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(54) Ni-Fe-Cr ALLOY

(57) An objective of the present invention is to provide a Ni-Fe-Cr alloy having an excellent intergranular corrosion resistance. A Ni-Fe-Cr alloy of the present embodiment has a chemical composition consisting of, in mass percent, C: 0.005 to 0.015%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.5%, P: 0.030% or less, S: 0.020% or less, Cu: 1.0 to 5.0%, Ni: 30.0 to 45.0%, Cr: 18.0 to 30.0%, Mo: 2.0 to 4.5%, Ti: 0.5 to 2.0%, N: 0.001 to 0.015%, and Al: 0 to 0.50%, with the balance being Fe and impurities. An average grain size d (μm) satisfies Formula (1):

$$d < 4.386 / (C_{rel} + 0.15) \qquad (1)$$

where, C_{rel} in Formula (1) is defined by Formula (2):

$$C_{rel} = C - 0.125Ti + 0.8571N \qquad (2)$$

where, symbols of elements in Formula (1) and Formula (2) are to be substituted by contents of corresponding elements (mass%).

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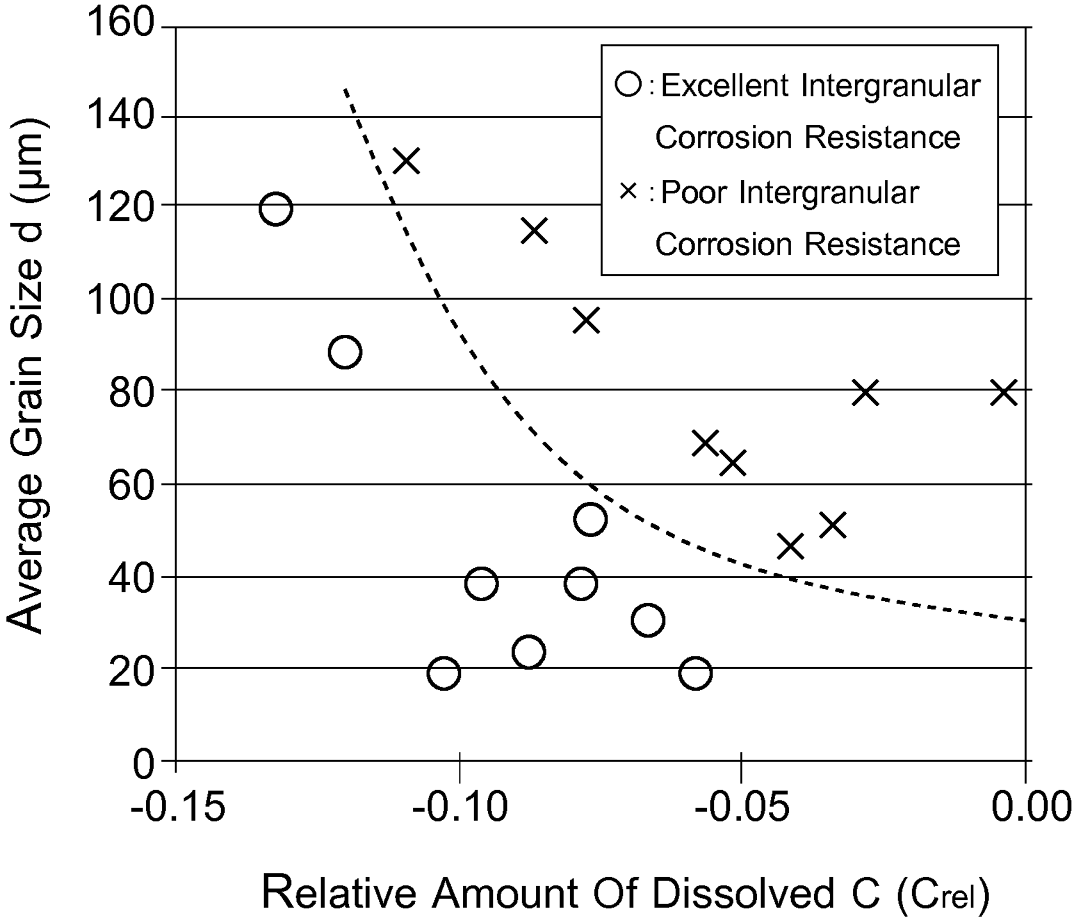
FIG. 1


160
140
120
100
80
60
40
20
0
-0.15
-0.10
-0.05
0.00
Average Grain Size d (μm)
Relative Amount Of Dissolved C (Crel)
○ : Excellent Intergranular Corrosion Resistance
× : Poor Intergranular Corrosion Resistance

Description

TECHNICAL FIELD

[0001] The present invention relates to a Ni-Fe-Cr alloy.

BACKGROUND ART

[0002] Installations, such as reheating furnace pipes, in a petroleum refining plant and a petrochemical plant are used under high-temperature environments. In addition, those installations are brought into contact with process fluid including sulfides and/or chlorides. Therefore, a material used for the installations is required to have an excellent corrosion resistance. For the installations, for example, Ni-based alloys or Ni-Fe-Cr alloys having excellent corrosion resistances, typically Alloy825 (TM), are used.

[0003] Ni-based alloys used for the installations described above are proposed in Japanese Patent Application Publication No. 61-227148 (Patent Literature 1) and Japanese Patent Application Publication No. 6-240407 (Patent Literature 2).

[0004] A high-nickel alloy disclosed in Patent Literature 1 consisting of, in mass percent, C: 0.1% or less, Si: 1.0% or less, Mn: 1.5% or less, S: 0.015% or less, Ni: 30.0 to 30.5%, Cr: 19.0 to 25.0%, Cu: 1.0% or less, Al: 0.1 to 1.0%, Ti: 0.05 to 1.0%, and Nb: 0.05 to 1.0%, with the balance being iron and unavoidable impurities, and satisfies conditions of $(3Ti + Nb) / S \geq 150$ and $(Ti + Nb) / C \geq 15$. Patent Literature 1 describes that the high-nickel alloy can be thereby given an excellent intergranular corrosion resistance.

[0005] A high-strength clad steel disclosed in Patent Literature 2 has a base-metal composition consisting of, in mass percent, C: 0.03 to 0.12%, Si: 0.5% or less, Mn: 1 to 1.8%, Nb: 0.06% or less, Mo: 0.25% or less, V: 0.06% or less, and Al: 0.01 to 0.06%, with the balance being Fe and unavoidable impurities. The high-strength clad steel is a Ni-based alloy having a cladding-material composition consisting of C: 0.05% or less, Si: 0.5% or less, Mn: 1% or less, Cr: 19.5 to 23.5%, Mo: 2.5 to 3.5%, Al: 0.2% or less, Ti: 0.6 to 1.2%, Cu: 1.5 to 3%, and Ni: 38 to 46%, with the balance being Fe and unavoidable impurities. Patent Literature 2 describes that the high-strength clad steel can be provided with an excellent corrosion resistance by heating to 900 to 1030°C, then quenched, and tempering at 500 to 630°C.

CITATION LIST

PATENT LITERATURE

[0006]

[Patent Literature 1] Japanese Patent Application Publication No. 61-227148
[Patent Literature 2] Japanese Patent Application Publication No. 6-240407

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0007] A Ni-based alloy or a Ni-Fe-Cr alloy may be sensitized in a weld heat affected zone when welding is performed. The sensitization may likely cause intergranular corrosion. Therefore, a Ni-based alloy or a Ni-Fe-Cr alloy used under the high-temperature environments described above is required to have an excellent intergranular corrosion resistance achieved by inhibiting the sensitization.

[0008] However, with the materials disclosed in Patent Literature 1 and Patent Literature 2 described above, the intergranular corrosion may occur due to insufficient inhibition of the sensitization.

[0009] An objective of the present invention is to provide a Ni-Fe-Cr alloy having an excellent intergranular corrosion resistance.

SOLUTION TO PROBLEM

[0010] A Ni-Fe-Cr alloy of the present embodiment has a chemical composition consisting of, in mass percent, C: 0.005 to 0.015%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.5%, P: 0.030% or less, S: 0.020% or less, Cu: 1.0 to 5.0%, Ni: 30.0 to 45.0%, Cr: 18.0 to 30.0%, Mo: 2.0 to 4.5%, Ti: 0.5 to 2.0%, N: 0.001 to 0.015%, and Al: 0 to 0.50%, with the balance being Fe and impurities. An average grain size d (μm) satisfies Formula (1):

$$d < 4.386 / (C_{rel} + 0.15) \qquad (1)$$

where, C_{rel} in Formula (1) is defined by Formula (2):

$$C_{rel} = C - 0.125Ti + 0.8571N \qquad (2)$$

where, symbols of elements in Formula (1) and Formula (2) are to be substituted by contents of corresponding elements (mass%).

ADVANTAGEOUS EFFECTS OF INVENTION

[0011] The Ni-Fe-Cr alloy according to the present invention has an excellent intergranular corrosion resistance.

BRIEF DESCRIPTION OF DRAWINGS

[0012]

[FIG. 1] FIG. 1 is a graph illustrating the relation between relative amount of dissolved C (C_{rel}), average grain size d (μm), and intergranular corrosion resistance.
[FIG. 2] FIG. 2 is a graph illustrating the relation between average grain size d (μm), the subtraction (F1 - d) of d from F1 = 4.386 / (C_{rel} + 0.15), and intergranular corrosion resistance.

DESCRIPTION OF EMBODIMENTS

[0013] An Embodiment of the present invention will be described below in detail with reference to the accompanying drawings. Hereafter, the sign % following each element means "mass percent".
[0014] The present inventors conducted studies about the sensitization and intergranular corrosion resistance of Ni-Fe-Cr alloys. As a result, the present inventors obtained the following findings.

(A) The sensitization occurs by the following mechanism. When a Ni-Fe-Cr alloy is affected by heat through welding or the like, Cr carbide precipitates in crystal grain boundaries. The precipitation of Cr carbide consumes Cr present around the crystal grain boundaries. Therefore, when Cr carbide precipitates, Cr-depleted zones develop along the crystal grain boundaries. This phenomenon is called sensitization. In the Cr-depleted zones, adequate formation of passivation films fails, which leads to a decrease in corrosion resistance, resulting in the occurrence of intergranular corrosion. If an amount of dissolved C in a Ni-Fe-Cr alloy is reduced, the sensitization can be inhibited, which increases the intergranular corrosion resistance.
(B) If the content of C in a Ni-Fe-Cr alloy is reduced, the amount of dissolved C in the Ni-Fe-Cr alloy is reduced. Thus, in the present embodiment, the content of C is set at 0.005 to 0.015%.
(C) If C is immobilized by Ti in the form of Ti carbide, the amount of dissolved C in the Ni-Fe-Cr alloy can be further reduced. However, if N is present in the Ni-Fe-Cr alloy, Ti nitride precipitates earlier than Ti carbide in solidification because N has a greater affinity for Ti than C. As a result, Ti runs short, failing to immobilize C. Therefore, the content of N is preferably low. Thus, in the present embodiment, the content of N is set at 0.015% or less.

[0015] As described above, the amount of dissolved C in an actual Ni-Fe-Cr alloy is a value determined from the contents of C, Ti, and N in a relative way. Hence, a theoretical amount of dissolved C is determined as follows.

$$\text{Amount of dissolved C} = \text{Content of C in Alloy} - \text{Content of C immobilized by Ti in the form of TiC.}$$

[0016] Here, when N is present, Ti precipitates in the form of Ti nitride, and thus the amount of Ti available for the immobilization of C is determined as follows.

$$\text{Amount of Ti available for the immobilization of C} = \text{Ti} - 48/14 \times \text{N}$$

[0017] Consequently, the theoretical amount of dissolved C in the alloy is determined as follows.

$$C_{total} = C - (Ti - 48/14 \times N) \times 12/48 = C - 0.250Ti + 0.8571N$$

[0018] However, in an actual, industrial producing process, chemical kinetics has to be factored in. Specifically, in an equilibrium condition, the amount of dissolved C is the theoretical amount of dissolved C (C_{total}) described above. In contrast, in the actual producing process, the reaction proceeds in a short time and may complete before the equilibrium condition comes about. Therefore, not all of Ti form TiC in some cases, and thus the adjustment of the Ti coefficient is needed in the formula of C_{total}.

[0019] As a result of a study conducted by the inventors, the actual amount of dissolved C in a Ni-Fe-Cr alloy (C_{real}) is as follows:

$$C_{real} = C - 0.125Ti + 0.8571N + k_1$$

where, k_1 is a constant of the amount of dissolved C.

[0020] Of the actual amount of dissolved C (C_{real}), an amount of C used in the precipitation of Cr carbide (total precipitation amount of C (C_{pre})) is as follows, with a solid-solubility limit of C denoted by k_2 (%).

$$C_{pre} = C - 0.125Ti + 0.8571N + k_1 - k_2$$

(D) To increase the intergranular corrosion resistance, in addition, refining grains is effective. The reason for this is as follows. When grains are refined, a total grain boundary area increases. The total precipitation amount of C (C_{pre}) in the alloy is constant, and therefore, the larger the total grain boundary area is, the less an amount of C, per unit grain boundary area, contributing to the precipitation of Cr carbide (unit precipitation amount of C (C_{unit})). As a result, the precipitation and growth of Cr carbide per unit grain boundary area are suppressed, and the development of the Cr-depleted zones is inhibited. Consequently, the sensitization is inhibited.

[0021] The relation between the average grain size d and unit precipitation amount of C (C_{unit}) is determined as follows. When the average grain size is d (μm), the grain boundary area of a grain is determined as $k_3 \times d_2$ μm^2 (k_3 is a constant). When the number of grains per unit volume is k_4/d_3 (k_4 is a constant), the total grain boundary area is determined as follows.

$$\text{Total grain boundary area} = (k_3 \times d_2) \times (k_4 / d_3) = k_3k_4 / d$$

[0022] Using the total grain boundary area and the total precipitation amount of C (C_{pre}), the unit precipitation amount of C (C_{unit}) is determined as follows.

$$C_{unit} = C_{pre} / (k_3k_4/d) = d \times (C_{pre} / k_3k_4)$$

[0023] According to this formula, the average grain size d is in proportion to the unit precipitation amount of C (C_{unit}). In other words, the smaller the average grain size d, the less the unit precipitation amount of C (C_{unit}), and as a result, the sensitization is inhibited.

(E) The present inventors introduced an idea of an index of the intergranular corrosion resistance based on the average grain size d and the amount of C contributing to the precipitation of Cr carbide described above. As a result, the present inventors found that increasing the intergranular corrosion resistance cannot be simply achieved only reducing the average grain size d, and an appropriate average grain size d exists in the relation with the amount of C contributing to the precipitation of Cr carbide.

[0024] FIG. 1 is a graph illustrating the relation between the amount of C contributing the precipitation of Cr carbide (relative amount of dissolved C (C_{rel})), the average grain size d (μm), and the intergranular corrosion resistance. In FIG. 1, the horizontal axis represents the formula of the total precipitation amount of C (C_{pre}) from which the constants k_1 and k_2 are omitted (the relative amount of dissolved C (C_{rel}) to be described later). FIG. 1 is obtained through Example to be described later. In FIG. 1, those showed excellent intergranular corrosion resistances are plotted as "○", and those showed poor intergranular corrosion resistances are plotted as "×".

[0025] From FIG. 1, to inhibit the sensitization, the average grain size d needs to be decreased with an increase in the total precipitation amount of C (C_{pre}). In contrast, the less the total precipitation amount of C (C_{pre}), the larger the average grain size d can be made. In other words, the total precipitation amount of C (C_{pre}) is in an inversely proportional relation with the average grain size, and is expressed as follows:

$$d = k_5 / (C_{pre} + k_6)$$

where, k_5 and k_6 are constants.

[0026] According to the relation between excellent intergranular corrosion resistances and poor intergranular corrosion resistances (○ and ×) illustrated in FIG. 1, F1 can be obtained by determining the constants k_1, k_2, k_5 and k_6, with the broken line of FIG. 1 set as a boundary:

$$F1 = 4.386 / (C_{rel} + 0.15)$$

where, C_{rel} is the amount of dissolved C determined from the contents of C, Ti, and N in a relative way (the relative amount of dissolved C (C_{rel})), and defined as follows:

$$C_{rel} = C - 0.125Ti + 0.8571N \qquad (2)$$

[0027] From FIG. 1, to inhibit the sensitization, the average grain size d needs to be decreased with an increase in the relative amount of dissolved C (C_{rel}). In contrast, the less the relative amount of dissolved C (C_{rel}), the larger the average grain size d can be made.

[0028] F1 is an index of the intergranular corrosion resistance. When the average grain size d is less than F1, the average grain size d is proper for the relative amount of dissolved C (C_{rel}). In this case, the unit precipitation amount of C (C_{unit}) is reduced sufficiently, which inhibits the sensitization. As a result, the intergranular corrosion resistance can be increased. In contrast, when the average grain size d is not less than F1, the average grain size d is excessively large for the relative amount of dissolved C (C_{rel}). In this case, the unit precipitation amount of C (C_{unit}) is not reduced sufficiently, which contributes to the sensitization. As a result, the intergranular corrosion resistance is decreased.

[0029] FIG. 2 is a graph illustrating the relation between the average grain size d (μm), the subtraction (F1 - d) of d from F1, and the intergranular corrosion resistance. FIG. 2 is obtained through Example to be described later, as with FIG. 1. In FIG. 2, those showed excellent intergranular corrosion resistances are plotted as "○", and those showed poor intergranular corrosion resistances are plotted as "×". Referring to FIG. 2, when the average grain size d satisfies Formula (1), namely, when F1 - d makes a positive value, an excellent intergranular corrosion resistance can be provided even when the average grain size d is large. When the average grain size d does not satisfy Formula (1), namely, when F1 - d makes a negative value, the intergranular corrosion resistance decreases even when the average grain size d is small.

[0030] A Ni-Fe-Cr alloy according to the present embodiment completed based on the above findings has a chemical composition consisting of, in mass percent, C: 0.005 to 0.015%, Si: 0.05 to 0.50%, Mn: 0.05 to 1.5%, P: 0.030% or less, S: 0.020% or less, Cu: 1.0 to 5.0%, Ni: 30.0 to 45.0%, Cr: 18.0 to 30.0%, Mo: 2.0 to 4.5%, Ti: 0.5 to 2.0%, N: 0.001 to 0.015%, and Al: 0 to 0.50%, with the balance being Fe and impurities. An average grain size d (μm) satisfies Formula (1):

$$d < 4.386 / (C_{rel} + 0.15) \qquad (1)$$

where, C_{rel} in Formula (1) is defined by Formula (2):

$$C_{rel} = C - 0.125Ti + 0.8571N \qquad (2)$$

where, symbols of elements in Formula (1) and Formula (2) are to be substituted by contents of corresponding elements (mass%).

[0031] The above chemical composition may contain Al: 0.05 to 0.50%.

[Chemical Composition]

[0032] The chemical composition of the Ni-Fe-Cr alloy according to the present embodiment consisting of the following elements.

C: 0.005 to 0.015%

[0033] Carbon (C) increases the strength of the alloy. In addition, C deoxidizes the alloy. An excessively low content of C results in failure to provide these effects. In contrast, an excessively high content of C leads to an increase in precipitation of Cr carbides to grain boundaries, resulting in a decrease in the intergranular corrosion resistance. Consequently, the content of C is 0.005 to 0.015%. A lower limit of the content of C is preferably 0.008%. An upper limit of the content of C is preferably 0.013%, more preferably 0.010%.

Si: 0.05 to 0.50%

[0034] Silicon (Si) deoxidizes the alloy. An excessively low content of Si results in failure to provide this effect. In contrast, an excessively high content of Si makes inclusions likely to be produced. Consequently, the content of Si is 0.05 to 0.50%. A lower limit of the content of Si is preferably 0.15%, more preferably 0.20%. An upper limit of the content of Si is preferably 0.45%, more preferably 0.40%.

Mn: 0.05 to 1.5%

[0035] Manganese (Mn) stabilizes an austenite phase. In addition, Mn deoxidizes the alloy. An excessively low content of Mn results in failure to provide these effects. In contrast, an excessively high content of Mn causes S to combine with Mn to form a sulfide, which becomes nonmetallic inclusions, resulting in a decrease in pitting resistance. Consequently, the content of Mn is 0.05 to 1.5%. A lower limit of the content of Mn is preferably 0.15%, more preferably 0.30%. An upper limit of the content of Mn is preferably 1.2%, more preferably 1.0%.

P: 0.030% or less

[0036] Phosphorus (P) is an impurity. P segregates in grain boundaries in weld solidification, increasing crack susceptibility that occurs due to embrittlement of a heat affected zone. Therefore, the content of P is 0.030% or less. An upper limit of the content of P is preferably 0.025%, more preferably 0.020%. The content of P is preferably as low as possible.

S: 0.020% or less

[0037] Sulfur (S) is an impurity. As with P, S segregates in grain boundaries in weld solidification, increasing the crack susceptibility that occurs due to embrittlement of a heat affected zone. In addition, S forms MnS, resulting in a decrease in the pitting resistance. Therefore, the content of S is 0.020% or less. An upper limit of the content of S is preferably 0.010%, more preferably 0.005%. The content of S is preferably as low as possible.

Cu: 1.0 to 5.0%

[0038] Copper (Cu) increases the corrosion resistance of the alloy. An excessively low content of Cu results in failure to provide this effect. In contrast, an excessively high content of Cu results in a decrease in the hot workability of the alloy. Therefore, the content of Cu is 1.0 to 5.0%. A lower limit of the content of Cu is preferably 1.2%, more preferably 1.5%. An upper limit of the content of Cu is preferably 4.0%, more preferably 3.0%.

Ni: 30.0 to 45.0%

[0039] Nickel (Ni) increases the pitting resistance of the alloy. An excessively low content of Ni results in failure to provide this effect. In contrast, an excessively high content of Ni leads to saturation of the effect. Therefore, the content of Ni is 30.0 to 45.0%. A lower limit of the content of Ni is preferably 35.0%, more preferably 38.0%. An upper limit of the content of Ni is preferably 44.5%, more preferably 44.0%.

Cr: 18.0 to 30.0%

[0040] Chromium (Cr) increases the corrosion resistance of the alloy. An excessively low content of Cr results in failure to provide this effect. In contrast, an excessively high content of Cr leads to a decrease in the stability of austenite at high temperature, resulting in a decrease strength of the alloy in the high temperature. Therefore, the content of Cr is 18.0 to 30.0%. A lower limit of the content of Cr is preferably 19.0%, more preferably 20.0%. An upper limit of the content of Cr is preferably 26.0%, more preferably 24.0%.

Mo: 2.0 to 4.5%

[0041] Molybdenum (Mo) increases the corrosion resistance of the alloy. An excessively low content of Mo results in failure to provide this effect. In contrast, an excessively high content of Mo causes Laves phases to precipitate in grain boundaries in an alloy having a high content of Cr, resulting in a decrease in the corrosion resistance of the alloy. Therefore, the content of Mo is 2.0 to 4.5%. A lower limit of the content of Mo is preferably 2.4%, more preferably 2.8%. An upper limit of the content of Mo is preferably 4.0%, more preferably 3.5%.

Ti: 0.5 to 2.0%

[0042] Titanium (Ti) forms Ti carbide, inhibiting the sensitization of the alloy. An excessively low content of Ti results in failure to provide this effect. In contrast, an excessively high content of Ti results in a decrease in the hot workability of the alloy. Therefore, the content of Ti is 0.5 to 2.0%. A lower limit of the content of Ti is preferably 0.55%, more preferably 0.60%. An upper limit of the content of Ti is preferably 1.5%, more preferably 1.3%.

N: 0.001 to 0.015%

[0043] Nitrogen (N) forms fine carbo-nitrides in grains, increasing the strength, and therefore may be contained. In contrast, an excessively high content of N causes Ti to combine with N to form TiN, which hinders C from being immobilized in the form of Ti carbide, resulting in a decrease in inhibition of sensitization. Therefore, the content of N is 0.001 to 0.015%. A lower limit of the content of N is preferably 0.002%, more preferably 0.005%. An upper limit of the content of N is preferably 0.013%, more preferably 0.010%.

[0044] The balance of the chemical composition of the Ni-Fe-Cr alloy according to the present embodiment is Fe and impurities. Here, the impurities mean elements that are mixed from ores and scraps used as raw material, a producing environment, or the like when the Ni-Fe-Cr alloy is produced in an industrial manner, and are allowed to be mixed within ranges in which the impurities have no adverse effect on the Ni-Fe-Cr alloy according to the present embodiment.

[Optional Elements]

[0045] The Ni-Fe-Cr alloy described above may further contain Al in lieu of Fe.

Al: 0 to 0.50%

[0046] Aluminum (Al) is an optional element and need not be contained. When contained, Al deoxidizes the alloy. However, an excessively high content of Al results in a decrease in the cleanliness of the alloy and decreases in the workability and ductility of the alloy. Therefore, the content of Al is 0 to 0.50%. A lower limit of the content of Al is preferably 0.05%. An upper limit of the content of Al is preferably 0.30%, more preferably 0.20%. In the present specification, the content of Al means sol.Al (acid-soluble Al).

[Formula (1)]

[0047] F1 is defined as $F1 = 4.386 / (C_{rel} + 0.15)$. F1 is an index of the intergranular corrosion resistance. When the average grain size d is less than F1, the average grain size d is proper for the relative amount of dissolved C (C_{rel}). In this case, the unit precipitation amount of C (C_{unit}) is reduced sufficiently, which inhibits the sensitization. As a result, the intergranular corrosion resistance can be increased. In contrast, when the average grain size d is not less than F1, the average grain size d is excessively large for the relative amount of dissolved C (C_{rel}). In this case, the unit precipitation amount of C (C_{unit}) is not reduced sufficiently, which promotes to the sensitization. As a result, the intergranular corrosion resistance is decreased.

[Formula (2)]

[0048] Because the relative amount of dissolved C (C_{rel}) in Formula (1) is determined from the contents of C, Ti, and N in a relative way, as described above, the relative amount of dissolved C (C_{rel}) is defined as follows.

$$C_{rel} = C - 0.125Ti + 0.8571N \qquad (2)$$

[Producing Method]

[0049] The Ni-Fe-Cr alloy according to the present embodiment can be produced by various producing methods. As one example of the producing methods, a producing method for a Ni-Fe-Cr alloy tube will be described below.

[0050] First, a starting material having the above chemical composition is prepared. The starting material is, for example, a hollow billet. The hollow billet can be produced by, for example, machining or vertical piercing. The hollow billet is subjected to hot extrusion working. The hot extrusion working is, for example, the Ugine-Sejournet process. Through the above steps, a Ni-Fe-Cr alloy pipe is produced. The Ni-Fe-Cr alloy tube may be produced by hot working other than the hot extrusion working. The hot working may be repeated several times.

[0051] Preferably, a cooling rate to reach a temperature of 900°C after final hot working is 0.3°C/sec or higher. When the cooling rate to reach a temperature of 900°C after the final hot working is 0.3°C/sec or higher, it is possible to adjust the average grain size d such that the average grain size d satisfies Formula (1). As a result, the Ni-Fe-Cr alloy can have an excellent intergranular corrosion resistance.

[0052] The cooling rate to reach a temperature of 900°C can be made 0.3°C/sec or higher by performing mist cooling after the final hot working.

[0053] On the Ni-Fe-Cr alloy tube subjected to the hot working, cold working including cold rolling and/or cold drawing may be performed. Performing the cold working enables the reduction of the average grain size d. In this case, the intergranular corrosion resistance is further increased.

[0054] In addition, on the Ni-Fe-Cr alloy tube subjected to the hot working or the cold working, a final heat treatment such as solution treatment may be performed to obtain a desired mechanical property. In a case of performing the heat treatment, a lower limit of a heat treatment temperature is preferably 900°C, more preferably 915°C, still more preferably 930°C. In a case of performing the solution treatment, a lower limit of the heat treatment temperature is preferably 1020°C. In this case, Cr carbide can be dissolved. As a result, the intergranular corrosion resistance can be further inhibited.

[0055] An upper limit of the heat treatment temperature is preferably 1100°C, more preferably 1080°C, still more preferably 1060°C. In a case of performing stabilization treatment, an upper limit of the heat treatment temperature is preferably less than 1000°C. A heat treatment temperature less than 1000°C enables the precipitation of TiC. In addition, the heat treatment temperature less than 1000°C enables the reduction of the average grain size d. In this case, the sensitization can be further inhibited. As a result, the intergranular corrosion resistance can be further inhibited. As to the Ni-Fe-Cr alloy according to the present embodiment, the sensitization can be inhibited even when the heat treatment is performed at a high temperature of 1000 to 1100°C. A heat treatment duration of the final heat treatment is preferably 2 to 30 minutes.

[0056] The description of the above one example of the producing methods has been made about the producing method of a Ni-Fe-Cr alloy tube. However, the Ni-Fe-Cr alloy may be a plate product, a welded tube, a bar product, or the like. In short, the Ni-Fe-Cr alloy is not limited to a particular product shape.

[0057] The Ni-Fe-Cr alloy produced by the above producing method has an excellent intergranular corrosion resistance.

[Examples]

[0058] Alloys of Test Number 1 to Test Number 23 shown in Table 1 were subjected to vacuum melting to be produced into materials.

[Table 1]

[0059]

TABLE 1

Test Number	Chemical Composition (mass%, Balance: Fe And Impurities)												C_{rel}	F1
	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	Ti	N	Al		
1	0.005	0.25	0.51	0.012	0.001	1.8	39.7	19.8	2.9	0.7	0.002	0.330	-0.078	61
2	0.010	0.32	0.67	0.013	0.001	1.2	40.3	22.5	3.2	0.7	0.008	0.250	-0.066	52
3	0.010	0.50	1.48	0.025	0.002	1.5	41.2	20.9	3.2	0.8	0.008	0.280	-0.077	60
4	0.010	0.09	0.08	0.009	0.001	2.2	42.6	25.7	3.0	1.1	0.005	0.310	-0.121	150
5	0.011	0.29	0.67	0.011	0.001	3.1	39.2	20.9	3.2	1.0	0.013	0.450	-0.103	93
6	0.013	0.42	1.24	0.012	0.001	1.1	40.6	24.3	3.1	0.6	0.008	0.210	-0.059	48
7	0.013	0.31	0.69	0.021	0.002	4.6	40.4	23.1	3.3	1.2	0.005	0.340	-0.133	254
8	0.008	0.44	0.25	0.028	0.001	1.2	44.1	20.4	2.5	0.9	0.007	-	-0.096	81
9	0.013	0.16	0.87	0.013	0.001	1.4	40.9	26.8	3.3	0.9	0.008	0.120	-0.088	70
10	0.010	0.33	1.45	0.028	0.001	2.2	40.0	21.0	3.2	0.7	0.025	0.240	-0.051	44
11	0.011	0.17	1.23	0.014	0.002	3.2	38.9	24.5	2.4	0.4	0.013	0.320	-0.028	36
12	0.013	0.15	0.65	0.011	0.001	1.1	40.1	19.8	3.1	0.9	0.008	0.280	-0.088	70
13	0.010	0.26	0.37	0.018	0.001	1.3	41.0	22.7	2.9	0.8	0.008	0.140	-0.077	60
14	0.015	0.48	0.97	0.026	0.002	2.1	43.1	20.5	3.5	0.5	0.015	0.230	-0.035	38
15	0.008	0.24	1.12	0.024	0.001	4.2	31.2	19.4	2.7	0.5	0.015	0.090	-0.042	40
16	0.010	0.33	1.34	0.008	0.001	2.5	39.4	20.7	3.5	1.0	0.010	-	-0.109	107
17	0.013	0.25	0.77	0.013	0.001	1.7	40.3	21.1	3.7	0.3	0.025	0.340	-0.003	30
18	0.020	0.18	0.60	0.017	0.001	1.2	41.4	26.3	3.0	0.7	0.008	0.440	-0.056	46
19	0.013	0.30	0.85	0.027	0.002	4.6	44.5	19.5	3.1	2.5	0.010	0.350	-0.291	-31
20	0.010	0.32	0.67	0.013	0.001	1.2	40.3	22.5	3.2	0.7	0.008	0.250	-0.066	52
21	0.010	0.50	1.48	0.025	0.002	1.5	41.2	20.9	3.2	0.8	0.008	0.280	-0.077	60
22	0.011	0.29	0.67	0.011	0.001	3.1	39.2	20.9	3.2	1.0	0.013	0.450	-0.103	93
23	0.011	0.29	0.67	0.011	0.001	3.1	39.2	20.9	3.2	1.0	0.013	0.450	-0.103	93

[0060] The "C_{rel}" columns and "F1" columns in Table 1 are filled with C_{rel} values and F1 values of Ni-Fe-Cr alloys of the respective test number.

[0061] From the materials, ingots were produced. For the Test Number 1 to Test Number 21, each of the respective ingots was subjected to hot forging at 1200°C, then subjected to hot rolling at 1200°C at a reduction of area of 50%, and further subjected to cold rolling at a reduction of area of 67% to be produced into a plate product having a thickness of 5 mm, a width of 80 mm, and a length of 650 mm. For the Test Number 22 and Test Number 23, each of the respective ingots was subjected to hot forging at 1200°C to be produced into a plate product having a thickness of 15 mm, a width of 60 mm, and a length of 290 mm. For the Test Number 22 and Test Number 23, the cold rolling was not performed. On each of the plate materials, the final heat treatment was performed at heat treatment temperatures and for heat treatment durations shown in Table 2. The plate products subjected to the heat treatment were subjected to rapid cooling (water cooling).

[Table 2]

[0062]

TABLE 2

Test Number	Cooling Rate To Reach Temperature Of 900°C After Final Hot Working (°C/s)	Cold Rolling	Heat Treatment Temperature (°C)	Heat Treatment Duration (min)	Average Grain Size d (μm)	F1	Intergranular Corrosion Resistance Determination
1	0.36	Performed	980	10	40	61	○
2	0.38	Performed	930	15	30	52	○
3	0.41	Performed	1050	5	55	60	○
4	0.39	Performed	1080	5	90	150	○
5	0.35	Performed	920	20	18	93	○
6	0.45	Performed	940	30	20	48	○
7	0.38	Performed	1080	10	120	254	○
8	0.52	Performed	960	25	40	81	○
9	0.42	Performed	940	20	25	70	○
10	0.45	Performed	1000	10	65	44	×
11	0.36	Performed	1050	5	80	36	×
12	0.35	Performed	1100	10	115	70	×
13	0.43	Performed	1040	5	95	60	×
14	0.46	Performed	980	30	50	38	×
15	0.51	Performed	950	30	45	40	×
16	0.38	Performed	1080	15	130	107	×
17	0.43	Performed	1050	10	80	30	×
18	0.50	Performed	970	30	70	46	×
19	-	-	-	-	-	-31	-
20	0.21	Performed	930	15	85	52	×
21	0.22	Performed	1050	5	135	60	×
22	0.52	Not Performed	920	20	80	93	○
23	0.18	Not Performed	920	20	113	93	×

[Measuring Average Grain Size]

[0063] The plate products were cut in a direction perpendicular to a rolling direction, and test specimens having a thickness of 5 mm, a width of 20 mm, and a length of 10 mm were taken. The test specimens were each embedded in resin in such a manner that a surface including the rolling direction of the plate product (longitudinal section of the test specimen) becomes an observation surface, and the observation surface was subjected to mirror polish. The polished surface was etched using mixed acid. The etched observation surface was observed under an optical microscope. As to the average grain size d, five visual fields were shot at 100x magnification to determine the average grain size d (μm).

[Intergranular Corrosion Resistance Test]

[0064] From the plate product of each Test Number, a test specimen having a thickness of 5 mm, a width of 10 mm, and a length of 50 mm was taken. The lengthwise direction of the test specimen was parallel to the lengthwise direction of the plate product. The test specimen was subjected to sensitization heat treatment at 700°C for 60 minutes, which was a simulation of a weld heat affected zone. The surface of the test specimen subjected to the sensitization heat treatment was finished by wet emery polishing at #600, degreased with acetone, and dried. The test specimen was subjected to the intergranular corrosion test according to the ASTM A262 C method, and the intergranular corrosion resistance of the etched test specimen was evaluated. A test bath was a boiled 65% nitric acid, and three batches of an immersion test were performed, the three batches each taking 48 hours. A corrosion loss in each of the batches was measured, and from the corrosion rate in the three batches, the average corrosion rate was calculated.

[0065] In the evaluation of the intergranular corrosion resistance, when an average corrosion rate of the three batches was not more than 1 g/m^2 hr, the intergranular corrosion resistance was determined to be excellent (shown with "O" in Table 2). When the average corrosion rate was more than 1 g/m^2 hr, the intergranular corrosion resistance was determined to be poor (shown with "×" in Table 2).

[Test Results]

[0066] Table 2 shows test results.

[0067] Referring to Table 1, as to Test Number 1 to Test Number 9 and Test Number 22, the element contents of the plate products were appropriate, and the chemical compositions and the average grain sizes d satisfied Formula (1). As a result, grains ware made fine, and excellent intergranular corrosion resistances were shown.

[0068] As to Test Number 22, the cold rolling was not performed, and thus the average grain size d was large as compared with Test Number 5. However, since the average grain size d satisfied Formula (1), an excellent intergranular corrosion resistance was shown.

[0069] In contrast, as to Test Number 10, the content of N was excessively high. As a result, Ti precipitated in the form of Ti nitride, by which C was not immobilized sufficiently. This made the relative amount of dissolved C (C_{rel}) high, making the average grain size d excessively large for the relative amount of dissolved C (C_{rel}). Consequently, the average grain size d became not less than F1, and the intergranular corrosion resistance was low.

[0070] As to Test Number 11, the content of Ti was excessively low. This made Ti fail to immobilize C sufficiently, which made relative amount of dissolved C (C_{rel}) high, making the average grain size d excessively large for the relative amount of dissolved C (C_{rel}). Consequently, the average grain size d became not less than F1, and the intergranular corrosion resistance was low.

[0071] As to Test Number 12 to Test Number 16, although their chemical compositions were appropriate, their average grain sizes d were not less than F1. As a result, the intergranular corrosion resistance was low.

[0072] As to Test Number 17, the content of Ti was excessively low, and the content of N was excessively high. This made the relative amount of dissolved C (C_{rel}) high, making the average grain size d excessively large for the relative amount of dissolved C (C_{rel}). Consequently, the average grain size d became not less than F1, and the intergranular corrosion resistance was low.

[0073] As to Test Number 18, the content of C was excessively high. This made the relative amount of dissolved C (C_{rel}) high, making the average grain size d excessively large for the relative amount of dissolved C (C_{rel}). Consequently, the average grain size d became not less than F1, and the intergranular corrosion resistance was low.

[0074] As to Test Number 19, the content of Ti was excessively high. This made the hot workability low, making the working unable, and thus Test Number 19 fell outside the test.

[0075] As to Test Number 20, the cooling rate to reach 900°C after the final hot working was less than 0.3°C/s. Therefore, even with the heat treatment temperature set at less than 1000°C, the average grain size d was large as compared with Test Number 2, being not less than F1. As a result, the intergranular corrosion resistance was low.

[0076] As to Test Number 21, the cooling rate to reach 900°C after the final hot working was less than 0.3°C/s. Therefore, the average grain size d was large as compared with Test Number 3, being not less than F1. As a result, the intergranular corrosion resistance was low.

[0077] As to Test Number 23, the cooling rate to reach 900°C after the final hot working was less than 0.3°C/s. In addition, for Test Number 23, the cold rolling was not performed after the hot working. Therefore, even with the heat treatment temperature set at less than 1000°C, the average grain size d was large as compared with Test Number 5, being not less than F1. As a result, the intergranular corrosion resistance was low.

[0078] The embodiment according to the present invention has been described above. However, the aforementioned embodiment is merely an example for practicing the present invention. Therefore, the present invention is not limited to the aforementioned embodiment, and the aforementioned embodiment can be modified and implemented as appropriate without departing from the scope of the present invention.

Claims

1. A Ni-Fe-Cr alloy comprising a chemical composition consisting of, in mass percent:

C: 0.005 to 0.015%;
Si: 0.05 to 0.50%;
Mn: 0.05 to 1.5%;
P: 0.030% or less;
S: 0.020% or less;
Cu: 1.0 to 5.0%;
Ni: 30.0 to 45.0%;
Cr: 18.0 to 30.0%;
Mo: 2.0 to 4.5%;
Ti: 0.5 to 2.0%;
N: 0.001 to 0.015%; and
Al: 0 to 0.50%, with the balance being Fe and impurities, wherein

an average grain size d (μm) satisfies Formula (1):

$$d < 4.386 / (C_{rel} + 0.15) \qquad (1)$$

where, C_{rel} in Formula (1) is defined by Formula (2):

$$C_{rel} = C - 0.125Ti + 0.8571N \quad (2)$$

where, symbols of elements in Formula (1) and Formula (2) are to be substituted by contents of corresponding elements (mass%).

2. The Ni-Fe-Cr alloy according to claim 1, wherein the chemical composition contains Al: 0.05 to 0.50%.

FIG. 1

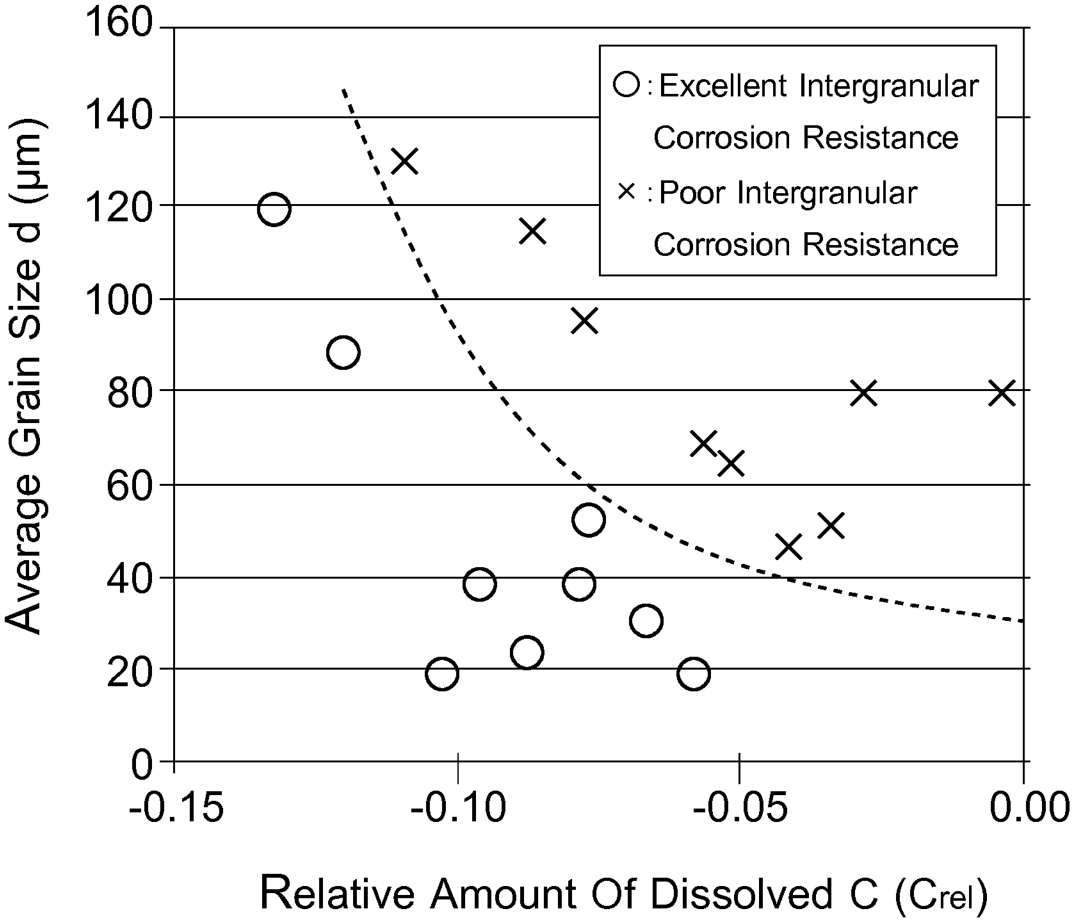
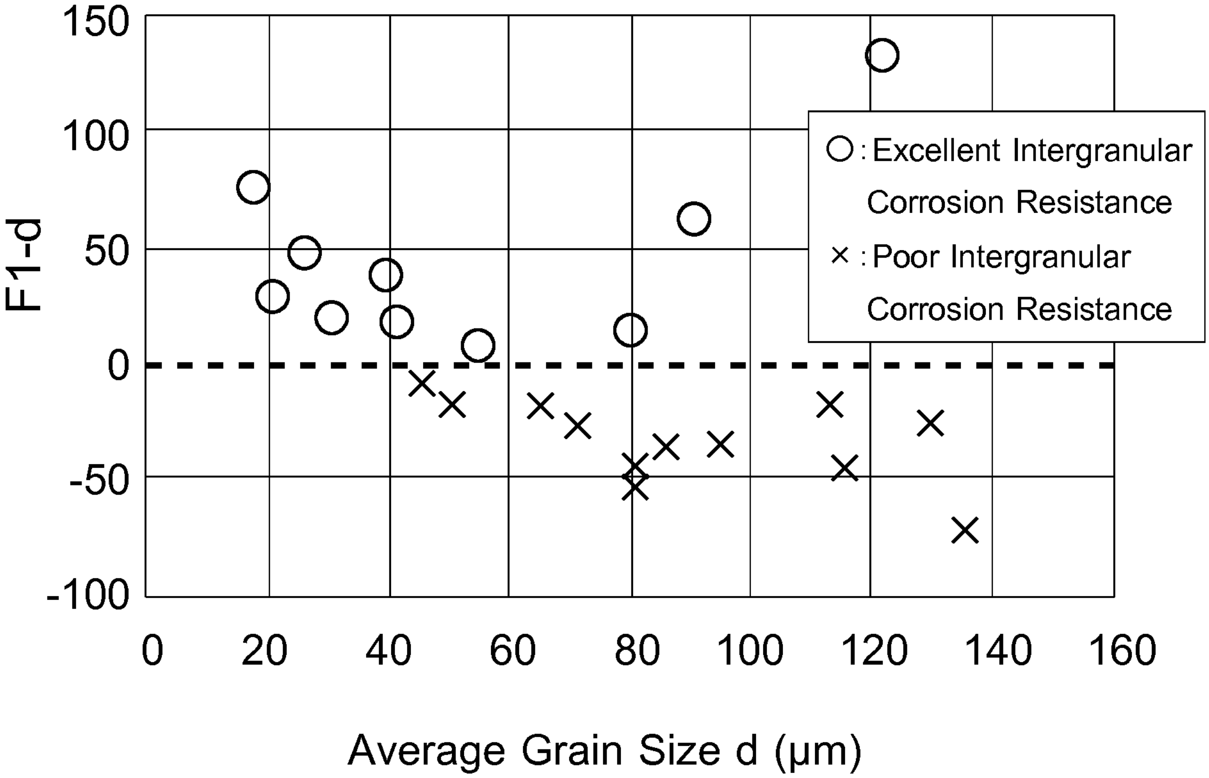

160
140
120
100
80
60
40
20
0
-0.15
-0.10
-0.05
0.00
Average Grain Size d (μm)
Relative Amount Of Dissolved C (Crel)
○ : Excellent Intergranular Corrosion Resistance
× : Poor Intergranular Corrosion Resistance

FIG. 2


150
100
50
0
-50
-100
F1-d
0
20
40
60
80
100
120
140
160
Average Grain Size d (μm)
○ : Excellent Intergranular Corrosion Resistance
× : Poor Intergranular Corrosion Resistance

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/089088

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/50*(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)
C22C38/00-38/60

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	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	JP 2-185943 A (Nippon Steel Corp.), 20 July 1990 (20.07.1990), table 1 (Family: none)	1-2
A	JP 2001-335893 A (Nippon Steel Corp.), 04 December 2001 (04.12.2001), fig. 1 (Family: none)	1-2

☒ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

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Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/089088

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	CN 103556029 A (LUOYANG SUNRUI SPECIAL EQUIPMENT CO., LTD.), 05 February 2014 (05.02.2014), examples (Family: none)	1-2
A	EP 0136998 A1 (VEREINIGTE EDELSTAHLWERKE A.G. (VEW)), 10 April 1985 (10.04.1985), examples & DE 3470329 D	1-2
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REFERENCES CITED IN THE DESCRIPTION

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