{Al}/27)$. fn2 is a ratio of the Ti content with respect to the total content of Al and Ti, the content of Al being converted into the amount of Ti. FIG. 1 shows a relation between fn2 and a sum of γ' and η phase after aging treatment. FIG. 1 is obtained by the following method. It is created by using fn2, and Ti, Al, and Ni contents in the γ' and η phase after aging treatment, which are obtained by the below described method, for NiCrFe alloys whose chemical compositions are within the range of the present invention, and in which the above described Formula (1) and the below described Formula (3) are within the range of the present invention. Further, γ' and η phase are discriminated by using a method to be described below. The symbol "○" in FIG. 1 indicates an Example in which the number density of η phase after aging treatment is less than $5/100 \mu\text{m}^2$. On the other hand, the symbol "●" in FIG. 1 indicates an Example in which the number density of η phase after aging treatment is not less than $5/100 \mu\text{m}^2$.

Referring to FIG. 1, when fn2 is less than 0.40, a sufficient precipitation amount of γ' will not be obtained. In this case, the NiCrFe alloy cannot obtain excellent creep strength. On the other hand, when fn2 is more than 0.80, γ' changes to η phase. As a result, the NiCrFe alloy cannot obtain excellent creep strength. Therefore, when fn2 is 0.40 to 0.80, it is possible to increase the creep strength of the NiCrFe alloy.

As described so far, if the chemical composition of the NiCrFe alloy of the present invention satisfies Formula (2), γ' precipitates in an appropriate amount, and the precipitation of η phase will be suppressed even after time has passed so that excellent creep strength will be obtained:

$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

where, each symbol of element in Formula (2) is substituted by the content (mass%) of the corresponding element. (C) One cause of stress relaxation cracking is segregation of S in grain boundaries. Therefore, it is possible to increase the stress relaxation cracking resistance of the NiCrFe alloy by decreasing an impurity S, which segregates in grain boundaries, thereby causing grain boundary embrittlement. On the other hand, rare earth metals (REM) combine with a minute amount of S, which cannot be removed by refining, in the alloy thereby forming inclusions. In other words, a REM can immobilize S as inclusions.

[0019] Therefore, adjusting the content of REM to be an appropriate amount will allow improving the stress relaxation

cracking resistance of the NiCrFe alloy. REM combines with S and is also likely to combine with O easily. Therefore, to immobilize S by REM, the REM content should be adjusted while the amount of REM that combines with O is taken into consideration.

[0020] If the chemical composition of the NiCrFe alloy of the present invention satisfies Formula (3), S will be sufficiently immobilized by REM, and excellent stress relaxation cracking resistance will be obtained:

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in Formula (3) is substituted by the content (mass%) of the corresponding element, and A(REM) is substituted by the atomic weight of each rare earth metal.

[0021] $\sum[\text{REM}/(\text{A}(\text{REM}))]$ is substituted by an addition sum of values which are obtained by dividing each REM content (mass%) contained in the NiCrFe alloy by the atomic weight of the REM.

[0022] Now define fn3 as $\text{fn3} = \sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16$. REM is a generic name of a total of 17 elements of Sc, Y, and lanthanoids. When fn3 is not less than 0, REM can sufficiently immobilize S as inclusions, thereby improving the stress relaxation cracking resistance.

[0023] The NiCrFe alloy according to the present invention, which has been completed based on the above described findings, has a chemical composition consisting of, in mass%, C: 0.03 to 0.15%, Si: not more than 1.00%, Mn: not more than 2.00%, P: not more than 0.040%, S: not more than 0.0050%, Cr: 18.0 to 25.0%, Ni: 25.0 to 40.0%, Ti: 0.10 to 1.60%, Al: 0.05 to 1.00%, N: not more than 0.020%, O: not more than 0.008%, rare earth metal (REM): 0.001 to 0.100%, B: 0 to 0.010%, Ca: 0 to 0.010%, Mg: 0 to 0.010%, V: 0 to 0.5%, Nb: 0 to 1.0%, Ta: 0 to 1.0%, Hf: 0 to 1.0%, Mo: 0 to 1.0%, W: 0 to 2.0%, Co: 0 to 3.0%, and Cu: 0 to 3.0%, with the balance being Fe and impurities, the chemical composition satisfying Formulae (1) to (3):

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in Formulae (1) to (3) is substituted by the content (mass%) of the corresponding element. A(REM) in Formula (3) is substituted by an atomic weight of each rare earth metal.

[0024] The above described chemical composition may contain B: 0.0001 to 0.010%.

[0025] The above described chemical composition may contain one or two types selected from the group consisting of Ca: 0.0001 to 0.010%, and Mg: 0.0001 to 0.010%.

[0026] The above described chemical composition may contain one or more types selected from the group consisting of V: 0.01 to 0.5%, Nb: 0.01 to 1.0%, Ta: 0.01 to 1.0%, and Hf: 0.01 to 1.0%.

[0027] The above described chemical composition may contain one or more types selected from the group consisting of Mo: 0.01 to 1.0%, W: 0.01 to 2.0%, Co: 0.01 to 3.0%, and Cu: 0.01 to 3.0%.

[0028] The NiCrFe alloy according to the present invention has excellent creep strength and excellent stress relaxation cracking resistance. To be more specific, the NiCrFe alloy will not rupture for 300 or more hours even if it is subjected to tensile strain of 10% at a strain rate of 0.05 min^{-1} and is kept as is under air atmosphere of 650°C after being subjected to cold rolling at a reduction of area of 20%.

[0029] Hereinafter, the NiCrFe alloy according to the present invention will be described in detail. The symbol "%" regarding elements means, unless otherwise stated, mass%.

[Chemical composition]

[0030] The chemical composition of NiCrFe alloy of the present invention contains the following elements.

C: 0.03 to 0.15%

[0031] Carbon (C) stabilizes austenite, and increases high temperature creep strength of the alloy. When the C content is too low, these effects cannot be obtained. On the other hand, when the C content is too high, coarse carbide will

precipitate in large amount, thus deteriorating the ductility of grain boundaries. Further, the toughness and creep strength of the alloy decrease. Therefore, the C content is 0.03 to 0.15%. The lower limit of the C content is preferably 0.04%, more preferably more than 0.04%, and further preferably 0.05%, and further preferably 0.06%. The upper limit of the C content is preferably 0.12%, and more preferably 0.10%.

Si: not more than 1.00%

[0032] Silicon (Si) is inevitably contained. Si deoxidizes the alloy, and improves the corrosion resistance and oxidation resistance at high temperatures of the alloy. However, when the Si content is too high, the stability of austenite deteriorates, and toughness and creep strength of the alloy decrease. Therefore, the Si content is not more than 1.00%. The upper limit of the Si content is preferably 0.80%, more preferably 0.60%, and further preferably less than 0.60%. Excessive reduction of the Si content deteriorates deoxidization effect, thus deteriorating the corrosion resistance and oxidation resistance at high temperatures of the alloy. And further, the production cost is significantly increased. Therefore, the lower limit of the Si content is preferably 0.02%, and more preferably 0.05%.

Mn: not more than 2.00%

[0033] Manganese (Mn) is inevitably contained. Mn deoxidizes the alloy, and stabilizes austenite. However, when the Mn content is too high, embrittlement is caused and the toughness and creep ductility of the alloy deteriorate. Therefore, the Mn content is not more than 2.00%. The upper limit of the Mn content is preferably 1.80%, and more preferably 1.50%. Excessive reduction of the Mn content deteriorates the deoxidization effect and stabilization of austenite, and further causes significant increase of the production cost. Therefore, the lower limit of the Mn content is preferably 0.10%, more preferably 0.30%, and further preferably more than 0.50%.

P: not more than 0.040%

[0034] Phosphorous (P) is an impurity. P deteriorates hot workability and weldability of the alloy, and also deteriorates creep ductility of the alloy after long hours of usage. Therefore, the P content is not more than 0.040%. The upper limit of the P content is preferably 0.035%, and more preferably 0.030%. The P content is preferably as low as possible. However, excessive reduction of the P content will increase the production cost. Therefore, the lower limit of the P content is preferably 0.0005%, and more preferably 0.0008%.

S: not more than 0.0050%

[0035] Sulfur (S) is an impurity. S deteriorates the stress relaxation cracking resistance of the alloy, and also deteriorates the hot workability, weldability, and creep ductility of the alloy. Therefore, the S content is not more than 0.0050%. The upper limit of the S content is preferably 0.0030%. The S content is preferably as low as possible. However, excessive reduction of the S content will increase the production cost. Therefore, the lower limit of the S content is preferably 0.0002%, and more preferably 0.0003%.

Cr: 18.0 to 25.0%

[0036] Chromium (Cr) improves the oxidation resistance and corrosion resistance at high temperatures of the alloy. When the Cr content is too low, these effects cannot be obtained. On the other hand, when the Cr content is too high, the stability of austenite at high temperatures deteriorates and the creep strength of the alloy decreases. Therefore, the Cr content is 18.0 to 25.0%. The lower limit of the Cr content is preferably 18.5%, and more preferably 19.0%. The upper limit of the Cr content is preferably 24.5%, and more preferably 24.0%.

Ni: 25.0 to 40.0%

[0037] Nickel (Ni) stabilizes austenite structure. Further, Ni forms γ' , thereby increasing the creep strength of the alloy. When the Ni content is too low, γ' is not likely to be formed, and the aforementioned effect cannot be obtained. On the other hand, when the Ni content is too high, the production cost increases. Therefore, the Ni content is 25.0 to 40.0%. The lower limit of the Ni content is preferably 26.0%, and more preferably 27.0%. The upper limit of the Ni content is preferably 37.0%, and more preferably 35.0%.

Ti: 0.10 to 1.60%

[0038] Titanium (Ti) combines with Ni to form γ' . Further, Ti combines with C to form TiC, thereby increasing the creep strength and tensile strength of the alloy at high temperatures. When the Ti content is too low, such effects cannot be obtained. On the other hand, when the Ti content is too high, γ' precipitates excessively, thereby deteriorating the stress relaxation cracking resistance of the alloy. Therefore, the Ti content is 0.10 to 1.60%. The lower limit of the Ti content is preferably 0.20%, more preferably 0.30%, and further preferably more than 0.60%. The upper limit of the Ti content is preferably 1.50%, more preferably less than 1.50%, and further preferably 1.40%.

Al: 0.05 to 1.00%

[0039] Aluminum (Al) deoxidizes the alloy. Further, Al combines with Ni to form γ' and increases the creep strength and tensile strength of the alloy at high temperatures. When the Al content is too low, such effects cannot be obtained. On the other hand, when the Al content is too high, γ' precipitates in a large amount, thereby deteriorating the stress relaxation cracking resistance, creep ductility, and toughness of the alloy. Therefore, the Al content is 0.05 to 1.00%. The lower limit of the Al content is preferably 0.08%, and more preferably 0.10%. The upper limit of the Al content is preferably 0.90%, and more preferably 0.80%.

N: not more than 0.020%

[0040] Nitrogen (N) is an impurity. N precipitates as coarse TiN, and decreases the amount of dissolved Ti, thereby decreasing the creep strength of the alloy. Further, N deteriorates toughness and hot workability of the alloy. Therefore, the N content is not more than 0.020%. The upper limit of the N content is preferably 0.017%, and more preferably 0.015%. The N content is preferably as low as possible. However, excessive reduction thereof will increase production cost. Therefore, the lower limit of the N content is preferably 0.002%, and more preferably 0.004%.

O: not more than 0.008%

[0041] Oxygen (O) is an impurity. Oxygen deteriorates the hot workability of the alloy, and also deteriorates the toughness and ductility of the alloy. Therefore, the O content is not more than 0.008%. The upper limit of the O content is preferably 0.006%, and more preferably 0.005%. The O content is preferably as low as possible. However, excessive reduction thereof will increase the production cost. Therefore, the lower limit of the O content is preferably 0.0005%, and more preferably 0.0008%.

REM: 0.001 to 0.100%

[0042] Rare earth metal (REM) forms a compound with S, thereby decreasing the content of S which has dissolved into the matrix, and improving the stress relaxation cracking resistance of the alloy. Further, REM improves the hot workability and oxidization resistance of the alloy. When the REM content is too low, these effects cannot be obtained. On the other hand, when the REM content is too high, the hot workability and weldability of the alloy will deteriorate. Therefore, the REM content is 0.001 to 0.100%. The lower limit of the REM content is preferably 0.003%, and more preferably 0.005%. The upper limit of the REM content is preferably 0.090%, and more preferably 0.080%.

[0043] REM is a generic name of a total of 17 elements of Sc, Y, and lanthanoids, and the REM content refers to a total content of one or more elements of REM. Moreover, REM is generally contained in misch metal. For that reason, REM may be added to molten metal as misch metal, and may be adjusted such that the REM content is within the above described range.

[0044] The balance of the chemical composition of the NiCrFe alloy according to the present invention consists of Fe and impurities. Here, the term impurity means an element which is introduced from ores and scraps as the raw material, or from a production environment, etc., when the NiCrFe alloy is industrially produced, and which is permitted within a range not adversely affecting the NiCrFe alloy of the present embodiment.

[Optional elements]

[0045] The NiCrFe alloy according to the present invention may contain B in place of part of Fe.

B: 0 to 0.010%

[0046] Boron (B) is an optional element and may not be contained. When contained, B increases the creep strength

of the alloy by causing grain boundary carbides to be finely dispersed. Further, B segregates in grain boundaries to assist the effects of REM. When B is contained in any small amount, the aforementioned effects will be obtained to some degree. However, when the B content is too high, the weldability and hot workability of the alloy will deteriorate. Therefore, the B content is 0 to 0.010%. The upper limit of the B content is preferably 0.008%. The lower limit of the B content to

effectively obtain the aforementioned effects is preferably 0.0001%, and more preferably 0.0005%.
[0047] The NiCrFe alloy according to the present invention may contain one or two types selected from the group consisting of Ca and Mg in place of part of Fe. Each of these elements forms a compound with S, thereby assisting the effects of REM.

Ca: 0 to 0.010%

[0048] Calcium (Ca) is an optional element and may not be contained. When contained, Ca forms a compound with S, thereby assisting the S immobilizing effect of REM. If Ca is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the Ca content is too high, Ca forms oxide, and deteriorates the hot workability of the alloy. Therefore, the Ca content is 0 to 0.010%. The upper limit of the Ca content is preferably 0.008%. The lower limit of the Ca content to effectively obtain the aforementioned effect is preferably 0.0001%, more preferably 0.0002% and further preferably 0.0003%.

Mg: 0 to 0.010%

[0049] Magnesium (Mg) is an optional element and may not be contained. When contained, Mg forms a compound with S, thereby assisting the S immobilizing effect of REM. When Mg is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the Mg content is too high, Mg forms oxide, thereby deteriorating the hot workability of the alloy. Therefore, the Mg content is 0 to 0.010%. The upper limit of the Mg content is preferably 0.008%. The lower limit of the Mg content to effectively obtain the aforementioned effect is preferably 0.0001%, more preferably 0.0002% and further preferably 0.0003%.

[0050] The NiCrFe alloy according to the present invention may contain one or more types selected from the group consisting of V, Nb, Ta, and Hf in place of part of Fe. Each of these elements forms carbide and carbonitride, thereby increasing the creep strength of the alloy.

V: 0 to 0.5%

[0051] Vanadium (V) is an optional element and may not be contained. When contained, V forms fine carbide and carbonitride with C and N, thereby increasing the creep strength of the alloy. When V is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the V content is too high, a large amount of carbide and carbonitride will precipitate, thereby deteriorating the creep ductility of the alloy. Therefore, the V content is 0 to 0.5%. The upper limit of the V content is preferably 0.4%. The lower limit of the V content to effectively obtain the aforementioned effect is 0.01%.

Nb: 0 to 1.0%

[0052] Niobium (Nb) is an optional element and may not be contained. When contained, Nb forms fine carbide and carbonitride with C and N, thereby increasing the creep strength of the alloy. When Nb is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the Nb content is too high, a large amount of carbide and carbonitride will precipitate, thereby deteriorating the creep ductility and toughness of the alloy. Therefore, the Nb content is 0 to 1.0%. The upper limit of the Nb content is preferably 0.4%. The lower limit of the Nb content to effectively obtain the aforementioned effect is 0.01%.

Ta: 0 to 1.0%

[0053] Tantalum (Ta) is an optional element and may not be contained. When contained, Ta forms fine carbide and carbonitride with C and N, thereby increasing the creep strength of the alloy. When Ta is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the Ta content is too high, a large amount of carbide and carbonitride will precipitate, thereby deteriorating the creep ductility and toughness of the alloy. Therefore, the Ta content is 0 to 1.0%. The upper limit of the Ta content is preferably 0.4%. The lower limit of the Ta content to effectively obtain the aforementioned effect is 0.01%.

Hf: 0 to 1.0%

[0054] Hafnium (Hf) is an optional element and may not be contained. When contained, Hf forms fine carbide and carbonitride with C and N, thereby increasing the creep strength of the alloy. When Hf is contained in any small amount, the aforementioned effect will be obtained to some degree. However, when the Hf content is too high, a large amount of carbide and carbonitride will precipitate, thereby deteriorating the creep ductility and toughness of the alloy. Therefore, the Hf content is 0 to 1.0%. The upper limit of the Hf content is preferably 0.4%. The lower limit of the Hf content to effectively obtain the aforementioned effect is 0.01%.

[0055] The NiCrFe alloy according to the present invention may contain one or more types selected from the group consisting of Mo, W, Co, and Cu in place of part of Fe.

Mo: 0 to 1.0%

[0056] Molybdenum (Mo) is an optional element and may not be contained. When contained, Mo dissolves into the alloy, thereby increasing the creep strength of the alloy at high temperatures. When Mo is contained in any small amount, such effect will be obtained to some degree. However, when the Mo content is too high, the stability of austenite will be lost, thereby deteriorating the toughness of the alloy. Therefore, the Mo content is 0 to 1.0%. The upper limit of the Mo content is preferably 0.9%. The lower limit to effectively obtain the aforementioned effect is preferably 0.01%.

W: 0 to 2.0%

[0057] Tungsten (W) is an optional element and may not be contained. When contained, W dissolves into the alloy, thereby increasing the creep strength of the alloy at high temperatures. When W is contained in any small amount, such effect will be obtained to some degree. However, when the W content is too high, the stability of austenite will be lost, thereby deteriorating the toughness of the alloy. Therefore, the W content is 0 to 2.0%. The upper limit of the W content is preferably 1.8%. The lower limit of the W content to effectively obtain the aforementioned effect is preferably 0.01%.

Co: 0 to 3.0%

[0058] Cobalt (Co) is an optional element and may not be contained. When contained, Co stabilizes austenite and dissolves into the alloy, thereby increasing the creep strength of the alloy at high temperatures. When Co is contained in any small amount, such effects will be obtained to some degree. However, when the Co content is too high, the production cost increases. Therefore, the Co content is 0 to 3.0%. The upper limit of the Co content is preferably 2.8%. The lower limit of the Co content to effectively obtain the aforementioned effects is preferably 0.01%.

Cu: 0 to 3.0%

[0059] Copper (Cu) is an optional element and may not be contained. When contained, Cu stabilizes austenite and suppresses precipitation of brittle phase such as σ phase during use at high temperatures. When Cu is contained in any small amount, such effects will be obtained to some degree. However, when the Cu content is too high, the hot workability of the alloy deteriorates. Therefore, the Cu content is 0 to 3.0%. The upper limit of the Cu content is preferably 2.5%, and more preferably less than 2.0%. The lower limit of the Cu content to effectively obtain the aforementioned effects is preferably 0.01%.

[Formula (1)]

[0060] The NiCrFe alloy according to the present invention further satisfies Formula (1):

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

where, each symbol of element in Formula (1) is substituted by the content (mass%) of the corresponding element.

[0061] $\text{fn1} = \text{Ti} + 48\text{Al}/27$ is an index to indicate the precipitation amount of γ' . fn1 indicates a total amount of Ti when the amount of Al is converted into the amount of Ti. When fn1 is less than 0.50, a sufficient precipitation amount of γ' will not be obtained, so that the NiCrFe alloy cannot obtain excellent creep resistance. On the other hand, when fn1 is more than 2.20, the stress relaxation cracking resistance, creep ductility, and toughness of the alloy will deteriorate due to an excessive precipitation amount of γ' . Therefore, fn1 is 0.50 to 2.20. In this range, an appropriate amount of γ' is

precipitated, and excellent creep resistance is obtained. The upper limit of the fn1 is preferably 2.00. The lower limit of fn1 is preferably 0.65.

[Formula (2)]

[0062] The above described chemical composition further satisfies Formula (2):

$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

where, each symbol of element in Formula (2) is substituted by the content (mass%) of the corresponding element.

[0063] $\text{fn2} = \text{Ti}/(\text{Ti} + 48\text{Al}/27)$ is a ratio of the Ti content with respect to the total content of Al and Ti, the content of Al being converted into the amount of Ti. When fn2 is less than 0.40, the Ti content is too low with respect to the Al content, and the precipitation amount of γ' decreases. As a result, the NiCrFe alloy cannot obtain excellent creep strength. On the other hand, when fn2 is more than 0.80, the Ti content becomes excessive with respect to the Al content so that although fine γ' precipitates in an early stage of creep, the γ' changes to coarse and acicular η phase over time. As a result, the creep strength and toughness of the alloy deteriorate. Therefore, fn2 is 0.40 to 0.80. In this range, γ' precipitates in an appropriate amount, and will not change to η phase even when further time passes so that excellent creep strength is obtained. The upper limit of fn2 is preferably 0.75.

[Formula (3)]

[0064] The above described chemical composition further satisfies Formula (3):

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in Formula (3) is substituted by the content (mass%) of the corresponding element, and A(REM) is substituted by the atomic weight of each REM.

[0065] $\text{fn3} = \sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16$ is an index to indicate the amount of S that segregates in grain boundaries. When fn3 is a negative value, S segregates in grain boundaries, thereby resulting in grain boundary embrittlement so that the stress relaxation cracking resistance of the alloy deteriorates. On the other hand, when fn3 is not less than 0, REM immobilizes S as inclusions, thereby decreasing the S content in the matrix. As a result, it is possible to improve the stress relaxation cracking resistance of the alloy. Therefore, fn3 is not less than 0.

[Production method]

[0066] One example of production method of the NiCrFe alloy of the present embodiment will be described. The production method of the present embodiment comprises a process of producing an ingot (steelmaking process), and a process of producing a hot-rolled plate (hot working process). Hereinafter, each process will be described in detail.

[Steelmaking process]

[0067] First, alloys having the above described chemical compositions are melted. The melting is performed by using, for example, the high-frequency induction vacuum melting. Next, an ingot is produced by an ingot-making method.

[Hot working process]

[0068] In the hot working process, normally, hot working is performed once or multiple times. First, the ingot is heated, and thereafter hot working is performed. The hot working refers to, for example, hot forging and hot rolling. The hot working may be performed by a well-known method.

[0069] Further, the hot-worked NiCrFe alloy may be subjected to cold working. The cold working is, for example, cold rolling.

[0070] Further, the NiCrFe alloy, which has been subjected to the above described working, may be subjected to heat treatment. The heat treatment temperature is preferably 1050 to 1200°C. Further, after being heated and held, the NiCrFe alloy is preferably water cooled.

[0071] In the above described exemplary production method, a production method of a NiCrFe alloy plate has been

described. However, the NiCrFe alloy may be a bar or an alloy pipe. In other words, the shape of the product will not be limited. Moreover, in the case of the alloy pipe, it is preferable that hot working by hot extrusion is performed.

[0072] The NiCrFe alloy produced by the processes described so far has excellent creep strength and excellent stress relaxation cracking resistance.

[Micro structure]

[0073] In the NiCrFe alloy according to the present invention, γ' and η phase precipitate in a use environment at high temperatures. In other words, the microstructure of the NiCrFe alloy according to the present invention after being kept at 650°C for 3000 hours contains a total of 2 to 6 mass% of γ' and η phase, wherein the number density of η phase is less than 5/100 μm^2 . Note that the γ' and η phase are herein also collectively referred to as "aging precipitates".

[0074] In a case where the NiCrFe alloy according to the present invention is subjected to aging treatment for keeping the alloy at 650°C for 3000 hours and then a total of γ' and η phase is less than 2 mass%, the precipitation amount of γ' in the alloy will be decreased. As a result, the NiCrFe alloy cannot obtain excellent creep strength. On the other hand, in a case where the same aging treatment is performed and then a total of γ' and η phase is more than 6 mass%, the precipitation amount of γ' may excessively increase. In that case, the alloy cannot obtain excellent stress relaxation cracking resistance. Therefore, the total of γ' and η phase after aging treatment is 2 to 6 mass%.

[0075] Specifically, the total of γ' and η phase can be measured by the following method. The NiCrFe alloy according to the present invention is subjected to aging treatment for keeping the alloy at 650°C for 3000 hours. A test specimen of 10 mm \times 5 mm \times 50 mm is sampled from the NiCrFe alloy after the aging treatment. When the alloy is an alloy plate, the test specimen is sampled from a middle part of plate thickness of the alloy pipe. On the other hand, when the alloy is an alloy pipe, the test specimen is sampled from a middle part of wall thickness. Note that the weight of the test specimen is measured in advance.

[0076] The sampled test specimen is electrolyzed in a 1% tartaric acid-1% $(\text{NH}_4)_2\text{SO}_4$ -water solution to sample the residue from the electrolyte. The sampled residue is melted by HCl (1+4)-20% tartaric acid solution of 60°C and the solution is filtered. The filtrate is measured by ICP emission spectrometry to determine Ti, Al, and Ni concentrations in the residue. From the determined Ti, Al, and Ni concentrations in the residue, and the weight of the test specimen, Ti, Al, and Ni contents in the γ' and η phase of the test specimen are determined. The sum of Ti, Al, and Ni contents, which have been determined by the method described so far, is defined as a sum of γ' and η phase (mass%).

[0077] In a case where the NiCrFe alloy according to the present invention is subjected to aging treatment for keeping the alloy at 650°C for 3000 hours and then the number density of η phase is not less than 5/100 μm^2 , part of γ' has changed to η phase. For that reason, the NiCrFe alloy cannot obtain excellent creep strength. Therefore, the number density of η phase after aging treatment is less than 5/100 μm^2 .

[0078] Specifically, the number density of η phase can be measured by the following method. The NiCrFe alloy according to the present invention is subjected to aging treatment for keeping the alloy at 650°C for 3000 hours. Microscopic observation is performed on the NiCrFe alloy after aging treatment. Specifically, a microscopic test specimen is sampled from the NiCrFe alloy after aging treatment. When the alloy is an alloy plate, the test specimen is sampled from a middle part of the plate thickness. On the other hand, when the alloy is an alloy pipe, the microscopic test specimen is sampled from a middle part of wall thickness of the alloy pipe. The sampled microscopic test specimen is subjected to mechanical polishing. The surface of the microscopic test specimen after mechanical polishing is electrolytically corroded by 10% oxalic acid. The microscopic test specimen after electrolytic corrosion is observed by a scanning electron microscope (SEM) in 5 visual fields, and an SEM image is created for each visual field. The observation magnification is 10000 times, and observation field is, for example, 12 $\mu\text{m} \times 9 \mu\text{m}$.

[0079] The γ' and η phase differ in their shapes. Specifically, γ' is observed to be spherical and η phase be acicular. More specifically, an aspect ratio of γ' is less than 3, and an aspect ratio of η phase is not less than 3. Here, the term "aspect ratio" means a value obtained by dividing the major axis length by the minor axis length for each aging precipitate.

[0080] In the above described SEM image of each visual field, aging precipitates (γ' and η phase) are identified from contrast. Further, by image processing, aspect ratios are calculated for the identified aging precipitates. To calculate an aspect ratios, general purpose application software may be used. When a calculated aspect ratio is not less than 3, the aging precipitate is identified to be η phase.

[0081] For an SEM image of each visual field, the number of identified η phase is counted to determine a sum of the numbers in all visual fields. By using the number of η phase in all visual fields and the area of the all visual fields, the number density of η phase in an observation field of 100 μm^2 (number/100 μm^2) is determined.

EXAMPLES

[0082] Alloys having chemical compositions indicated by Reference marks 1 to 15 shown in Table 1 were melted by the high-frequency induction vacuum melting method.

[Table 1]

5

10

15

20

25

30

35

40

45

50

55

[0083]

TABLE 1

Reference mark	Chemical composition (in mass%, with the balance being Fe and impurities)											fn1	fn2	fn3	REM element
	C	Si	Mn	P	S	Cr	Ni	Ti	Al	N	O	REM	Others		
1	0.06	0.41	0.85	0.013	0.0020	20.4	34.8	0.85	0.37	0.008	0.003	0.028	-	0.0000069	Nd
2	0.07	0.38	1.04	0.011	0.0006	23.5	35.0	1.35	0.36	0.012	0.002	0.015	B:0.002,Mo:0.5	0.0000021	Nd
3	0.07	0.25	0.98	0.014	0.0010	19.8	31.4	0.95	0.43	0.007	0.005	0.035	Ca:0.003	0.0000035	Nd
4	0.08	0.29	1.48	0.008	0.0003	19.3	29.5	0.84	0.55	0.006	0.002	0.019	W:1.2	0.0000392	Nd
5	0.07	0.25	0.78	0.011	0.0007	21.7	30.7	1.19	0.43	0.009	0.005	0.044	Mg:0.004, V:0.3	0.0000753	Nd
6	0.05	0.36	0.89	0.010	0.0006	23.6	33.0	0.64	0.35	0.009	0.004	0.031	Nb:0.3,Co:2.3	0.0000376	La
7	0.05	0.38	0.95	0.012	0.0010	20.5	27.3	0.72	0.45	0.003	0.003	0.030	Ta:0.1,Hf:0.4	0.0000580	Ce
8	0.08	0.22	0.99	0.015	0.0010	22.1	32.9	0.77	0.65	0.004	0.003	0.018	Cu:1.3,Co:2.1	0.0000460	Y
9	0.08	0.55	1.45	0.013	0.0010	21.8	31.6	0.28	0.11	0.013	0.001	0.028	Co:2.5	0.0001215	Nd
10	0.09	0.21	0.64	0.016	0.0010	21.8	29.8	1.33	0.70	0.008	0.002	0.032	Nb:0.3	0.0001076	Nd
11	0.10	0.25	1.12	0.008	0.0008	21.3	34.5	0.45	0.84	0.008	0.005	0.042	-	0.0000583	Nd
12	0.08	0.18	1.51	0.009	0.0004	19.5	29.9	0.65	0.57	0.008	0.002	0.024	W:1.5	0.0000708	Nd
13	0.10	0.33	0.88	0.011	0.0005	20.9	38.2	1.67	0.11	0.011	0.002	0.065	B:0.002,Cu:1.3	0.0003524	Nd
14	0.10	0.25	1.07	0.009	0.0010	19.9	32.8	0.88	0.41	0.009	0.005	0.026	B:0.003	-0.0000590	Nd
15	0.07	0.42	0.88	0.013	0.0010	20.8	34.5	0.88	0.36	0.007	0.003	-	-	-0.0001563	-

EP 3 524 705 A1

[0084] An ingot of 50 kg was produced by using an alloy of each Reference mark. The ingot was subjected to hot forging and hot rolling to obtain a plate material having a thickness of 15 mm. Each plate material was kept at 1150°C for 30 minutes, and thereafter the plate material was rapidly cooled (water cooling) and subjected to solution treatment. By the production processes described so far, NiCrFe alloy plate materials were produced. Using thus produced NiCrFe alloy plate materials, the following tests were conducted.

[Creep rupture test]

[0085] A test specimen was fabricated from the produced alloy plate material. The test specimen was sampled from a central part of thickness of the alloy plate material in parallel with the longitudinal direction (rolling direction). The specimen was a round bar test specimen, whose parallel part had a diameter of 6 mm, and which had a gauge length of 30 mm. By using the test specimen, a creep rupture test was conducted. The creep rupture test was performed under a tensile load of 70 MPa in the air atmosphere of 750°C. A test specimen whose rupture time was not less than 3000 hours was evaluated as "E" (Excellent), and those whose rupture time was less than 3000 hours as "NA" (Not Acceptable).

[Table 2]

[0086]

TABLE 2

Reference mark	Microstructure evaluation	Sum of γ' and η phase (mass%)	Creep rupture test	Stress relaxation cracking test
1	E	3.0	E	E
2	E	5.2	E	E
3	E	3.7	E	E
4	E	3.3	E	E
5	E	5.0	E	E
6	E	3.4	E	E
7	E	2.9	E	E
8	E	2.8	E	E
9	L	0.0	NA	E
10	TM	7.6	E	NA
11	L	0.8	NA	E
12	L	1.9	NA	E
13	TM, η	7.0	NA	E
14	E	3.6	E	NA
15	E	3.8	E	NA

[Microstructure observation]

[0087] From thus produced alloy plate materials, test specimens were fabricated by the above described method. The fabricated test specimens were subjected to aging treatment to keep them at 650°C for 3000 hours, and the sum (mass%) of γ' and η phase of each test specimen was determined by the above described method. Further, the number density of η phase (number/100 μm^2) was determined by the above described method. A sum of γ' and η phase of less than 2 mass% was evaluated as "L" (Less), that of 2 to 6 mass% as "E" (Excellent), and that of more than 6 mass% as "TM" (Too Much). Further, those showed a number density of η phase of not less than 5/100 μm^2 were evaluated as " η ".

[Stress relaxation cracking test]

[0088] The produced alloy plate material was further subjected to cold working. Specifically, cold rolling was performed

on the alloy plate material until its thickness became 12 mm. The reduction of area of this cold rolling was 20%. A test specimen was fabricated from this alloy plate material. The test specimen was sampled from a central part of thickness of the alloy plate material in parallel with the longitudinal direction (rolling direction). The specimen was a round bar test specimen, whose parallel part had a diameter of 6 mm, and which had a gauge length of 30 mm. By using the specimen, a stress relaxation cracking test was conducted. The stress relaxation cracking test was conducted such that the test specimen is subjected to tensile strain 10% at a strain rate of 0.05 min^{-1} and is kept as is for 300 hours in air atmosphere of 650°C . A specimen which did not rupture after being kept for 300 hours was evaluated as "E" (Excellent), and one which ruptured as "NA" (Not Acceptable).

[Test results]

[0089] Test results are shown in Table 2.

[0090] Referring to Table 2, the chemical compositions of Reference marks 1 to 8 were appropriate, so that fn1 was 0.50 to 2.20, fn2 was 0.40 to 0.80, and fn3 was not less than 0. For that reason, in the microstructure, the sum of γ' and η phase was 2 to 6 mass%. Further, the number density of η phase was less than $5/100 \mu\text{m}^2$. As a result, the creep rupture time was not less than 3000 hours, thus exhibiting excellent creep strength. Further, none of the specimens ruptured in the stress relaxation cracking test, exhibiting excellent stress relaxation cracking resistance.

[0091] On the other hand, in Reference mark 9, the value of fn1 was too low. For that reason, in the microstructure, the sum of γ' and η phase was less than 2 mass%, which was too low. As a result, the creep rupture time was less than 3000 hours, not exhibiting excellent creep strength.

[0092] In Reference mark 10, the value of fn1 was too high. For that reason, in the microstructure, the sum of γ' and η phase was more than 6 mass%. Further, the number density of η phase was less than $5/100 \mu\text{m}^2$. In other words, in the microstructure, γ' was more than 6 mass%, which was too high. As a result, the test specimen ruptured in the stress relaxation cracking test, thus not exhibiting excellent stress relaxation cracking resistance.

[0093] In Reference marks 11 and 12, the value of fn2 was too low. For that reason, in the microstructure, the sum of γ' and η phase was less than 2 mass%, which was too low. As a result, the creep rupture time was less than 3000 hours, not exhibiting excellent creep strength.

[0094] In Reference mark 13, the value of fn2 was too high. For that reason, in the microstructure, the number density of η phase was not less than $5/100 \mu\text{m}^2$. As a result, the creep rupture time was less than 3000 hours, not exhibiting excellent creep strength.

[0095] In Reference mark 14, the value of fn3 was too low. As a result, the specimen ruptured in the stress relaxation cracking test, thus not exhibiting excellent stress relaxation cracking resistance. This is considered because S in the matrix could not be immobilized.

[0096] In Reference mark 15, the REM content was too low. Further the value of fn3 was too low. As a result, the test specimen ruptured in the stress relaxation cracking test, not exhibiting excellent stress relaxation cracking resistance. This is considered because S in the matrix could not be immobilized.

[0097] So far, the embodiments of the present invention have been described. However, the above described embodiments are merely illustration for practicing the present invention. Therefore, the present invention will not be limited to the above described embodiments, and can be practiced by appropriately modifying the above described embodiments within a range not departing from the spirit of the invention.

INDUSTRIAL APPLICABILITY

[0098] The present invention can be widely applied to uses for which high creep strength and stress relaxation cracking resistance are demanded. Particularly, the present invention can be suitably used for high temperature members of thermal power generation boilers, petroleum refining and chemical industry plants, or the like.

Claims

1. A NiCrFe alloy, comprising a chemical composition consisting of: in mass%,
C: 0.03 to 0.15%,
Si: not more than 1.00%,
Mn: not more than 2.00%,
P: not more than 0.040%,
S: not more than 0.0050%,
Cr: 18.0 to 25.0%,
Ni: 25.0 to 40.0%,

Ti: 0.10 to 1.60%,
 Al: 0.05 to 1.00%,
 N: not more than 0.020%,
 O: not more than 0.008%,
 5 Rare earth metal (REM): 0.001 to 0.100%,
 B: 0 to 0.010%,
 Ca: 0 to 0.010%,
 Mg: 0 to 0.010%,
 V: 0 to 0.5%,
 10 Nb: 0 to 1.0%,
 Ta: 0 to 1.0%,
 Hf: 0 to 1.0%,
 Mo: 0 to 1.0%,
 W: 0 to 2.0%,
 15 Co: 0 to 3.0%,
 and Cu: 0 to 3.0%, with the balance being Fe and impurities, the chemical composition satisfying the following
 Formulae (1) to (3):

$$0.50 \leq \text{Ti} + 48\text{Al}/27 \leq 2.20 \quad (1)$$

$$0.40 \leq \text{Ti}/(\text{Ti} + 48\text{Al}/27) \leq 0.80 \quad (2)$$

$$\sum[\text{REM}/(\text{A}(\text{REM}))] - \text{S}/32 - 2/3 \cdot \text{O}/16 \geq 0 \quad (3)$$

where, each symbol of element in Formulae (1) to (3) is substituted by the content (mass%) of the corresponding
 element, and A(REM) in Formula (3) is substituted by the atomic weight of each rare earth metal.

2. The NiCrFe alloy according to claim 1, wherein
 the chemical composition contains
 B: 0.0001 to 0.010%.

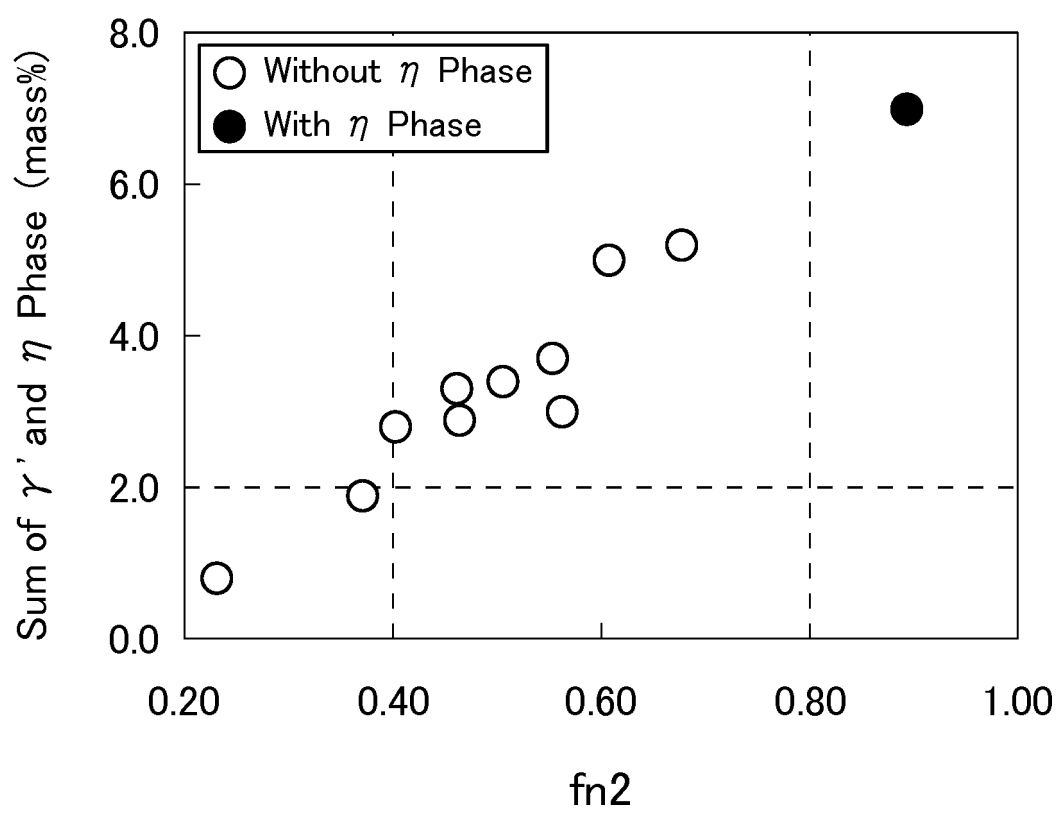
3. The NiCrFe alloy according to claim 1 or 2, wherein
 the chemical composition contains one or two types selected from the group consisting of
 Ca: 0.0001 to 0.010%, and
 Mg: 0.0001 to 0.010.

4. The NiCrFe alloy according to any one of claims 1 to 3, wherein
 the chemical composition contains one or more types selected from the group consisting of
 V: 0.01 to 0.5%,
 Nb: 0.01 to 1.0%,
 Ta: 0.01 to 1.0%, and
 Hf: 0.01 to 1.0%.

5. The NiCrFe alloy according to any one of claims 1 to 4, wherein
 the chemical composition contains one or more types selected from the group consisting of
 Mo: 0.01 to 1.0%,
 W: 0.01 to 2.0%,
 Co: 0.01 to 3.0%, and
 Cu: 0.01 to 3.0%.

6. The NiCrFe alloy according to any one of claims 1 to 5, wherein
 the NiCrFe alloy does not rupture for 300 hours or more in a stress relaxation test in which the NiCrFe alloy is
 subjected to tensile strain of 10% at a strain rate of 0.05 min^{-1} and kept as is in air atmosphere of 650°C after being
 subjected to cold rolling at a reduction of area of 20%.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/036059

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C38/00 (2006.01) i, C22C30/02 (2006.01) i, C22C38/58 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C22C1/00-49/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2017

Registered utility model specifications of Japan 1996-2017

Published registered utility model specifications of Japan 1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2010/113843 A1 (SUMITOMO METAL INDUSTRIES, LTD.) 07 October 2010, & US 2012/0031534 A1 & EP 2415883 A1 & CN 102369300 A	1-6
A	WO 2012/176586 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 27 December 2012, & US 2014/0127073 A1 & EP 2725112 A1 & KR 10-2014-0005357 A & CN 103620077 A	1-6
A	WO 2013/073423 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 23 May 2013, & EP 2781612 A1 & CN 103946403 A & KR 10-2014-0091061 A	1-6
A	JP 2015-196837 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 09 November 2015, (Family: none)	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
13 December 2017 (13.12.2017)Date of mailing of the international search report
26 December 2017 (26.12.2017)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2013227644 A [0005] [0010]
- JP 6264169 A [0005] [0010]
- JP 2002256398 A [0005] [0010]
- JP 8013104 A [0005] [0010]

Non-patent literature cited in the description

- **HANS VAN WORTEL.** Control of Relaxation Crack-
ing in Austenitic High Temperature Components.
CORROSION2007, 2007 [0011]