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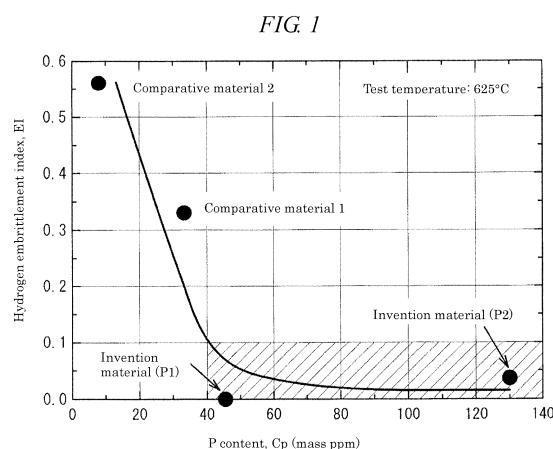
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(54) **NI-BASED ALLOY HAVING EXCELLENT HYDROGEN EMBRITTLEMENT RESISTANCE, AND METHOD FOR PRODUCING NI-BASED ALLOY MATERIAL**

(57) An object is to provide a Ni-based alloy having high strength and excellent hydrogen embrittlement resistance even in a high-temperature and high-pressure environment and particularly capable of being used for an ammonothermal pressure vessel and the like. The present invention relates to a Ni-based alloy including, in terms of mass ratios, Fe: 30 to 40%, Cr: 14 to 16%, Ti: 1.2 to 1.7%, Al: 1.1 to 1.5%, Nb: 1.9 to 2.7%, and P: 40 to 150 ppm, with the remainder being Ni and unavoidable impurities.



Hydrogen embrittlement index of invention material and comparative material

**Description**

## TECHNICAL FIELD

5     **[0001]** The present invention relates to a Ni-based alloy having excellent hydrogen embrittlement resistance and a method for producing a Ni-based alloy material.

## BACKGROUND ART

10    **[0002]** An ammonothermal method has been known as a kind of single crystal growing method and the ammonothermal method has been, for example, applied to single crystal growth of gallium nitride that is a nitride semiconductor for a blue light emitting diode.

15    **[0003]** Gallium nitride has been expected to be utilized as an optical device such as a high-brightness LED and a semiconductor laser, and an electronic device for use in a transistor for electric vehicle, an amplifier for mobile phone base station, or the like. For the application to these devices, it is necessary to enlarge the size of the gallium nitride single crystal and a size of 2 inches or more to 6 inches or more, further a size larger than that has been desired.

20    **[0004]** Hitherto, a vapor-phase growth method has been a main stream for the growth of the gallium nitride single crystal. However, for coping with the enlargement and mass production of the crystal as described above or cost reduction, the method is being replaced by the ammonothermal method in which a crystal is grown in high-temperature and high-pressure ammonia. Since a temperature of 600 to 650°C and a pressure of 200 to 250 MPa are generally used as synthetic conditions in the ammonothermal method, application of a Ni-Fe-based alloy is attempted as a pressure vessel material having high strength under a high-temperature environment.

25    **[0005]** Since operations are conducted under high temperature and high pressure in the ammonothermal method, ammonia as a raw material is decomposed to generate a large amount of high-pressure hydrogen. Therefore, as characteristics required for the pressure vessel material, excellent hydrogen embrittlement resistance at high temperature is first mentioned. In addition, since the vessel is used under a high-temperature environment, creep properties are also required.

30    **[0006]** Hitherto, some techniques relating to a Ni-Fe-based alloy having high strength and excellent hydrogen embrittlement resistance have been developed. For example,

35    **[0007]** Patent Document 1 discloses a technique relating to an Fe-Ni-based alloy having high strength and excellent hydrogen embrittlement resistance, which is used as a high-pressure hydrogen piping material for hydrogen station. The document presents a two-layer structure piping material consisting of an outer layer having high strength imparted thereto by aging and an inner layer having hydrogen embrittlement resistance imparted thereto.

40    **[0008]** Patent Document 2 discloses a Ni-Fe alloy in which high strength and hydrogen embrittlement resistance are exhibited by controlling particle size of the  $\gamma'$  phase and fractions of individual precipitation phases.

45    **[0009]** Moreover, Patent Document 3 discloses a technique dealing with hydrogen embrittlement resistance and the like at high temperature.

## BACKGROUND ART DOCUMENT

40

## PATENT DOCUMENT

**[0010]**

45     Patent Document 1: JP-A-2010-174360

Patent Document 2: JP-A-2009-68031

Patent Document 3: JP-A-5-255788

## SUMMARY OF THE INVENTION

50

## PROBLEMS THAT THE INVENTION IS TO SOLVE

55    **[0011]** However, the temperature at which the alloys have high strength and excellent hydrogen embrittlement resistance is room temperature in Patent Documents 1 and 2 and it is unclear whether these characteristics may be assured or not under high temperature and high pressure. Moreover, although Patent Document 3 deals with a high Ni-based alloy having high strength and excellent hydrogen embrittlement resistance, which is usable at 200 to 500°C, it is considered that characteristics at 600 to 650°C, which are problems of the present invention, cannot be secured in the alloy and also characteristics under high pressure cannot be assured at all.

**[0012]** As mentioned above, any of the conventional Ni-Fe-based alloys having high strength and excellent hydrogen embrittlement resistance cannot assure those characteristics under the conditions dealt with in the present invention.

**[0013]** The present invention has been made based on the above circumstances and an object thereof is to provide a Ni-based alloy having high strength and excellent hydrogen embrittlement resistance even in a high-temperature and high pressure environment, such as 600 to 650°C and 200 to 250 MPa, and a method for producing a Ni-based alloy material.

#### MEANS FOR SOLVING THE PROBLEMS

**[0014]** The present inventors have found that a Ni-based alloy having high strength and excellent hydrogen embrittlement resistance even under high temperature and high pressure is obtained by restricting the composition of the Ni-based alloy to a specific range and thus they have accomplished the present invention. Namely, the gist of the invention lies on the following <1> to <7>.

<1> A Ni-based alloy including, in terms of mass ratios, Fe: 30 to 40%, Cr: 14 to 16%, Ti: 1.2 to 1.7%, Al: 1.1 to 1.5%, Nb: 1.9 to 2.7%, and P: 40 to 150 ppm, with the remainder being Ni and unavoidable impurities.

<2> The Ni-based alloy according to <1>, which further includes at least either one of Mg: 0.01% or less and Zr: 0.1% or less in terms of mass ratios.

<3> The Ni-based alloy according to <1> or <2>, in which a hydrogen embrittlement index EI defined by  $EI = (RA_A - RA_H) / RA_A$  when a reduction of area of a hydrogen charged material and a reduction of area of a hydrogen non-charged material at a tensile test are indicated as  $RA_H$  and  $RA_A$ , respectively, is 0.1 or less at 625°C.

<4> The Ni-based alloy according to any one of <1> to <3>, in which a creep rupture time at 700°C and 333 MPa is 1,500 hours or more.

<5> The Ni-based alloy according to any one of <1> to <4>, in which a minimum creep rate at 700°C and 333 MPa is  $1 \times 10^{-8} \text{ s}^{-1}$  or less.

<6> The Ni-based alloy according to any one of <1> to <5>, which is used as an ammonothermal pressure vessel material.

<7> A method for producing a Ni-based alloy material, the method including subjecting the Ni-based alloy according to <1> or <2> to a solution treatment and subsequently to an aging treatment twice at a temperature of 825 to 855°C and at a temperature of 710 to 740°C.

#### ADVANTAGE OF THE INVENTION

**[0015]** According to the present invention, it becomes possible to provide a Ni-based alloy having good hydrogen embrittlement resistance at such a high temperature as 600°C or higher and excellent creep properties in such a higher-temperature region as 700°C. Furthermore, as a secondary effect, application of the Ni-based alloy to a pressure vessel material for an ammonothermal method enables production of a pressure vessel capable of coping with a higher-temperature and higher-pressure environment and thus, for example, it is expected that enlargement, mass production, and cost reduction of a gallium nitride single crystal useful as an electronic device may be remarkably advanced.

#### BRIEF DESCRIPTION OF THE DRAWINGS

##### **[0016]**

[FIG. 1] FIG. 1 shows a relationship between hydrogen embrittlement index and P content of invention materials and comparative materials.

[FIG. 2] FIG. 2 shows a relationship between creep stress and creep rupture time of the invention materials and the comparative materials.

[FIG. 3] FIG. 3 shows a relationship between creep test time and creep rate of the invention materials and the comparative materials.

#### MODE FOR CARRYING OUT THE INVENTION

**[0017]** The following will explain embodiments of the present invention in detail but the invention is not limited to the following explanations and can be carried out with appropriately changing it in the range without departing from the gist of the invention.

**[0018]** Here, "% by weight", "ratio by weight", and "ppm by weight" are the same as "% by mass", "ratio by mass", and "ppm by mass", respectively.

**[0019]** The Ni-based alloy according to the invention includes, in terms of mass ratios, Fe: 30 to 40%, Cr: 14 to 16%, Ti: 1.2 to 1.7%, Al: 1.1 to 1.5%, Nb: 1.9 to 2.7%, and P: 40 to 150 ppm, with the remainder being Ni and unavoidable impurities.

**[0020]** Moreover, it is more preferable that the Ni-based alloy further includes at least either one of Mg: 0.01% or less and Zr: 0.1% or less.

**[0021]** The following will explain reasons for determining the above-mentioned alloy composition. Hereinafter, the content of each element other than P is shown in terms of % by mass and the content of P is shown in terms of ppm by mass.

Fe: 30 to 40%

**[0022]** Fe is effective for cost reduction of the alloy when the content thereof increases but a Laves phase forms when Fe is excessively incorporated together with Nb incorporation and the formation invites deterioration of material characteristics, such as an increase in hydrogen embrittlement susceptibility. Therefore, the content of Fe is controlled to 30 to 40%. For the same reason, it is preferable to determine the lower limit thereof to 33% and the upper limit thereof to 38%.

Cr: 14 to 16%

**[0023]** Cr is an element necessary for enhancing oxidation resistance, corrosion resistance, and strength. Also, it combines with C to form a carbide, thereby enhancing high-temperature strength. However, too large content thereof invites destabilization of matrix and promotes the formation of harmful TCP phases such as a  $\sigma$  phase and  $\alpha$ -Cr, resulting in adverse influences on ductility and toughness. Also, there is a concern that the  $\sigma$  phase acts as a hydrogen accumulation site in the alloy to enhance the hydrogen embrittlement susceptibility. Therefore, the content of Cr is limited to 14 to 16%.

Ti: 1.2 to 1.7%

**[0024]** Ti mainly forms a MC carbide to suppress crystal grain coarsening of the alloy and also combines with Ni to precipitate a  $\gamma'$  phase, thereby contributing to precipitation strengthening of the alloy. However, when Ti is exceedingly incorporated, the stability of the  $\gamma'$  phase at high temperature is lowered and an  $\eta$  phase is formed, thereby impairing strength, ductility, toughness, and high-temperature long-term structural stability. Moreover, there is a concern that the  $\eta$  phase also acts as a hydrogen accumulation site in the alloy to enhance the hydrogen embrittlement susceptibility. Therefore, the content of Ti is limited to the range of 1.2 to 1.7%.

Al: 1.1 to 1.5%

**[0025]** Al combines with Ni to precipitate a  $\gamma'$  phase, thereby contributing to precipitation strengthening of the alloy. However, when the content thereof is too large, the  $\gamma'$  phase aggregates at grain boundaries and is coarsened, thereby drastically impairing mechanical properties at high temperature and also lowering hot workability. Therefore, the content of Al is limited to 1.1 to 1.5%.

Nb: 1.9 to 2.7%

**[0026]** Nb is an element that stabilizes the  $\gamma'$  phase and contributes to strength enhancement but when Nb is exceedingly incorporated, the precipitation of the  $\eta$  phase, the  $\sigma$  phase, and the Laves phase that are harmful phases is promoted, thereby remarkably lowering the structural stability and enhancing the hydrogen embrittlement susceptibility. Therefore, the content of Nb is limited to 1.9 to 2.7%.

P: 40 to 150 ppm

**[0027]** P is considered to have an effect of suppressing excessive accumulation of hydrogen at grain boundaries by increasing consistency of the grain boundaries and lowering the hydrogen embrittlement susceptibility, so that P is incorporated. In order to obtain the above effect, a P content of 40 ppm or more is necessary. Also, P has effects of lengthening the creep rupture time and decreasing the minimum creep rate. However, when P is exceedingly incorporated, there is a possibility that grain boundary segregation of P becomes excessive to contrarily lower the consistency of the grain boundaries and the effect of reducing the hydrogen embrittlement susceptibility is lost. Therefore, the content of P is limited to 40 to 150 ppm. For the same reason, it is preferable to determine the lower limit thereof to 45 ppm and the upper limit thereof to 140 ppm.

Mg: 0.01% or less

**[0028]** Mg mainly combines with S to form a sulfide and enhances hot workability, so that Mg is incorporated as desired. However, when the content thereof is too large, the grain boundaries are contrarily embrittled and hot workability decreases, so that the content of Mg is preferably controlled to 0.01% or less. Incidentally, for sufficiently exhibiting the above effect, the lower limit of the Mg content is more preferably controlled to 0.0005% or more.

Zr: 0.1 % or less

**[0029]** Zr segregates at grain boundaries to contribute to an improvement in high-temperature characteristics, so that Zr is incorporated as desired. However, when Zr is exceedingly incorporated, the hot workability of the alloy is lowered, so that the content of Zr is preferably controlled to 0.1% or less. Moreover, in order to obtain the above effect, it is more preferable to incorporate it in an amount of 0.01% or more.

**[0030]** It is preferable that at least either one of Mg and Zr is contained in the above ranges but it is more preferable to contain both of Mg and Zr in view of securing good hot workability.

**[0031]** The remainder in the Ni-based alloy according to the invention is Ni and unavoidable impurities.

**[0032]** The unavoidable impurities mean elements which are initially contained in raw materials of the alloy or are unavoidably mixed in during the smelting of the alloy, and examples thereof include O, N and S. The content of the unavoidable impurities in the whole Ni-based alloy is preferably as low as possible and is more preferably 50 ppm or less in view of high purification of the alloy.

**[0033]** The Ni-based alloy of the invention has excellent hydrogen embrittlement resistance and can be suitably used as a material to be exposed to a hydrogen atmosphere. Also, it is excellent in high strength characteristic at high temperature and can be suitably used as an ammonothermal pressure vessel material.

**[0034]** The Ni-based alloy of the invention can be smelted by a usual method and, as the invention, the smelting method is not particularly limited.

**[0035]** The Ni-based alloy of the invention can be subjected to processing such as forging as desired and can be subjected to a solution treatment or a thermal treatment by aging (aging treatment).

**[0036]** The solution treatment can be performed, for example, under conditions of 1,040 to 1,140°C for 4 to 10 hours. Moreover, the aging treatment is preferably a treatment performed in at least two stages. For example, the aging treatment can be performed twice at a temperature of 825 to 855°C and at a temperature of 710 to 740°C. As the temperature for the aging treatment, the treatment is preferably performed first at a temperature of 825 to 855°C (first stage) and subsequently at a temperature of 710 to 740°C (second stage) in this order. Furthermore, the time for the aging treatment is more preferably from 4 to 10 hours at the first stage and from 4 to 24 hours at the second stage.

**[0037]** By adopting the above-mentioned conditions for the solution treatment and the aging treatment, high tensile strength at room temperature and high tensile strength at a high temperature of 600°C or higher can be secured and a Ni-based alloy material having excellent hydrogen embrittlement resistance can be obtained. The resulting tensile strength is preferably 1,000 MPa or more at room temperature and 820 MPa or more at 625°C.

**[0038]** Incidentally, when the temperature at the first stage of the aging treatment is lower than 825°C or higher than 855°C, there is a concern that the  $\gamma'$  phase cannot be sufficiently grown and the above tensile strength cannot be secured.

**[0039]** Moreover,  $M_{23}C_6$  type carbide precipitates in excess when the temperature at the second stage of the aging treatment is lower than 710°C, and MC type carbide is coarsened when the temperature is higher than 740°C. Thereby, there is a concern that adverse influences such as a decrease in high-temperature ductility are caused in both cases.

**[0040]** Among the Ni-based alloys obtained in the above, more preferred is the Ni-based alloy affording such hydrogen embrittlement resistance that hydrogen embrittlement index EI defined by  $EI = (RA_A - RA_H) / RA_A$  when a reduction of area of a hydrogen charged material and a reduction of area of a hydrogen non-charged material at a tensile test are indicated as  $RA_H$  and  $RA_A$ , respectively, is 0.1 or less at 625°C. The hydrogen charge is simulated by intrusion of a hydrogen quantity of 50 ppm.

**[0041]** Moreover, among the Ni-based alloys obtained in the above, more preferred is also the Ni-based alloy affording such a high-temperature creep property that a creep rupture time at 700°C and 333 MPa is 1,500 hours or more.

**[0042]** Furthermore, among the Ni-based alloys obtained in the above, more preferred is also the Ni-based alloy affording such a high-temperature creep property that a minimum creep rate at 700°C and 333 MPa is  $1 \times 10^{-8} \text{ s}^{-1}$  or less.

**[0043]** Incidentally, the Ni-based alloy having the above-mentioned hydrogen embrittlement index and high-temperature creep properties can be obtained by satisfying the compositional requirements mentioned above, and particularly containing P in an amount of 40 ppm or more.

**[0044]** The material using the Ni-based alloy according to the invention can be used for any desired uses capable of exhibiting the hydrogen embrittlement resistance through plastic working or machining, and particularly can be suitably used as an ammonothermal pressure vessel material. Thereby, it becomes possible to realize the enlargement, mass production, and cost reduction of a gallium nitride single crystal, for example.

## EXAMPLES

**[0045]** The following will explain examples of the present invention.

**[0046]** Smelting and forging of a material of 50 kg round steel ingot were performed by a vacuum induction melting method to form plates so as to achieve compositions shown in Table 1, in order to obtain two kinds of invention materials and two kinds of comparative materials, respectively.

**[0047]** The obtained forged plates were cut into ones having an appropriate size, which were then subjected to a solution treatment of  $1,040^{\circ}\text{C} \times 4$  hours and to a two-stage aging treatment of  $840^{\circ}\text{C} \times 10$  hours and subsequent  $730^{\circ}\text{C} \times 24$  hours, thereby obtaining test materials (invention materials P1, P2 and comparative materials 1, 2). Subsequently, the test materials were machined to form tensile test pieces for evaluation of hydrogen embrittlement resistance and creep test pieces.

[Table 1]

| Test material           | Chemical composition of test material (% by mass; ppm by mass for P, S, N, and O) |      |      |         |         |       |       |      |      |      |       |         |        |         |         |
|-------------------------|-----------------------------------------------------------------------------------|------|------|---------|---------|-------|-------|------|------|------|-------|---------|--------|---------|---------|
|                         | C                                                                                 | Si   | Mn   | P (ppm) | S (ppm) | Ni    | Cr    | Al   | Ti   | Nb   | Fe    | Mg      | Zr     | N (ppm) | O (ppm) |
| Invention material (P1) | 0.011                                                                             | 0.01 | 0.01 | 45      | 2       | 41.40 | 15.41 | 1.26 | 1.45 | 2.05 | 38.26 | 0.0015  | 0.030  | 13      | 16      |
| Invention material (P2) | 0.012                                                                             | 0.01 | 0.01 | 130     | 2       | 41.37 | 15.40 | 1.26 | 1.44 | 2.06 | 38.30 | 0.0015  | 0.030  | 12      | 15      |
| Comparative material 1  | 0.011                                                                             | 0.01 | 0.02 | 33      | <1      | 41.66 | 15.10 | 1.11 | 1.68 | 2.06 | 38.20 | <0.0005 | <0.010 | 31      | 7       |
| Comparative material 2  | 0.011                                                                             | 0.01 | 0.01 | 8       | 3       | 41.39 | 15.40 | 1.24 | 1.41 | 2.08 | 38.24 | 0.0012  | 0.036  | 7       | 16      |

**[0048]** Evaluation of the hydrogen embrittlement resistance was performed by the following procedure.

**[0049]** First, a test piece having a diameter and a length of the parallel part of 10 mm and 50 mm, respectively, was held in an atmosphere of a temperature of 450°C and a hydrogen pressure of 25 MPa for 72 hours to charge hydrogen. The hydrogen charging conditions are set so as to simulate 50 ppm that is a hydrogen quantity which is assumed to intrude into the material in an actual ammonothermal method. Using a hydrogen charged material after the hydrogen charge, a tensile test was performed at 625°C and a tensile strength and a reduction of area were measured.

**[0050]** Also, for a test piece in a hydrogen uncharged state (hydrogen non-charged material), a tensile strength and a reduction of area were similarly measured.

**[0051]** As for the hydrogen embrittlement resistance, also using the tensile test results of the hydrogen non-charged material at 625°C, the hydrogen embrittlement index EI defined by the following equation (1) was calculated to perform evaluation:

hydrogen embrittlement index  $EI = (RA_A - RA_H) / RA_A \dots (1)$  in which  $RA_A$  is a reduction of area of a hydrogen non-charged material and  $RA_H$  is a reduction of area of a hydrogen charged material.

A smaller value of the hydrogen embrittlement index indicates more excellent hydrogen embrittlement resistance.

**[0052]** The creep properties were evaluated by performing a creep rupture test and a creep rate test. In both tests, test temperature was 700°C, and test stress was 333 MPa and 275 MPa in the rupture test and was 333 MPa in the rate test.

**[0053]** Table 2 shows the tensile strength, reduction of area, and hydrogen embrittlement index of each of the hydrogen charged materials and the hydrogen non-charged materials at 625°C. Incidentally, the hydrogen embrittlement index of the invention material P1 became negative but this is indicated as 0.00 for convenience sake in Table 2.

[Table 2]

| Tensile strength, reduction of area, and hydrogen embrittlement index of invention material and comparative material at 625°C |                           |                              |                               |                              |                                 |
|-------------------------------------------------------------------------------------------------------------------------------|---------------------------|------------------------------|-------------------------------|------------------------------|---------------------------------|
| Test material                                                                                                                 | Hydrogen charged material |                              | Hydrogen non-charged material |                              | Hydrogen embrittlement index EI |
|                                                                                                                               | Tensile strength /MPa     | Reduction of area $RA_H$ (%) | Tensile strength /MPa         | Reduction of area $RA_A$ (%) |                                 |
| Invention material (P1)                                                                                                       | 725                       | 30.1                         | 733                           | 28.7                         | 0.00                            |
| Invention material (P2)                                                                                                       | 729                       | 38.8                         | 794                           | 39.9                         | 0.03                            |
| Comparative material 1                                                                                                        | 721                       | 17.0                         | 711                           | 25.2                         | 0.33                            |
| Comparative material 2                                                                                                        | 732                       | 15.5                         | 717                           | 35.1                         | 0.56                            |

**[0054]** FIG. 1 shows a relationship between the hydrogen embrittlement index of each of the invention materials P1 and P2 (hereinafter sometimes collectively referred to as "invention material") and the comparative materials 1 and 2 (hereinafter sometimes collectively referred to as "comparative material") at 625°C and the P content in each Ni-based alloy.

**[0055]** From the figure, the hydrogen embrittlement index of the invention material is remarkably small as compared with that of the comparative material and thus it is realized that the invention material is extremely excellent in the hydrogen embrittlement resistance at high temperature. As shown at the shaded section in the figure, when the P content becomes 40 ppm or more, the hydrogen embrittlement index decreases to 0.1 or less and the hydrogen embrittlement susceptibility reduces to such a degree that the influence of hydrogen can be almost ignored. From the results, it is realized that P has effects of suppressing excessive accumulation of hydrogen at grain boundaries by increasing the consistency of the grain boundaries and lowering the hydrogen embrittlement susceptibility and a P content of 40 ppm or more is necessary for improving the hydrogen embrittlement resistance by increasing the P content.

**[0056]** FIG. 2 and FIG. 3 show results of the creep rupture test and results of the creep rate test, respectively. From FIG. 2, the rupture time of the invention material is greatly longer than that of the comparative material. The rupture time of the invention material in the case where the test stress is 333 MPa is at least ten times that of the comparative material 1 and the rupture time is about 1,500 hours in the case of the invention material P1 and is about 2,000 hours in the case of the invention material P2. Furthermore, from FIG. 3, it is realized that the minimum creep rate of the invention material is at least one fourth or less as compared with that of the comparative material 2 and the value is  $1 \times 10^{-8} \text{ s}^{-1}$  ( $3.6 \times 10^{-5}$



$\text{h}^{-1}$ ) or less.

**[0057]** From the above, it becomes obvious that the invention material according to the present invention has excellent creep properties.

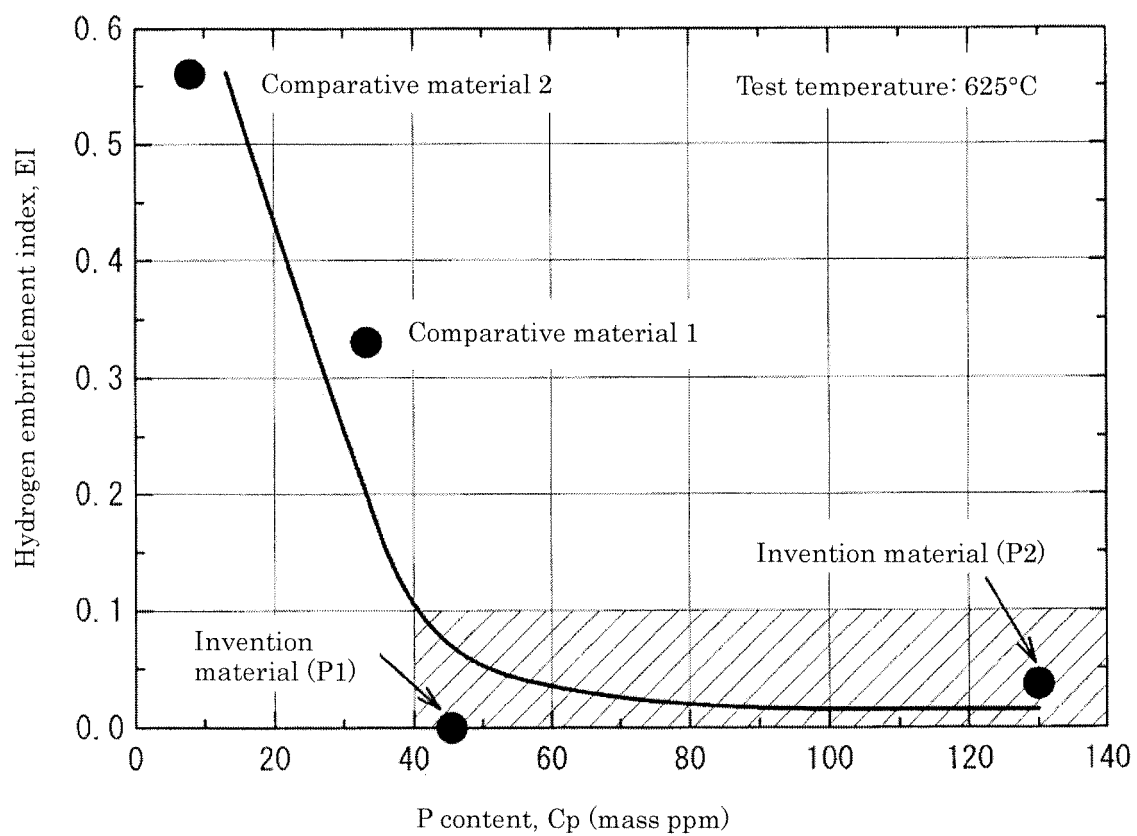
**[0058]** While the invention has been described based on the above embodiments and examples, it will be apparent to one skilled in the art that the invention is not limited to the contents of the above embodiments and examples and various changes and modifications can be made therein without departing from the spirit and scope of the invention.

**[0059]** The present application is based on Japanese Patent Application No. 2012-184966 filed on August 24, 2012, and the contents are incorporated herein by reference.

## Claims

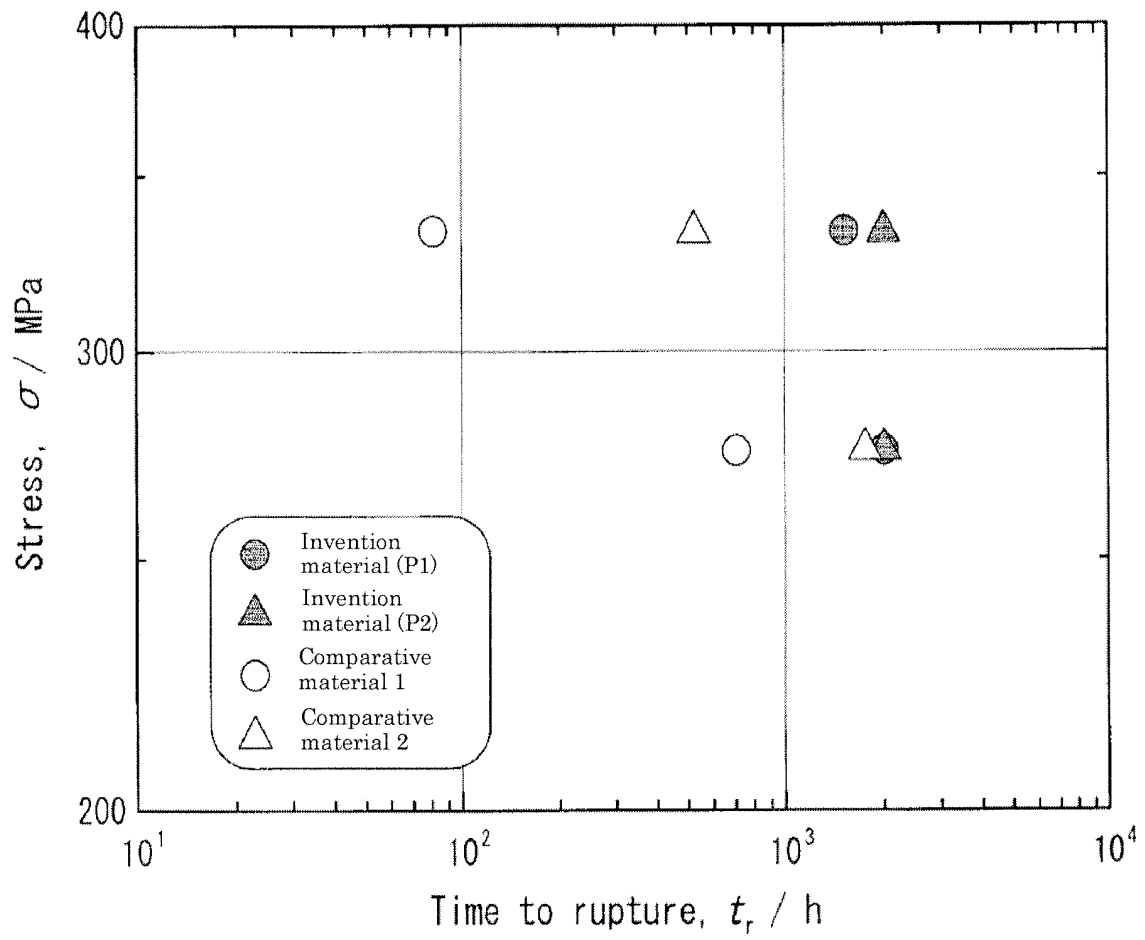
1. A Ni-based alloy comprising, in terms of mass ratios, Fe: 30 to 40%, Cr: 14 to 16%, Ti: 1.2 to 1.7%, Al: 1.1 to 1.5%, Nb: 1.9 to 2.7%, and P: 40 to 150 ppm, with the remainder being Ni and unavoidable impurities.
2. The Ni-based alloy according to claim 1, which further comprises at least either one of Mg: 0.01% or less and Zr: 0.1% or less in terms of mass ratios.
3. The Ni-based alloy according to claim 1 or 2, wherein a hydrogen embrittlement index EI defined by  $EI = (RA_A - RA_H) / RA_A$  when a reduction of area of a hydrogen charged material and a reduction of area of a hydrogen non-charged material at a tensile test are indicated as  $RA_H$  and  $RA_A$ , respectively, is 0.1 or less at 625°C.
4. The Ni-based alloy according to any one of claims 1 to 3, wherein a creep rupture time at 700°C and 333 MPa is 1,500 hours or more.
5. The Ni-based alloy according to any one of claims 1 to 4, wherein a minimum creep rate at 700°C and 333 MPa is  $1 \times 10^{-8} \text{ s}^{-1}$  or less.
6. The Ni-based alloy according to any one of claims 1 to 5, which is used as an ammonothermal pressure vessel material.
7. A method for producing a Ni-based alloy material, said method comprising subjecting the Ni-based alloy according to claim 1 or 2 to a solution treatment and subsequently to an aging treatment twice at a temperature of 825 to 855°C and at a temperature of 710 to 740°C.

FIG. 1



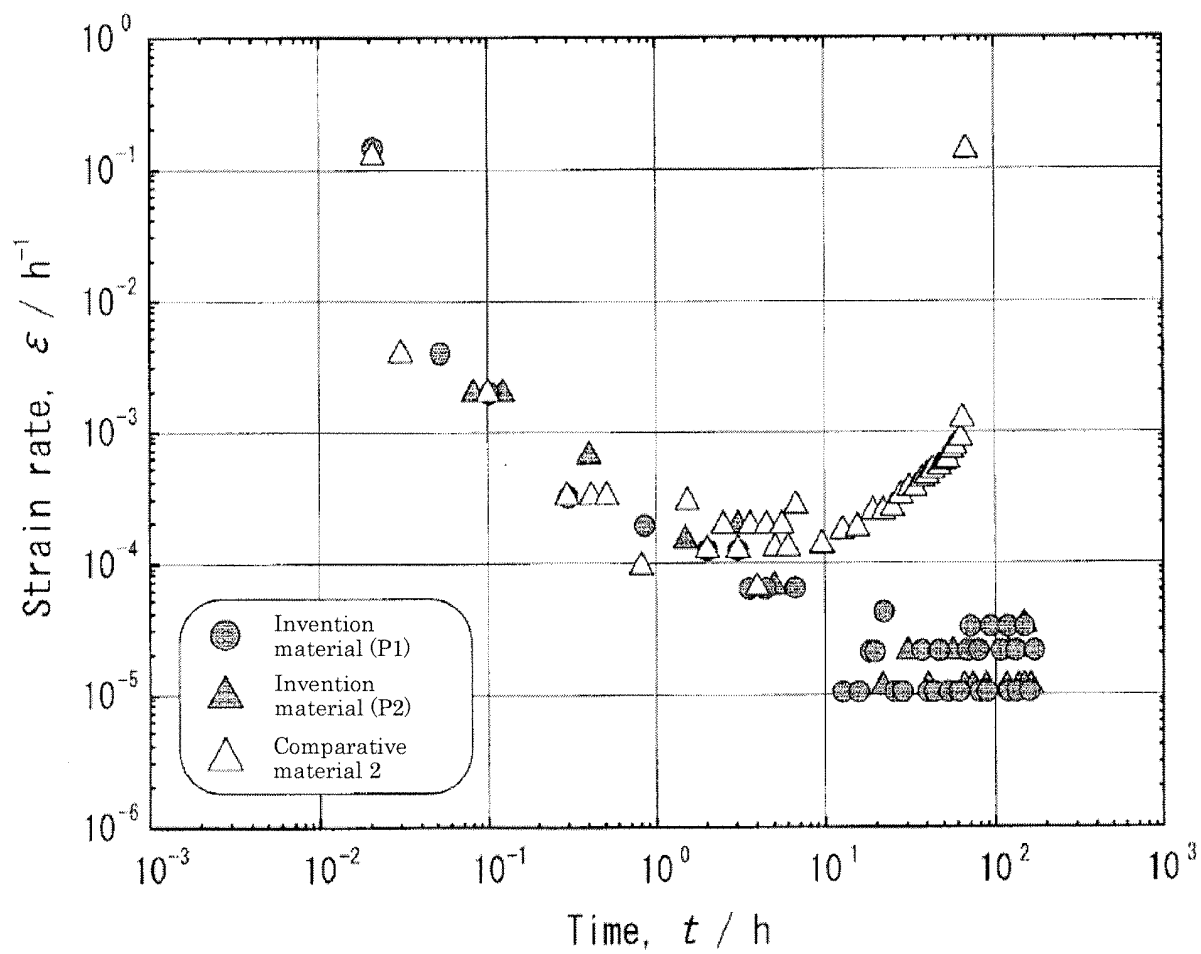
Hydrogen embrittlement index of invention material and comparative material

FIG. 2



Creep rupture time of invention material and comparative material

FIG. 3



Creep rate of invention material and comparative material

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2013/072431

## A. CLASSIFICATION OF SUBJECT MATTER

C22C19/05(2006.01)i, C22F1/10(2006.01)i, C22F1/00(2006.01)n

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)

C22C19/05, C22F1/10, C22F1/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2013

Kokai Jitsuyo Shinan Koho 1971-2013 Toroku Jitsuyo Shinan Koho 1994-2013

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         | JP 2011-127204 A (Hitachi Metals, Ltd.),<br>30 June 2011 (30.06.2011),<br>claims; table 1<br>(Family: none)                                                                                                                                         | 1-7                   |
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☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search

01 October, 2013 (01.10.13)

Date of mailing of the international search report

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