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(54) **HIGH-GRADE DUPLEX STAINLESS STEEL WITH MUCH SUPPRESSED FORMATION OF INTERMETALLIC PHASES AND HAVING AN EXCELLENT CORROSION RESISTANCE , EMBRITTLEMENT RESISTANCE, CASTABILITY AND HOT WORKABILITY**

HOCHWERTIGER ROSTFREIER DUPLEXSTAHL MIT STARK UNTERDRÜCKTER BILDUNG VON INTERMETALLISCHEN PHASEN UND HERVORRAGENDER KORROSIONSBESTÄNDIGKEIT, VERSPRÖDUNGSBESTÄNDIGKEIT, GIESSBARKEIT UND WARMUMFORMBARKEIT

ACIER INOXYDABLE DUPLEX DE QUALITE SUPERIEURE PRESENTANT UNE FORMATION A SUPPRESSION ELEVEE DE PHASES INTERMETALLIQUES ET POSSEDANT UNE EXCELLENTE RESISTANCE A LA CORROSION, UNE EXCELLENTE RESISTANCE A LA FRIABILITE, UNE EXCELLENTE COULABILITE ET UNE EXCELLENTE APTITUDE AU FA ONNAGE A CHAUD

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(73) Proprietor: **Park, Yong Soo**
Seocho-ku,
Seoul 137-849 (KR)

(72) Inventors:
• **PARK, Yong-Soo**
Bangbae-Dong
Seocho-Ku
Seoul 137-849 (KR)

- **KIM, Soon-Tae**
Mapo-Ku
Seoul 121-841 (KR)
- **LEE, In-Sung**
Yongdungpo-Ku
Seoul 150-044 (KR)

(74) Representative: **Hoffmann, Jörg Peter**
Müller Hoffmann & Partner
Patentanwälte
Innere Wiener Strasse 17
81667 München (DE)

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- **PATENT ABSTRACTS OF JAPAN vol. 008, no. 222 (C-246), 9 October 1984 (1984-10-09) & JP 59 107019 A (NIHON STAINLESS KK), 21 June 1984 (1984-06-21)**

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DescriptionTECHNICAL FIELD

5 **[0001]** The present invention relates to duplex stainless steel having excellent corrosion resistance, and more particularly to, high-grade duplex stainless steel having excellent corrosion resistance, embrittlement resistance, castability and hot workability by suppressing formation of intermetallic phases, such as sigma (θ) and khi (χ), formed during the production (casting, hot rolling or welding).

10 BACKGROUND ART

[0002] Duplex stainless steel where austenite (γ) phase providing high workability and ferrite (α) phase providing high corrosion resistance are minutely combined has higher strength than austenitic stainless steel by at least 1.7 times, and also shows high pitting resistance and high stress corrosion cracking (SCC) resistance. Commercial high-grade duplex stainless steels having a pitting resistance equivalent (PREW=wt%Cr+3.3(wt%Mo+0.5wt%W)+30wt%N) of about 46, such as SAF 2507 (UNS S32750), UR 52N+ (UNSS32550) and ZERON 100 (UNSS32760) have been used for various purposes since 1990s. Quality of duplex stainless steel has improved due to development of refining processes, and thus it has been increasingly used in various fields for a few years.

20 **[0003]** However, as compared with commercial PREW 38-level duplex stainless steel such as SAF 2205, the PREW 46-level high-grade duplex stainless steel contains a large amount of Cr, Mo and W which are major elements of sigma and khi phases deteriorating mechanical properties and corrosion resistance, and thus easily forms precipitation phases thereof during the production or application. Actually, embrittlement by the precipitation phases has been observed in cooling after continuous casting of duplex stainless steel, slow cooling after hot rolling, slow cooling of a heat affected zone after welding, and slow cooling of an ingot center unit after casting. In addition, Mo for improving local corrosion and SCC resistances among the added alloying elements is a high-priced element facilitating formation of sigma phases and 475°C brittleness, and thus restrictively used. Sigma phase is a very brittle intermetallic compound formed from temperature of 650°C to 1000°C. More than 1 vol.% of sigma phase can remarkably reduce impact toughness and corrosion resistance of duplex stainless steel.

25 **[0004]** Accordingly, a lot of research and development have been made to suppress formation of sigma phase during the production or application of duplex stainless steel. But, the conventional research and development have the following problems.

30 1) When 1 to 3% of Al or Al and Nb are added to ferritic stainless steel containing 39% of Cr, a formation speed of sigma phase is lowered, a formation temperature range of sigma phase is reduced, and thus a precipitation speed of sigma phase is lowered (K. Permachandra et al., Materials Science and Technology, Vol. 8, p.2477(1997)). However, it is not relevant to duplex stainless steel containing austenite and ferrite.

35 2) When Zr is added to stainless steel, a formation speed of sigma phase is lowered. However, alloying elements such as Al or Zr are ferrite former which reduce an austenite phase fraction and form different kinds of intermetallic compounds containing N, to deteriorate corrosion resistance and mechanical properties (M.B Cotrie et al., Metallurgical and Materials Transaction 28A (1997) 2477).

40 3) When Sn is added to ferritic stainless steel containing 43 to 46% of Cr, Sn is precipitated in a nucleation area of sigma phase such as a grain boundary or grain boundary triple point, to reduce a formation speed of sigma phase. When an alloy is exposed to a high temperature over 232°C, the ferritic stainless steel may be cracked due to a low melting point (232°C) of Sn. It is not relevant to duplex stainless steel either (Costa et. Al., Physica Status Solidi, A 139(1993)83).

45 4) Okamoto et al. disclosed that DP3W (UNS S39274) which was high-grade duplex stainless steel containing 3%Mo+2%W could delay a precipitation speed of sigma phase more than commercial high-grade duplex stainless steels containing 3.8%Mo, such as SAF 2507, UR 52N+ and ZERON 100 by adding W in aging heat-treatment for 10 minutes at 850°C. However, when a large-sized ingot and slab are hot-rolled, or a large-sized product is molten and cast, corrosion resistance and mechanical properties are deteriorated due to precipitation of khi and sigma phases showing high brittleness (H. Okamoto et al., 4th International Conferences on Duplex Stainless Steels, (1994) Paper91 and US Patent 5,298,093).

50 **[0005]** Especially, in accordance with US Patent 5,298,093, although a large amount of W (1.5 to 5.0%) is added to improve corrosion resistance, formation of intermetallic phases is not accelerated. Therefore, W is positively added, S and O are fixedly used, and at least one element selected from the group consisting of 0.02% or less of Ca, 0.02% or less of Mg, 0.02% or less of B, and 0.2% or less of at least one REM in total is added to improve hot workability by fixing S and O. In the case that Ca, B, Mg and REM exceed their upper limits, a lot of oxides and sulfides are formed. The

non-metallic inclusions such as oxides and sulfides are operated as the pitting point, which reduces corrosion resistance.

[0006] In addition, US Patent 5,733,387 suggests duplex stainless steel containing 0.03% or less of C, 1.0% or less of Si, 2.0% or less of Mn, 0.04% or less of P, 0.004% or less of S, 2.0% or less of Cu, 5.0 to 8.0% of Ni, 22 to 27% of Cr, 1.0 to 2.0% of Mo, 2.0 to 5.0% of W, 0.13 to 0.30% of N, at least one element selected from the group consisting of a certain amount of Ca, Ce, B and Ti, and a balance of Fe. The aforementioned patent reduces the content of Mo that facilitates formation of intermetallic phases, and increases the content of W in order to improve corrosion resistance. However, as confirmed in PREW formula that will later be described, effects of Mo for improving pitting resistance are twice as many as W. It is thus inefficient to decrease the content of Mo.

[0007] On the other hand, rapid cooling is essential in heat-treatment of duplex stainless steel to suppress formation of intermetallic phases having high brittleness. When duplex stainless steel is cooled from a heat-treatment temperature, it passes through a precipitation temperature of intermetallic phases. If the cooling speed is not sufficiently high in the temperature zone, intermetallic phases are rapidly precipitated. When intermetallic phases are precipitated at a high speed in the slow cooling, duplex stainless steel becomes embrittled and also shows low corrosion resistance. Accordingly, another conventional methods for suppressing precipitation of intermetallic phases are intended to control a cooling process during heat-treatment.

[0008] In accordance with Japan Patent Laid-Open Publication No. 5-271776, in order to suppress precipitation of intermetallic phases, duplex stainless steel is cooled to a temperature just below the lowest temperature of precipitation zone of intermetallic phases at a much higher speed than a precipitation cooling speed of intermetallic phases during heat-treatment, and maintained for 5 minutes at a temperature lower than the lowest precipitation temperature zone of intermetallic phases by over 200°C.

[0009] In addition, Japan Patent Publication No. 62-6615 suggests a method for suppressing formation of intermetallic phases when duplex stainless steel is manufactured as a mechanical component by casting. In general, when the mechanical component is manufactured by using duplex stainless steel, molten steel is poured into a sand mold, solidified and left at a room temperature. However, when a cast product is manufactured using high-grade duplex stainless steel where intermetallic phases are easily precipitated, some ferritic phase is transformed into sigma and austenitic phases during the cooling process to the room temperature after casting, and thus sigma phase includes embrittlement. In order to suppress precipitation of sigma phase, the aforementioned Japan Patent Publication teaches a method for removing a mold when the temperature is over 1,000°C and rapidly cooling the product. If the cooling speed is not sufficiently high in passing the precipitation temperature zone, sigma phase is rapidly precipitated. That is, when sigma phase is precipitated during the cooling process, stainless steel is embrittled and also shows low corrosion resistance.

[0010] However, the above-described methods for adding the third alloying elements or controlling the cooling process during the heat-treatment cannot sufficiently suppress sigma phase in high-grade duplex stainless steel.

DISCLOSURE OF THE INVENTION

[0011] The main object of the present invention is to remove brittleness and improve corrosion resistance by reducing a precipitation speed and amount of brittle intermetallic phases, by delaying diffusion and precipitation of intermetallic phases by adding appropriate amounts of Ba, Y, Ce, La, Nd, Pr, Ta, Zr and Ti atoms having a large atomic diameter, and additionally blocking diffusion of Cr, Mo, Si and W by using minute Rare Earth compounds or Ba oxides.

[0012] Another object of the invention is to prevent individual formation of Al₂O₃ and MnS inclusions which have detrimental effects on properties of steel by performing proper preliminary deoxidation according to a common method using Ti, Mg, Ca, Al and Ca+Al, as well as adding MM (Mischmetal: rare earth metallic mixtures consisting of atoms with atomic numbers from 57 to 71, containing at least 50% or more of Ce, a certain amount of La, Nd and Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Se, and 1% or less of Fe. Hereinafter, the detailed description and embodiment of the present invention uses MM containing major elements of 51%Ce-26%La-15.5%Nd-5.5%Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 1% or less of Fe) and/or Y.

[0013] Yet another object of the invention is to control solubility products in molten steel of rare-earth metal elements of MM and/or Y (REM, hereinafter, referred as 'RE' in compound formulae) within a certain range, supplying heterogeneous nucleation sites to make fine and minute structure during dendrite formation of the solidification, and controlling segregation of the solute elements such as Cr, Mo, W, Ni, Mn and Si by forming a rare-earth metallic compound mixture (RExOy or (RE,Al)xOy+RExOyS+RExSy) having a diameter below 5µm in molten steel, resulting in improving mechanical properties, physical properties and corrosion resistance.

[0014] Yet another object of the invention is to remarkably suppress formation of intermetallic phases such as sigma in duplex stainless steel by adding new alloying elements, and to improve the production yield during mass production.

[0015] Yet another object of the invention is to considerably increase the production yield in casting and hot working, by improving embrittlement resistance and preventing cracks by lowering a precipitation speed of intermetallic phases such as sigma.

[0016] Yet another object of the invention is to improve corrosion resistance and mechanical properties and upgrade

durability of equipments, by suppressing precipitation of sigma and khi phases deteriorating corrosion resistance and mechanical properties in a casting state, and controlling precipitation of such phases in heat-affected zone after welding when equipment components are necessarily welded in various application fields.

[0017] In order to achieve the above-described objects, the summary of the invention will now be explained:

5 (1) High-grade duplex stainless steel with high corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases, consisting essentially of 21.0 to 38.0% of Cr, 3.0 to 12.0% of Ni, 1.5 to 6.5% of Mo, 0 to 6.5% of W, 3.0% or less of Si, 8.0% or less of Mn, 0.2 to 0.7% of N, 0.1% or less of C, 0.0001 to 0.6% of Ba, and a balance of Fe and incidental impurities on a weight basis, a pitting resistance equivalent (PREW) defined by following formula ① satisfying $40 \leq \text{PREW} \leq 67$:

$$\text{PREW} = \text{wt}\% \text{Cr} + 3.3(\text{wt}\% \text{Mo} + 0.5\text{wt}\% \text{W}) + 30\text{wt}\% \text{N} \text{ --- } \textcircled{1}$$

15 (2) The high-grade duplex stainless steel of (1), further containing 0.0001 to 1.0% of MM and/or Y in total.
 (3) The high-grade duplex stainless steel of (2), wherein Ba is added within the range of 0.001 to 0.2%.
 (4) High-grade duplex stainless steel with high corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases, consisting essentially of 21.0 to 38.0% of Cr, 3.0 to 12.0% of Ni, 1.5 to 6.5% of Mo, 0 to 6.5% of W, 3.0% or less of Si, 8.0% or less of Mn, 0.2 to 0.7% of N, 0.1% or less of C, 0.0001 to 1.0% of MM and/or Y in total, and a balance of Fe and incidental impurities on a weight basis
 20 wherein MM is rare-earth metallic mixtures consisting of atoms with atomic numbers from 57 to 71, containing major elements of 51% of Ce, 26% of La, 15.5% of Nd and 5.5% of Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Sc, and 1% or less Fe, and a pitting resistance equivalent (PREW) defined by following formula ① satisfying $40 \leq \text{PREW} \leq 67$:

$$\text{PREW} = \text{wt}\% \text{Cr} + 3.3(\text{wt}\% \text{Mo} + 0.5\text{wt}\% \text{W}) + 30\text{wt}\% \text{N} \text{ --- } \textcircled{1}$$

25 (5) The high-grade duplex stainless steel of one of (2) to (4), wherein a value of $[\text{MM and/or Y+Al}][\text{O+S}]$ which is an equation of solubility products of MM and/or Y, and Al, O and S of steel ranges from 0.001×10^{-5} to $30000 \times 10^{-5} [\%]^2$.
 (6) The high-grade duplex stainless steel of (5), wherein, in the case of a cast product, the value of the equation of the solubility products ranges from 1×10^{-5} to $5000 \times 10^{-5} [\%]^2$.
 (7) The high-grade duplex stainless steel of (5), wherein, in the case of a hot working product, the value of the equation of the solubility products ranges from 0.1×10^{-5} to $2000 \times 10^{-5} [\%]^2$.
 30 (8) The high-grade duplex stainless steel of one of (2) to (4), wherein a total amount of MM and/or Y ranges from 0.01 to 0.6%.
 (9) The high-grade duplex stainless steel of (8), wherein the total amount of MM and/or Y ranges from 0.2 to 0.5%.
 (10) The high-grade duplex stainless steel of one of (1) to (4), further containing at least one element selected from the group consisting of 0.5% or less of Ca, 0.5% or less of Mg, 1.0% or less of Al, 0.5% or less of Ta, 0.5% or less of Nb, 1.5% or less of Ti, 1.0% or less of Zr, 1.0% or less of Sn and 1.0% or less of In.
 35 (11) The high-grade duplex stainless steel of one of (1) to (4), further containing 0.1% or less of B.
 (12) The high-grade duplex stainless steel of one of (1) to (4), further containing one or more among 3.0% or less of Cu and 3.0% or less of Co.
 (13) The high-grade duplex stainless steel of one of (1) to (4), wherein a value of $[\text{PREW}(\gamma) - \text{PREW}(\alpha)]$ which is a corrosion resistance balance of austenitic phase and ferritic phase ranges from -5 to 10.
 40 (14) The high-grade duplex stainless steel of one of (1) to (4), wherein a volume fraction of ferritic phase ranges from 20 to 70%, and a volume fraction of austenitic phase ranges from 30 to 80% on a volume basis.

50 BRIEF DESCRIPTION OF THE DRAWINGS

[0018]

55 Figs. 1A to 1F are pictures showing microstructures of invention steel 4 (Fig. 1A), invention steel 10 (Fig. 1B) and invention steel 36 (Fig. 1C) aging heat-treated at 850°C for 30 minutes, comparative steel 47 (Fig. 1D), and UR 52N+ (Fig. 1E) and SAF 2507 (Fig. 1F) which are commercial steels;
 Figs. 2A to 2D are graphs showing X-ray diffraction test results of invention steel 4 (Fig. 2A) aging heat-treated at 850°C for 30 minutes, comparative steel 47 (Fig. 2B), and UR 52N+ (Fig. 2C) and SAF 2507 (Fig. 2D) which are

commercial steels;

Figs. 3A to 3D are pictures showing macrostructures of invention steel 10 (Fig. 3A) and comparative steel 47 (Fig. 3B) in a middle portion of an ingot ($\text{Ø}110\text{mm}\times\text{L}550\text{mm}$), and microstructures of invention steel 10 (Fig. 3C) and comparative steel 47 (Fig. 3D);

Fig. 4 is a graph showing anodic polarization resistance test results of invention steels and commercial steel in a casting state in 50°C deaerated $0.5\text{N HCl}+1.0\text{N NaCl}$ solution;

Fig. 5 is a graph showing critical pitting temperature test results of invention steels and commercial steels in 6% FeCl_3 solution;

Figs. 6A, 6B and 6C are graphs showing anodic polarization resistance test results of invention steels (Fig. 6A) solution heat-treated at 1130°C , commercial high-grade duplex stainless steels (Fig. 6B), and commercial high-grade austenitic stainless steels (Fig. 6C) in 70°C deaerated $0.5\text{N HCl}+1.0\text{N NaCl}$ solution;

Figs. 7A and 7B are graphs showing anodic polarization resistance test results of invention steels (Fig. 7A) aging heat-treated at 850°C for 10 minutes and commercial high-grade duplex stainless steels (Fig. 7B) in 50°C deaerated $0.5\text{N HCl}+1.0\text{N NaCl}$ solution; and

Figs. 8A and 8B are graphs showing anodic polarization resistance test results of invention steels (Fig. 8A) aging heat-treated at 850°C for 30 minutes and commercial high-grade duplex stainless steels (Fig. 8B) in 50°C deaerated $0.5\text{N HCl}+1.0\text{N NaCl}$ solution.

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] High-grade duplex stainless steel having excellent corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases in accordance with the present invention will now be described in detail with reference to the accompanying drawings.

[0020] Based on the fact that, even if corrosion resistance and mechanical properties are remarkably improved in a thin laboratory size of mother alloy manufactured by optimal alloy design, special conditions should be satisfied to increase the production yield of thick cast products and hot working products in the mass production, and to improve corrosion resistance and mechanical properties thereof, the present inventors have thoroughly researched into mechanism of intermetallic phases such as sigma (θ) and khi (χ) showing detrimental effects on corrosion resistance, embrittlement resistance, castability and hot workability, and reached the following results.

[0021] That is, the present inventors found out that, when alloying elements such as Ba, MM (Ce, La, Nd, Pr) and/or Y which have a much larger atomic diameter than basic alloying elements such as Fe, Cr, Mo, Ni, W, Mn and Si which composed duplex stainless steel containing Cr, Mo, Si and W facilitating formation of intermetallic phases were added, the alloying elements atoms having a larger atomic diameter filled atomic vacancies operating as a diffusion path for Cr, Mo, Si and W composing sigma and khi phases, especially filled atomic vacancies in austenitic and ferritic phase boundaries and crystal grains of ferritic phase, to lower a formation speed of intermetallic phases at a temperature ranging from 1000 to 650°C .

[0022] In addition, the present inventors discovered that, because the alloying elements having a large atomic diameter have much lower free energy for thermodynamically forming oxides or oxy-sulfides than Fe, Cr, Mo, W, Ni, Mn and Si, and thus could form minute and uniform oxides and oxy-sulfides having a diameter below $5\mu\text{m}$. Those minute rare-earth metallic mixtures or Ba oxides could additionally block diffusion of Cr, Mo, Si and W at a temperature ranging from 1000 to 650°C , to lower a precipitation speed of intermetallic phases.

[0023] The present inventors also found out that MnS non-metallic inclusion was generally operated as a starting point of corrosion due to its lower corrosion resistance than a matrix, but rare-earth non-metallic inclusion was not operated as a starting point of corrosion due to its higher corrosion resistance than the matrix.

[0024] That is, the present invention suppresses formation of intermetallic phases by adding 0.0001 to 0.6% of Ba (2.18Å) (number of bracket represents atomic diameter) having a larger atomic diameter than Fe (1.24Å), Cr (1.25Å), Mo (1.36Å), W (1.37Å), Ni (1.25Å), Mn (1.12Å) and Si (1.17Å) which are major alloying elements of commercial duplex stainless steel.

[0025] Moreover, the present invention actively suppresses formation of intermetallic phases by adding MM (comprising major elements such as Ce: 1.83Å , La: 1.88Å , Nd: 1.82Å and Pr: 1.83Å , minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 1% or less of Fe) and/or Y (1.82Å) having a larger atomic diameter than Fe (1.24Å), Cr (1.25Å), Mo (1.36Å), W (1.37Å), Ni (1.25Å), Mn (1.12Å) and Si (1.17Å) which are major alloying elements of commercial duplex stainless steel, or adding it with Ba. Here, in order to facilitate such effects, $[\text{MM and/or Y+Al}]\cdot[\text{O+S}]$ which is a equation of solubility products of MM and/or Y, and Al, O and S of steel should exist within the range of 0.001×10^{-5} to 30000×10^{-5} .

[0026] In addition, when an appropriate amount of at least one alloying element of Ca (1.97Å), Mg (1.6Å), Al (1.43Å), Ta (1.43Å), Nb (1.43Å), Ti (1.47Å), Zr (1.62Å), Sn (1.51Å) and In (1.68Å) which have a larger atomic diameter than the alloying elements is added, formation of sigma and khi phases is more efficiently suppressed.

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[0027] When B which has a much smaller atomic diameter than Fe, Cr, Mo, W, Ni, Mn and Si to fill the spaces of the alloying elements having a large atomic diameter is added with the alloying elements, B serves to lower a precipitation speed of sigma and khi phases with the alloying elements.

[0028] At least one alloying element of Cu and Co can be additionally used to improve acid resistance and strength.

[0029] The role of alloying elements added to duplex stainless steels in accordance with the present invention, and the reasons for restricting chemical composition ranges thereof will now be described.

Cr: 21.0 to 38.0%

[0030] Cr is a basic important element for maintaining corrosion resistance of stainless steel. At least 12% of Cr is required to maintain corrosion resistance. In the present invention, the alloy needs to have austenite-ferrite duplex structure, and thus at least 21% of Cr must be used in consideration of Cr_{eq} and Ni_{eq} defined in the following formula and austenite/ferrite phase ratio determined by them. So as to manufacture duplex stainless steel by balance of C, N, Ni, Mo, W, Si, Mn and Cu, the upper limit of Cr is set up 38%, more preferably, 24 to 28%.

$$Cr_{eq} = \%Cr + 2\%Si + 1.5\%Mo + 0.75\%W + 5\%V + 5.5\%Al + 1.75\%Nb + 1.5\%Ti \quad \text{--- } \textcircled{2}$$

$$Ni_{eq} = \%Ni + 0.5\%Mn + 30\%C + 0.3\%Cu + 25\%N + \%Co \quad \text{--- } \textcircled{3}$$

$$\text{Austenitic phase fraction (vol\%)} = 100 - [55 \times (Cr_{eq}/Ni_{eq}) - 66.1] \quad \text{--- } \textcircled{4}$$

$$\text{Ferritic phase fraction (vol\%)} = 55 \times (Cr_{eq}/Ni_{eq}) - 66.1 \quad \text{--- } \textcircled{5}$$

[0031] In addition, a range of phase ratios for maximizing corrosion resistance of duplex stainless steel is obtained by the following examples of the invention. The ferritic ratio ranges from 20 to 70 vol.% (30 to 80 vol.% in austenitic phase fraction).

Ni: 3 to 12%

[0032] At least 3% of Ni is required because it is an austenitic stabilizer for increasing uniform corrosion resistance. 3.0 to 12.0%, more preferably 6 to 9% of Ni is used in consideration of Cr_{eq} , Ni_{eq} , phase ratio and its high cost.

Mo: 1.5 to 6.5%

[0033] Mo is an important element for maintaining corrosion resistance of the alloy like Cr. Mo serves to stabilize ferritic phase. Since the alloy of the invention needs to have austenite-ferrite duplex structure, at least 1.5% of Mo should be added in consideration of Cr_{eq} , Ni_{eq} and phase ratio. Especially, when Mo is added with Cu, it can remarkably improve corrosion resistance in high density SO_4^{2-} and Cl^- environment. Mo is very useful to improve mechanical properties and corrosion resistance in an annealing state, but forms intermetallic phases having detrimental effects such as sigma in aging heat-treatment, hot rolling or welding. Accordingly, 6.5% or less of Mo is used in consideration of Cr_{eq} , Ni_{eq} , corrosion resistance and phase stability. As confirmed in PREW formula, effects of Mo for improving pitting resistance are twice as many as W. Thus, the content of Mo is more preferably over 2% to obtain superior pitting resistance.

W: 0 to 6.5%

[0034] W is a ferritic stabilizer and a homologous alloying element having similar chemical properties to Mo. W improves corrosion resistance in high density SO_4^{2-} and Cl^- environment, and also improves corrosion resistance and mechanical properties by delaying a precipitation speed of brittle sigma and khi phases after sensitization heat-treatment or welding. However, W is a high-priced alloying element, and if a large amount of W is used, it facilitates formation of intermetallic compounds. Therefore, 6.5% or less, more preferably 4.0% or less of W is used in consideration of phase stability,

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mechanical properties and corrosion resistance.

Si: 3% or less

5 **[0035]** Si is a ferritic stabilizer which has deoxidation effects in refining, and which increases fluidity of molten steel and reduces surface defects in cast production. When Si is used over 3%, it increases a precipitation speed of brittle intermetallic phases, and reduces ductility of steel. 3.0% or less, more preferably, 1.0% or less of Si is used in consideration of corrosion resistance.

10 Mn: 8% or less

15 **[0036]** Mn is an austenitic stabilizer which can replace high-priced Ni. Mn serves to increase solid solubility of N and reduce high temperature deformation resistance. In order to improve corrosion resistance by increasing the content of N, an appropriate amount of Mn is essentially used. It has deoxidation effects in dissolution and refining. However, a large amount of Mn deteriorates corrosion resistance, and facilitates formation of brittle intermetallic phases. Accordingly, the content of Mn is set up 8% or less, more preferably 1.0 to 3.0%.

N: 0.2 to 0.7%

20 **[0037]** N is very useful to improve pitting resistance, which is more effective than Cr by about 30 times. N is a strong austenitic stabilizer, and also is one of the most important elements for improving corrosion resistance. When N exists with Mo, it can considerably improve corrosion resistance. When the content of C is reduced to improve grain boundary corrosion resistance, N can compensate for mechanical properties. In addition, N suppresses formation of Cr carbides, and improves tensile strength and yield strength without reducing elongation. The content of N must be controlled in
25 consideration of balance with C, Cr, Ni, Mo and W and austenitic-ferritic phase ratio. At least 0.2% of N is preferably used in respect of corrosion resistance. However, when N is used over 0.7%, it may reduce castability (blowhole, shrinkage) and rollability. More preferably, the content of N ranges from 0.32 to 0.45%.

C: 0.1 % or less

30 **[0038]** C is a representative element for stabilizing austenite phase and an important element for maintaining mechanical strength. However, if a large amount of C is used, it precipitates carbides and thus reduces corrosion resistance. Therefore, 0.1% or less, preferably 0.05% or less of C is used, and more preferably, 0.03% or less of C is used to improve corrosion resistance in aging.

35 PREW value: 40 to 67

[0039] In addition to that the contents of Cr, Mo, W and N are restricted as described above, the value of the PREW defined by following formula ① satisfies $40 \leq \text{PREW} \leq 67$:

$$\text{PREW} = \text{wt}\% \text{Cr} + 3.3(\text{wt}\% \text{Mo} + 0.5\text{wt}\% \text{W}) + 30\text{wt}\% \text{N} \text{ --- } \textcircled{1}$$

45 **[0040]** When the value of the PREW is lower than the lowest limit, corrosion resistance is not sufficiently obtained, and when the value of the PREW is higher than the upper limit, formation of intermetallic phases is facilitated. Preferably, the value of the PREW is greater than 45.

[0041] Moreover, $[\text{PREW}(\gamma) - \text{PREW}(\alpha)]$ which is a corrosion resistance balance of phases for maximizing corrosion resistance of duplex stainless steel preferably ranges from -5 to 10 according to the examples of the invention which
50 will later be discussed.

Ba: 0.0001 to 0.6%

55 **[0042]** As described above, Ba is one of the most important elements of the invention. Ba has an atomic diameter of 2.18Å. Ba having a much larger atomic diameter than the other alloying elements (Fe, Cr, Mo, W, Ni, Mn, Si, etc.) of duplex stainless steel is operated as a barrier for blocking diffusion of Cr, Mo and W which are main constituents of brittle intermetallic phases, and thus effective to reduce a diffusion speed, a precipitation speed and a precipitation amount. In addition, Ba is coupled with solute atoms and oxygen to form oxides, thereby lowering a precipitation speed

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of sigma and khi phases. In order to obtain the aforementioned effects, 0.6% or less of Ba is required. When Ba is used over 0.6%, it is not economically advantageous. Furthermore, a large amount of Ba is precipitated in grain boundaries, to reduce grain boundary strength at a high temperature and offset improvements of high temperature cracking sensitivity. Accordingly, the upper limit of Ba is set up 0.6%. On the other hand, if Ba is used below 0.0001%, addition effects thereof are not expectable.

MM and/or Y: 0.0001 to 1.0%

[0043] MM (Mischmetal: rare-earth metallic mixtures consisting of atoms with atomic numbers from 57 to 71, containing at least 50% or more of Ce, a certain amount of La, Nd and Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 1% or less of Fe. As described above, the detailed description and embodiment of the present invention uses MM containing major elements of 51%Ce-26%La-15.5%Nd-5.5%Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, and 1% or less of Fe) and/or Y is one of the most important alloying elements which can be added with/without Ba. When MM and/or Y is added, it can prevent individual formation of Al_2O_3 and MnS non-metallic inclusions which have detrimental effects on general properties of steel, form a rare-earth metallic compound mixture ($RExOy$ or $(RE,Al)xOy+RExOyS+RExSy$) having a diameter below $5\mu m$ in molten steel, operate as heterogeneous nucleation sites to make a solidified structure fine and minute in solidification, and control segregation of solute elements, to improve mechanical properties, physical properties and corrosion resistance.

[0044] In addition, Y, MM(Ce, La, Nd, Pr, etc.), Ba, Zr and Ti having a large atomic diameter maintained in steel in an atomic state are very efficient to delay a precipitation speed of brittle intermetallic phases. MM and/or Y is a very important element for improving weldability, high temperature oxidation resistance, machinability and high temperature workability. The content of MM and/or Y ranges from 0.0001 to 1.0%. If MM and/or Y is used over 1.0%, the addition is not economically advantageous, and the excessive amounts have detrimental effects on general properties of steel. When MM and/or Y is used below 0.0001%, the aforementioned addition effects cannot be obtained.

[0045] Moreover, in order to obtain micro-uniformity of a segregation area of solute elements resulting from fine and minute structure induced by heterogeneous nucleation during dendrite formation of solidification of a rare-earth metallic compound mixture ($RExOy$ or $(RE,Al)xOy+RExOyS+RExSy$), and reduction of a precipitation speed of intermetallic phases by allowing Y, MM(Ce, La, Nd, Pr, etc.), Ba, Zr and Ti to block diffusion of Cr, Mo, Si and W facilitating formation of intermetallic phases, $[MM \text{ and/or } Y+Al] \cdot [O+S]$ which is an equation of solubility products of MM and/or Y in steel, and Al, O and S of steel is supposed to range from 0.001×10^{-5} to $30000 \times 10^{-5} [\%]^2$. When the value of the equation of the solubility products is below 0.001×10^{-5} , it is difficult to control the solidified structure, decrease segregation of solute elements and suppress formation of intermetallic phases. If the value of the equation of the solubility products is over $30000 \times 10^{-5} [\%]^2$, rare-earth metallic compound mixtures are excessively formed, to deteriorate mechanical properties, physical properties and corrosion resistance of steel. More preferably, in the case of a cast product, the value of the equation of the solubility products ranges from 1×10^{-5} to $5000 \times 10^{-5} [\%]^2$, and in the case of a hot working product, the value of the equation of the solubility products ranges from 0.1×10^{-5} to $2000 \times 10^{-5} [\%]^2$.

[0046] The content of MM preferably ranges from 0.01 to 0.6%, more preferably 0.2 to 0.5%.

Ca: 0.5% or less

[0047] Ca is a deoxidation element for improving embrittlement resistance, and reducing high temperature deformation resistance and machinability resistance. When a large amount of Ca is used, it reduces purity and corrosion resistance of steel. Preferably, 0.5% or less of Ca is used.

Al, O and S

[0048] Al is a ferritic stabilizer for improving oxidation resistance and embrittlement resistance. When Al is added to steel, it increases purity of steel by deoxidation effects, and reduces high temperature deformation resistance. Preferably, 1.0% or less of Al is used.

[0049] In addition, steel essentially contains O and S which generate cracks during solidification process and decrease ductility after production. Accordingly, O and S which generate brittleness should be restrictively used. In the case of a cast product, 200ppm or less of O and 50ppm or less of S should be used, and in the case of wrought product, 100ppm or less of O and 20ppm or less of S should be used.

Ti: 1.5% or less

[0050] Ti shows deoxidation effects in refining process, and forms titanium sulfides to improve machinability. In order to improve intergranular corrosion resistance, the content of Ti is determined in consideration of an amount of C. 1.5%

or less of Ti is used to improve corrosion resistance in environments including chloride ions after sensitization heat-treatment.

Mg: 0.5% or less, Ta: 0.5% or less, Nb: 0.5% or less, Zr: 1.0% or less, Sn: 1.0% or less, In: 1.0% or less

[0051] As disclosed by the present inventors, in addition to Ca (1.97Å), Al (1.43Å) and Ti (1.47Å) which have a larger atomic diameter than Fe, Cr, Mo and W, Mg (1.6Å), Ta (1.43Å), Nb (1.43Å), Zr (1.62Å), Sn (1.51Å) and In (1.68Å) are efficient to suppress sigma and khi phases. Therefore, 0.5% or less of Mg, 0.5% or less of Ta, 0.5% or less of Nb, 1.0% or less of Zr, 1.0% or less of Sn and 1.0% or less of In are used.

[0052] When the aforementioned alloying elements exceed their upper limits, they are not economically advantageous, and generate grain boundary embrittlement to deteriorate castability and hot workability.

B: 0.1% or less

[0053] B is useful to improve embrittlement resistance and reduce high temperature deformation resistance, and prevent high temperature cracks in welding. When B is used with N, boron nitrides having a low melting point are formed to improve machinability. Especially, B has a much smaller atomic diameter than Fe, Cr, Mo, W, Ni, Mn and Si, and thus fills minute gaps. Accordingly, when B coexists with alloying elements having a large atomic diameter, it can enhance blocking effects to decrease a precipitation speed of sigma and khi phases. Preferably, 0.1% or less of B is used.

Cu: 3% or less

[0054] Cu is an austenitic stabilizer for improving corrosion resistance. Especially, when Cu is used with Mo, it considerably increases corrosion resistance in acid environments of concentrated sulfuric acid and hydrochloric acid. Cu also induces substitutional solid solution hardening effects to improve tensile strength and yield strength.

[0055] If an appropriate amount of Cu is not used in consideration of phase ratio, Cr and Mo, Cu may reduce pitting resistance. In addition, Cu is an important element for improving machinability by lowering a working hardening speed. When Cu is over 3%, it generates hot shortness. Therefore, 3% or less of Cu is used.

Co: 3.0% or less

[0056] Co is an austenitic stabilizer which can replace Ni. Co is very effective to improve corrosion resistance and strength, but its cost is high. 3.0% or less of Co is used in consideration of phase ratio and corrosion resistance balance.

Example 1: Method for Manufacturing and Testing Steel of Invention

[0057] A method for designing and manufacturing optimal alloys in accordance with the present invention will now be explained. The method for designing the alloy is obtained by optimally combining alloy design factors such as PREW of equation ①, [PREW(γ)-PREW(α)] for corrosion resistance balance of phases, Cr_{eq} of equation ②, and Ni_{eq} of equation ③, and resultant values are shown in Table 2.

[0058] Cr_{eq} and Ni_{eq} were calculated by the equation ② and ③ to determine the composition, the alloying elements are melted in high frequency induction furnace using commercial pure grade of Fe, Cr, Mo, Ni, W, Cu, Si, Mn and Fe-Cr-N as recited in the claims of the invention, and deoxidized according to a common method such as Ti, Mg, Al, Ca or Al+Ca composite deoxidation, samples for casting melted in air, and samples for wrought products were melted in vacuum and nitrogen gas atmosphere. As shown in Table 4, the value of [PREW(γ)-PREW(α)] for corrosion resistance balance of phases of Table 2 was obtained by analyzing Cr, Mo, W and N elements composing austenitic and ferritic phases, and introducing the resultant values to the PREW equation ①.

[0059] According to another aspect of the invention, molten steel containing the elements as recited in the claims of the invention was preliminarily deoxidized according to a common method such as Al, Ca or Al+Ca composite deoxidation, and Ba and/or MM and/or Y was added to molten steel to form Ba oxides or rare-earth metallic compound mixtures (RExOy or (RE,Al)xOy+RExOyS+RExSy), so that solubility products could satisfy '[Ba and/or MM and/or Y+Al]·[O+S] = 0.001 × 10⁻⁵ to 30000 × 10⁻⁵[%]²'.

[0060] Thereafter, 25Kg of plate-type cast product (9mm thick) was manufactured by pouring molten metal into a plate type ceramic mold, and 30Kg of ingot was manufactured by pouring molten metal into a preheated rectangular steel mold. In the case of the ingot for wrought products, it was processed in a proper size using a grinding or machining process, soaked at 1250°C, and hot rolled to a thickness of 6mm. The solution heat-treatment was performed for both the cast product and 6mm thick - hot rolled product at a temperature ranging from 1050 to 1150°C. Table 1 shows the chemical compositions of the solution heat-treated steels of the invention in comparison with comparative and commercial

steels.

[0061] In order to evaluate general properties of the solution heat-treated product and the product aging heat-treated at 850°C for 10 minutes, microstructures, X-ray diffraction test results, anodic polarization test results, critical pitting temperature, critical crevice corrosion temperature, and mechanical properties thereof were measured.

[0062] The samples were polished to 2000grit using SiC polishing paper, finally polished using alumina, processed in Murakami solution (30g $K_3Fe(CN)_6$ +30gKOH+100ml distilled water) at 80°C, etched, and washed ultrasonically in acetone and distilled water. Then, the microstructures of the samples were observed using an optical microscope.

[0063] The X-ray diffraction test was performed to confirm sigma and khi phases precipitated according to the aging heat-treatment at 850°C for 30 minutes. Rikagu D/MAX-B was used as a test device, the samples were analyzed at an accelerating voltage of 35kv and a current of 35mA, and Ni filter was used with Cu target. According to the observation results, the samples where a lot of phases had been precipitated were analyzed at angles ranging from 30 to 120° with a speed of 12°/min., and analyzed precisely again at a angles ranging from 40 to 50° where peak concentration of the precipitated phases are observed with a speed of 1°/min.

[0064] The anodic polarization test was performed per ASTM G5 in 50 and 70°C deaerated 0.5N HCl+1.0N NaCl solution with a scanning speed of 1 mV/sec.

[0065] The critical pitting resistance temperature was measured per ASTM G 48A-92, and the critical crevice corrosion temperature was measured per ASTM G 48D.

[0066] The samples were polished to 600grit, and the hardness of the samples was measured in C-scale by using Rockwell hardness tester.

Example 2: Comparison of Microstructures of Aged Products

[0067] Figs. 1A to 1F are pictures of microstructures showing precipitation of brittle intermetallic phases deteriorating corrosion resistance and mechanical properties, such as sigma and khi of invention steel 4 (Fig. 1A), invention steel 10 (Fig. 1B) and invention steel 36 (Fig. 1C) aging heat-treated at 850°C for 30 minutes, comparative steel 47 (Fig. 1D), and UR 52N+ (Fig. 1E) and SAF 2507 (Fig. 1F) which are commercial high-grade duplex stainless steels. Bright parts show austenitic phase, and dark parts show ferritic phase decomposed into sigma phase+austenite phase in the aging heat-treatment. The degree of precipitation of the intermetallic phases was 'invention steel 4=invention steel 10=invention steel 36<<commercial steel UR 52+<commercial steel SAF 2507<<comparative steel 47'. As a result, invention steels 4, 10 and 36 suppressed precipitation of the intermetallic phases more than commercial steels UR 52+ and SAF 2507 and comparative steel 47, to remarkably improve embrittlement resistance.

Example 3: X-ray Diffraction Analysis Test

[0068] Figs. 2A to 2D are graphs of X-ray diffraction analysis test results showing precipitation of brittle intermetallic phases deteriorating corrosion resistance and mechanical properties, such as sigma and khi of invention steel 4 (Fig. 2A) aging heat-treated at 850°C for 30 minutes, comparative steel 47 (Fig. 2B), and UR 52N+ (Fig. 2C) and SAF 2507 (Fig. 2D) which are commercial high-grade duplex stainless steels. As compared with comparative steel 47 and commercial steels UR 52+ and SAF 2507, invention steel 4 did not precipitate sigma phase, and precipitated little khi phase, to considerably improve embrittlement resistance.

Example 4: Comparison of Macrostructures and Microstructures in Cast State

[0069] Figs. 3A to 3D are pictures showing macrostructures (Figs. 3A and 3B) and microstructures (Figs. 3C and 3D) in a middle portion of an ingot (Ø110mm×L550mm) of invention steel 10 manufactured according to the method for controlling solidified structures, segregation of solute elements, and formation of intermetallic phases, and comparative steel 47 in a casting state.

[0070] As compared with the macrostructure (Fig. 3B) of comparative steel 47 (0.015%O, 0.007%S) where a value of solubility products was zero because MM and Al were not added, the macrostructure (Fig. 3A) of invention steel 10 (0.09%MM, 0.02%Al, 0.025%O and 0.007%S) where $[MM+Al] \cdot [O+S]$, a value of solubility products of MM (Ce, La, Nd, Pr) of molten steel, and/or Y, and Al, O and S was $352.0 \times 10^{-5} [\%]^2$ was a minute equiaxed crystal structure where growth of columnar crystals was restricted, had dense solidified structures, and did not generate V segregation and inverse V segregation.

[0071] In addition, as compared with the microstructure (Fig. 3D) of comparative steel 47, the microstructure (Fig. 3C) of invention steel 10 remarkably suppressed precipitation of intermetallic phases deteriorating corrosion resistance and mechanical properties such as sigma and khi, and reduced a size of austenitic and ferritic phases.

Example 5: Anodic Polarization Test Results in Cast State

[0072] Fig. 4 is a graph showing anodic polarization resistance test results of invention steels 4, 10, 26 and 36 which are not solution heat-treated and comparative steel 47 in a cast state. The degree of pitting resistance was 'invention steel 10>invention steel 4>invention steel 36> invention steel 26>comparative steel 47'.

Example 6: Results of Critical Pitting and Crevice Corrosion Temperature Tests

[0073] Fig. 5 is a graph showing a critical pitting temperature of solution heat-treated invention steels 4, 10, 26 and 36, UR 52N+, SAF 2507 and ZERON 100 which are commercial high-grade duplex stainless steels, SAF 2205 which is commercial duplex stainless steel, SR-50A which is commercial high-grade austenitic stainless steel, and AISI 316L which is commercial austenitic stainless steel. When the critical pitting temperature increased, the pitting resistance improved. The degree of corrosion resistance of invention steels and commercial steels was 'invention steel 10=invention steel 26=invention steel 36>commercial steel SR-50A>invention steel 4>commercial steel UR 52N+=commercial steel ZERON 100>commercial steel SAF 2507>commercial steel SAF 2205>commercial steel AISI 316L'.

[0074] Invention steels 10, 26 and 26 showed higher pitting resistance than commercial high-grade duplex stainless steels UR 52N+, SAF 2507 and ZERON 100, and higher corrosion resistance than SR-50A which was commercial high-priced austenitic stainless steel. Invention steels had a much higher critical pitting temperature than comparative and commercial steels, and thus had a higher critical crevice corrosion temperature as shown in Table 2, thereby remarkably improving crevice corrosion resistance. Table 2 shows the critical pitting temperature and the critical crevice corrosion temperature of the steels.

Example 7: Anodic Polarization Test Results of Solution Heat-Treated Product

[0075] Figs. 6A to 6C are graphs showing anodic polarization resistance test results of solution heat-treated invention steels 4, 10, 26 and 36 (Fig. 6A), commercial high-grade duplex stainless steels UR 52N+, SAF 2507 and ZERON 100 (Fig. 6B) and commercial high-grade austenitic stainless steels AL-6XN, SR-50A and 254SMO (Fig. 6C). The degree of pitting resistance was 'invention steel 26=invention steel 36=commercial steel SR-50A>invention steel 10>invention steel 4>commercial steel AL-6XN>commercial steel 254SMO>commercial steel UR 52N+=SAF 2507=ZERON 100'.

[0076] In Example 6, invention steels had a much higher critical pitting temperature and critical crevice corrosion temperature than comparative and commercial steels, and thus had a high pitting potential in the anodic polarization test (refer to Table 2). That is, the three tests showed similar results.

Example 8: Anodic Polarization Test Results of Aged Product (850°C×10min.)

[0077] Figs. 7A and 7B are graphs showing anodic polarization resistance test results of invention steels 4, 10, 26 and 36 (Fig. 7A) aging heat-treated at 850°C for 10 minutes and commercial high-grade duplex stainless steels UR 52N+, SAF 2507 and ZERON 100 (Fig. 7B). The degree of pitting resistance was 'invention steel 4=invention steel 10=invention steel 26> invention steel 36>commercial steel ZERON 100>commercial steel SAF 2507>commercial steel UR 52N+'.

[0078] As a result, as compared with commercial steels UR52N+, SAF 2507 and ZERON 100, invention steels 4, 10 and 26 lowered a precipitation speed of intermetallic phases such as sigma and khi during the aging heat-treatment, to improve pitting resistance.

Example 9: Anodic Polarization Test and Hardness Measurement Results of Aged Product (850°C×30min.)

[0079] Figs. 8A and 8B are graphs showing anodic polarization resistance test results of invention steels 4, 10, 26 and 36 (Fig. 8A) aging heat-treated at 850°C for 30 minutes and commercial high-grade duplex stainless steels UR 52N+, SAF 2507 and ZERON 100 (Fig. 8B). The degree of pitting resistance was 'invention steel 10>invention steel 4>invention steel 36= invention steel 26=commercial steel SAF 2507>commercial steel ZERON 100>commercial steel UR 52N+'.

[0080] Accordingly, as compared with commercial steels UR52+, SAF 2507 and ZERON 100, invention steels 4 and 10 lowered a precipitation speed of intermetallic phases such as sigma and khi during the aging heat-treatment, to remarkably improve pitting resistance, and invention steels 36 and 26 showed pitting resistance similar to or higher than commercial steels.

[0081] Table 2 shows differences of hardness values ($\Delta H = H_A - H_{S,A}$) obtained by subtracting hardness values $H_{S,A}$ of solution heat-treated invention steels from hardness values H_A of aging heat-treated invention steels at 850°C for 30 minutes. In general, when sigma and khi phases having high brittleness increased, ΔH also increased, to seriously

reduce corrosion resistance, strength, elongation and impact strength. As shown in Table 2, ΔH of invention steels ranged from 0.1 to 3.7 due to delay of a precipitation speed of intermetallic phases, ΔH of comparative steels ranged from 10.3 to 16.2, and ΔH of commercial steels ranged from 5.6 to 6.2. That is, invention steels showed more excellent embrittlement resistance than comparative steels.

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Example 10: Mechanical Properties

[0082] Table 3 shows yield strength, tensile strength and elongation after solution heat-treatment of cast product at 1130°C and performing a tensile test thereon. Invention steels had high strength due to interstitial solution hardening effects by high N addition, and fixed crystal grain boundaries by Ba, and rare-earth oxides or sulfuric oxides (< 5 μ m), to simultaneously improve strength and elongation. Therefore, invention steels have much better mechanical properties than comparative steels.

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Example 11: Properties of Hot Rolled Samples

[0083] Table 5 shows critical pitting temperature, mechanical properties and hot workability of hot-rolled samples after casting in vacuum and nitrogen atmosphere. The hot-rolled samples showed better mechanical properties and microstructures than invention steels cast in air by over 10%, and showed corrosion resistance similar to them.

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[0084] The hot-rolled samples generated less cracks on the edge than comparative products during the hot rolling, to maintain high hot workability.

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Table 1. Chemical Composition of Invention Steel, Comparative Steel and Commercial Steel (wt.%)

Classification ¹⁾	C	Cr	Ni	Mo	W	N	Cu	Mn	Si	MM ²⁾ or Y	Ba	Ta	Zr	B	Others
○	0.015	29.0	7.0	1.7	3.0	0.43	0.01	3.0	0.82	Y:0.45	-	-	0.02	0.0015	Sn:0.01, Nb: 0.01, Mg: 0.01, Co: 0.01, In:0.01, Al:0.02
○	0.014	26.9	7.3	2.5	3.2	0.34	0.4	2.0	0.17		0.01		0.0015	0.0015	Al:0.03
○	0.020	25.3	7.1	3.9	0.7	0.27	0.80	0.8	0.32	MM:0.05	0.01	-	1.0	0.0021	Al:0.01
○	0.017	27.0	7.4	2.4	3.1	0.40	0.02	1.6	0.55	MM:0.11	-	-	-	0.0028	Al:0.02
○	0.012	27.5	7.1	2.5	3.24	0.34		2.1	0.22	MM:0.008	0.002		0.0020	0.0020	Al:0.02
○	0.015	21.0	7.0	6.4	3.2	0.36	0.05	2.1	0.37	MM:0.08	0.04	-	-	-	Nb:0.04, Mg: 0.02, Al:0.03
○	0.014	27.1	7.3	2.7	2.9	0.33	0.04	1.7	0.36	MM:0.08	0.01	-	-	0.0050	Al:0.02
○	0.013	26.8	6.8	2.5	3.2	0.35	1.2	2.1	0.2		0.01			0.0015	Al:0.03
○	0.012	26.6	5.2	2.6	3.9	0.34	2.30	2.2	0.34	MM:0.4	0.02	-	0.01	0.0019	In:0.42, Al: 0.03
○	0.021	26.3	7.3	2.6	3.0	0.36	0.08	1.4	0.59	MM:0.09	0.01	-	-	0.0024	Al:0.02
○	0.015	27.1	6.6	2.5	3.2	0.36	1.2	2.0	0.21	MM:0.01				0.0018	Al:0.02
○	0.014	30.0	9.6	2.8	1.8	0.44	0.04	2.8	0.60	Y:0.3, MM: 0.2	0.02	0.004	0.05	-	Sn:0.56, Al: 0.03
○	0.017	27.3	7.4	2.5	3.0	0.41	0.06	1.6	0.55	MM:0.12	-	-	-	0.08	Ti:0.04, Al: 0.01
○	0.014	26.7	7.3	2.5	3.3	0.35	1.2	2.2	0.25	MM:0.009	0.001			0.0016	Al:0.03
○	0.012	27.0	7.0	2.4	3.2	0.35	0.07	2.2	0.32	MM:0.02	-	-	0.20	-	Mg:0.48, Ti: 0.7, Al:0.02
○	0.014	27.2	7.1	2.2	2.8	0.36	0.09	1.8	0.40	MM:0.22	0.01	-	-	-	Mg:0.01, Al: 0.03
○	0.012	27.5	7.2	2.5	3.2	0.36		2.0	0.24					0.0015	Al:0.02, Ca: 0.01

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Classification ¹⁾	C	Cr	Ni	Mo	W	N	Cu	Mn	Si	MM ²⁾ or Y	Ba	Ta	Zr	B	Others
○ 18	0.016	27.1	7.3	2.3	3.1	0.40	0.01	1.8	0.57	MM:0.22	-	0.26	-	0.0500	Co:0.02, Al:0.02
○ 19	0.012	26.8	6.9	2.5	3.0	0.32	0.05	2.0	0.31	MM:0.04	0.03	-	-	0.0030	Al:0.02
○ 20	0.014	35.0	10.0	1.8	5.9	0.50	0.03	1.2	0.36	MM:0.86	-	-	-	-	Al:0.03
○ 21	0.014	27.0	6.8	2.5	3.2	0.34	1.2	2.1	0.17					0.0017	Al:0.03, Ca:0.01
○ 22	0.023	26.2	8.5	5.4	3.3	0.22	2.70	0.7	0.97	-	0.60	-	-	-	Al:0.02
○ 23	0.032	23.6	8.2	5.7	0.02	0.3	0.01	0.04	0.59	MM:0.15	0.02	-	-	0.0001	Al:0.005, V:0.024, Ti:0.015, Ca:0.001
○ 24	0.016	27.6	7.2	2.6	3.2	0.35		2.1	0.23	MM:0.025				0.0015	Al:0.03
○ 25	0.020	27.2	6.3	2.6	3.2	0.36	1.50	2.0	0.38	MM:0.1	0.01	-	-	0.0021	Mg:0.02 Co:0.02, Al:0.02
○ 26	0.017	27.3	7.2	4.5	-	0.39	0.04	2.0	0.64	MM:0.32	-	-	-	0.0020	Al:0.02
○ 27	0.020	25.1	7.0	3.8	0.2	0.26	0.03	0.5	0.25	MM:0.17	0.005	-	-	-	Mg:0.04, Co:0.06, Al:0.02
○ 28	0.028	24.1	8.7	5.7	0.2	0.25	0.06	1.0	0.48	MM:0.46	0.50	-	-	0.0050	Al:0.03
○ 29	0.034	24.0	7.6	5.5	-	0.26	2.00	1.2	0.75	MM:0.62	-	-	0.04	0.0050	Ti:0.80, Sn:0.02, In:0.04, Al:0.03,
○ 30	0.025	24.2	8.7	5.3	0.3	0.26	0.07	1.2	0.80	-	0.05	0.45	-	0.0080	Ti:0.02, Al:0.02
○ 31	0.020	24.0	8.7	5.7	-	0.24	0.08	0.9	0.54	MM:0.21	-	-	-	0.0030	Nb:0.5, Co:0.04, Al:0.02
○ 32	0.024	24.0	8.1	5.6	0.2	0.23	0.04	1.4	0.44	MM:0.32	-	-	0.50	0.0040	Al:0.02
○ 33	0.015	23.5	10.0	5.4	0.2	0.25	0.02	1.1	0.45	MM:0.46	-	-	-	0.0020	Co:0.95, In:0.01, Al:0.03

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Classification ¹⁾	C	Cr	Ni	Mo	W	N	Cu	Mn	Si	MM ²⁾ or Y	Ba	Ta	Zr	B	Others
○	34	23.7	8.7	5.5	-	0.25	0.01	2.8	0.53	MM:0.6	0.01	0.01	0.01	0.0010	Sn:0.01, In: 0.01, Mg: 0.01, Co: 0.01, Nb: 0.01, Al:0.03
○	35	26.8	8.4	5.0	0.3	0.35	0.06	2.7	0.73	MM:0.4, Y: 0.1	0.10	-	0.02	0.0040	Al:0.02
○	36	26.7	7.4	4.6	0.2	0.34	0.07	1.6	0.43	MM:0.06	0.01	-	-	0.0015	Al:0.02
○	37	34.5	10.0	1.5	0.4	0.37	0.05	1.1	0.41	MM:0.8, Y: 0.1	-	0.02	-	0.0022	Co:0.04, Nb: 0.02, Al:0.03
○	38	27.1	6.4	4.5	-	0.36	1.60	2.2	0.56	MM:0.03	0.01	-	-	0.0015	Al:0.02
○	39	25.7	3.2	2.8	3.9	0.40	2.4	2.7	1.0	MM:0.04	0.01	-	0.01	-	Sn:0.8, Co: 1.4, Al:0.01
○	40	34.0	12.0	2.1	6.5	0.50	0.03	1.2	2.9	MM:0.03	0.02	-	-	0.0200	In:0.9, Al: 0.01
○	41	23.6	7.0	5.4	0.22	0.25	0.02	1.2	2.2	MM:0.04	0.01	0.01	-	-	Co:2.9, Al: 0.01
○	42	37.5	12.0	1.52	0.41	0.37	0.05	1.6	1.1	MM:0.02	0.02	-	-	0.0800	Mg:0.47, Al: 0.02
○	43	25.3	7.1	3.7	0.21	0.27	0.04	0.6	0.3	MM:0.02	0.01	-	-	-	Ti:1.4, Al: 0.01
×	44	34.9	9.8	1.5	2.1	0.49	0.02	1.3	0.45	-	-	-	-	-	-
×	45	29.3	7.2	1.9	3.2	0.45	0.02	2.8	0.70	-	-	-	-	-	-
×	46	22.1	7.3	6.5	3.3	0.34	0.03	2.3	0.45	-	-	-	-	-	-
×	47	23.0	8.1	5.6	0.1	0.40	0.05	1.2	0.54	-	-	-	-	-	-
×	48	34.8	9.8	1.6	0.1	0.35	1.40	2.0	0.60	-	-	-	-	-	-
×	49	29.4	9.5	3.7	0.2	0.45	0.01	2.5	0.65	-	-	-	-	-	-
×	50	27.2	7.4	4.2	0.2	0.35	0.02	1.8	0.45	-	-	-	-	-	-
	UR 52N+	25.2	6.3	3.8	-	0.25	1.70	1.0	0.38	-	-	-	-	-	-

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Classification ¹⁾	C	Cr	Ni	Mo	W	N	Cu	Mn	Si	MM ²⁾ or Y	Ba	Ta	Zr	B	Others
SAF 2507	0.014	24.8	6.9	3.9	-	0.26	-	0.4	0.30	-	-	-	-	-	-
ZERON 100	0.012	25.2	6.9	3.8	0.7	0.26	0.70	0.9	0.31	-	-	-	-	-	-
SAF 2205	0.016	22.3	5.2	3.2	-	0.18	-	0.6	0.24	-	-	-	-	-	-
AL-6XN	0.018	21.2	24.5	6.3	-	0.21	0.50	0.8	0.33	-	-	-	-	-	-
SR-50A	0.015	23.2	21.3	6.3	-	0.25	-	1.1	0.28	-	-	-	-	-	-
254SMO	0.016	20.1	18.2	6.3	-	0.21	0.70	1.2	0.31	-	-	-	-	-	-
AISI 316L	0.018	17.2	12.3	2.5	-	-	-	1.2	0.34	-	-	-	-	-	-

(Notes) 1) Invention Steel ○ ; Comparative Steel ×

2) MM(Mischmetal) represent total weight of Ce, La, Nd, Pr, etc. added into Invention Steel.

Table 2. Properties of Invention Steel, Comparative Steel and Commercial Steel (Cast Product)

Classification ¹⁾	PREW	Austenite (vol.%)	Ferrite (vol.%)	Corrosion Resistance Balance of Phases [PREW(γ)-PREW(α)]	Pitting Potential (mV _{SCE})	CPT(°C)	CCCT(°C)	Differences of Hardnesses ($\Delta H=H_A-H_{S,A}$)
○	52.5	67.2	32.8	9.7	2)	80	40	0.32
○	50.7	59.5	40.5	5.0	2)	90	50	2.1
○	47.4	48.3	51.7	5.9	60	70	40	0.24
○	52.0	66.1	33.9	7.6	2)	85	45	0.10
○	51.4	55.3	44.7	6.0	2)	95	60	2.3
○	58.2	59.9	40.1	1.8	2)	80	40	0.12
○	50.7	54.9	45.1	7.1	2)	90	50	0.10
○	50.8	59.8	40.2	5.4	2)	95	55	2.5
○	51.8	47.8	52.2	9.6	2)	85	45	0.28
○	50.6	61.3	38.7	6.8	2)	95	60	0.10
○	51.5	59.2	40.8	6.0	2)	90	50	2.2
○	55.4	76.0	24.0	7.1	2)	85	45	0.21
○	52.8	66.2	33.8	7.9	2)	90	50	1.00
○	51.0	62.9	37.1	4.5	2)	95	60	2.4
○	50.7	55.4	44.6	8.2	2)	90	50	0.44
○	49.9	60.8	39.2	7.7	2)	90	50	0.52
○	52.0	58.7	41.3	6.0	2)	90	50	2.8
○	51.9	66.1	33.9	7.7	2)	85	45	0.90
○	49.6	53.2	46.8	7.3	2)	90	50	0.60
○	65.7	65.9	34.1	10.0	2)	80	40	0.64
○	50.8	57.9	42.1	5.4	2)	90	50	2.9
○	56.1	31.8	68.2	4.7	2)	85	45	0.72

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Classification 1)	PREW	Austenite (vol.%)	Ferrite (vol.%)	Corrosion Resistance Balance of Phases [PREW(γ)-PREW(α)]	Pitting Potential (mV _{SCE})	CPT(°C)	CCCT(°C)	Differences of Hardnesses ($\Delta H=H_A-H_{S,A}$)
○	23	55.1	44.9	3.5	2)	95	60	3.7
○	24	57.8	42.2	5.8	2)	90	50	3.1
○	25	57.6	42.4	7.7	2)	85	55	0.86
○	26	60.9	39.1	8.2	2)	95	60	1.40
○	27	46.1	53.9	6.5	-10	70	40	1.10
○	28	52.2	47.8	1.5	2)	90	50	1.81
○	29	48.3	51.7	3.6	2)	95	55	1.43
○	30	53.2	46.8	2.3	2)	90	50	1.21
○	31	53.3	46.1	2.8	2)	90	50	1.32
○	32	52.7	45.8	2.2	2)	90	55	1.61
○	33	48.8	64.7	-0.7	2)	90	50	1.14
○	34	52.7	58.4	0.6	2)	85	45	1.63
○	35	53.8	66.8	3.7	2)	85	45	1.42
○	36	52.1	55.0	7.1	2)	95	55	0.82
○	37	51.1	63.9	10.0	2)	85	45	1.32
○	38	52.8	56.7	8.0	2)	95	55	1.90
○	39	53.4	55.0	10.0	2)	90	50	0.87
○	40	66.7	64.0	9.8	2)	95	55	0.63
○	41	49.3	50.0	2.5	2)	90	50	1.21
○	42	54.3	63.2	10.0	2)	95	55	1.59
○	43	46.0	39.2	9.9	2)	75	40	1.06
×	44	58.0	72.6	11.5	2)	75	35	13.40

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Classification 1)	PREW	Austenite (vol.%)	Ferrite (vol.%)	Corrosion Resistance Balance of Phases [PREW(γ)-PREW(α)]	Pitting Potential (mV _{SCE})	CPT(°C)	CCCT(°C)	Differences of Hardnesses ($\Delta H=H_A-H_{S,A}$)
×	54.4	68.7	31.3	9.6	2)	80	40	10.40
×	59.2	55.4	44.6	3.8	2)	90	50	16.20
×	53.5	73.1	26.9	3.8	2)	95	55	14.10
×	50.1	64.7	35.3	9.0	2)	80	40	12.20
×	55.1	76.8	23.2	7.4	2)	80	40	10.30
×	51.6	57.2	42.8	7.6	2)	90	50	12.00
UR 52N+	45.2	41.5	58.5	7.5	-32	70	35	6.20
SAF 2507	45.5	43.2	56.8	7.5	-14	65	35	5.60
ZERON 100	46.7	44.4	55.6	6.7	57	70	40	-
SAF 2205	38.3	19.7	80.3	14.3	-	35	-	-
AL-6XN	48.3	100	0	-	518	85	35	-
SR-50A	51.5	100	0	-	2)	90	40	-
254SMO	47.2	100	0	-	204	75	30	-
AISI 316L	25.5	100	0	-	-	10	-10	-

(Notes) 1) Invention Steel ○; Comparative Steel ×

2) Above equilibrium oxygen evolution potential: No pitting generated.

Table 3. Mechanical Properties of Invention Steel and Comparative Steel (Cast Product)

Classification ¹⁾	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation(%)	Classification ¹⁾	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation(%)
○	712	816	40	○	724	842	34
○	650	809	33	○	682	814	34
○	696	812	40.5	○	580	798	38.6
○	720	840	44	○	690	806	38
○	645	811	32	○	688	812	39
○	714	836	36	○	702	830	40.6
○	734	880	38	○	604	826	40.8
○	655	815	35	○	704	822	40
○	712	820	40.4	○	720	806	34.1
○	680	820	46	○	696	798	34
○	638	825	31	○	680	822	44
○	720	860	40.6	○	660	814	32.2
○	702	814	36	○	690	880	30.2
○	655	807	35	○	685	890	34
○	708	810	38	○	618	782	32
○	724	846	41.2	○	709	831	37
○	661	825	32	○	601	817	39.2
○	712	842	41	○	687	820	35
○	704	832	40	×	624	804	24
○	620	785	32	×	620	786	27.2
○	659	818	31	×	596	780	24
○	612	808	38	×	591	598	18
○	660	842	36	×	612	814	22
○	647	819	33	×	598	800	24.5

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Classification ¹⁾	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation(%)	Classification ¹⁾	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation(%)		
○	25	684	882	32.4	×	50	614	790	26.4
(Notes) 1) Invention Steel ○; Comparative Steel ×									

Table 4. Corrosion Resistance Balances of Austenite(γ)/Ferrite(α) Phases of Invention Steel, Comparative Steel and Commercial Steel

Classification ¹⁾	No.	PREW (γ)						PREW (α)						Corrosion Resistance Balances of Phases [PREW(γ)-PREW(α)]		
		Cr	Mo	W	N	PREW	Cr	Mo	W	N	PREW	30N	16N			
○	1	28.35	1.44	2.46	0.62	55.6	30.33	2.23	4.11	0.05	PREW	30N	16N			
○	2	26.25	2.12	2.58	0.5	52.5	28.08	3.28	4.32	0.05	PREW	30N	16N			
○	3	24.42	3.04	0.52	0.51	50.5	26.13	4.71	0.87	0.05	PREW	30N	16N			
○	4	26.37	2.02	2.53	0.58	54.6	28.22	3.14	4.22	0.05	PREW	30N	16N			
○	5	26.75	2.08	2.56	0.53	53.8	28.63	3.22	4.27	0.05	PREW	30N	16N			
○	6	20.43	5.24	2.52	0.57	58.9	21.86	8.13	4.21	0.05	PREW	30N	16N			
○	7	26.27	2.16	2.23	0.56	53.9	28.11	3.35	3.72	0.05	PREW	30N	16N			
○	8	26.15	2.09	2.61	0.51	52.8	27.99	3.23	4.36	0.05	PREW	30N	16N			
○	9	25.66	2.02	2.89	0.66	56.8	27.46	3.13	4.82	0.05	PREW	30N	16N			
○	10	25.61	2.14	2.38	0.56	53.3	27.40	3.32	3.98	0.05	PREW	30N	16N			
○	11	26.44	2.10	2.60	0.53	53.6	28.29	3.25	4.34	0.05	PREW	30N	16N			
○	12	29.5	2.47	1.55	0.56	57.1	31.57	3.83	2.59	0.05	PREW	30N	16N			
○	13	26.67	2.11	2.45	0.59	55.5	28.54	3.27	4.09	0.05	PREW	30N	16N			
○	14	26.11	2.16	2.72	0.49	52.5	27.94	3.34	4.55	0.05	PREW	30N	16N			
○	15	26.18	1.93	2.46	0.59	54.4	28.01	2.99	4.11	0.05	PREW	30N	16N			
○	16	26.47	1.81	2.22	0.56	52.9	28.33	2.81	3.7	0.05	PREW	30N	16N			
○	17	26.82	2.12	2.59	0.54	54.2	28.69	3.28	4.32	0.05	PREW	30N	16N			
○	18	26.47	1.94	2.53	0.58	54.4	28.32	3.00	4.22	0.05	PREW	30N	16N			
○	19	25.95	1.99	2.28	0.56	53.0	27.77	3.08	3.81	0.05	PREW	30N	16N			
○	20	34.19	1.52	4.80	0.73	69.1	36.58	2.35	8.02	0.05	PREW	30N	16N			
○	21	26.32	2.09	2.56	0.51	52.8	28.16	3.24	4.28	0.05	PREW	30N	16N			
○	22	25.01	3.93	2.26	0.59	59.3	26.76	6.09	3.78	0.05	PREW	30N	16N			
○	23	22.87	4.6	0.02	0.5	53.0	24.47	7.12	0.03	0.05	PREW	30N	16N			

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Classification ¹⁾	No.	PREW (γ)					PREW(α)					Corrosion Resistance Balances of Phases [PREW(γ)-PREW(α)]		
		Cr	Mo	W	N	PREW	Cr	Mo	W	N	PREW	30N	16N	
○	24	26.90	2.12	2.58	0.53	54.0	28.78	3.29	4.31	0.05	48.3	5.8	-0.1	
○	25	26.42	2.11	2.49	0.59	55.1	28.27	3.27	4.16	0.05	47.4	7.7	0.2	
○	26	26.57	3.70	0	0.61	57.0	28.43	5.74	0	0.05	48.9	8.2	0.3	
○	27	24.19	2.93	0.15	0.51	49.3	25.88	4.54	0.25	0.05	42.8	6.5	0.1	
○	28	23.32	4.51	0.15	0.43	51.5	24.95	7.0	0.25	0.05	50.0	1.5	-3.9	
○	29	23.16	4.28	0	0.48	51.8	24.78	6.64	0	0.05	48.2	3.6	-2.4	
○	30	23.43	4.22	0.23	0.44	51.1	25.07	6.53	0.38	0.05	48.8	2.3	-3.2	
○	31	23.13	4.4	0	0.46	51.5	24.75	6.81	0	0.05	48.7	2.8	-3.0	
○	32	23.12	4.31	0.15	0.44	50.9	24.74	6.69	0.25	0.05	48.7	2.2	-3.3	
○	33	22.93	4.52	0.16	0.36	48.9	24.54	7.01	0.27	0.05	49.6	-0.7	-5.0	
○	34	23.03	4.48	0	0.39	49.6	24.64	6.94	0	0.05	49.0	0.6	-4.3	
○	35	26.19	4.23	0.25	0.5	55.5	28.02	6.55	0.41	0.05	51.8	3.7	-2.6	
○	36	25.89	3.69	0.15	0.58	55.6	27.7	5.72	0.26	0.05	48.5	7.1	-0.2	
○	37	33.65	1.25	0.32	0.55	54.8	36.0	1.94	0.54	0.05	44.8	10.0	3.0	
○	38	26.30	3.63	0	0.6	56.2	28.14	5.63	0	0.05	48.2	8.0	0.3	
○	39	24.92	2.24	3.0	0.69	57.9	26.66	3.48	5.0	0.05	47.9	10.0	1.1	
○	40	33.16	1.75	5.24	0.75	70.2	35.49	2.72	8.75	0.05	60.4	9.8	0.0	
○	41	22.80	4.23	0.16	0.45	50.6	24.4	6.56	0.28	0.05	48.0	2.5	-3.1	
○	42	36.56	1.26	0.33	0.56	58.0	39.12	1.96	0.55	0.05	48.0	10.0	2.9	
○	43	24.27	2.77	0.15	0.61	52.0	25.97	4.30	0.25	0.05	42.1	9.9	2.1	
×	44	34.24	1.3	1.77	0.66	61.2	36.64	2.02	2.96	0.05	49.7	11.5	3.0	
×	45	28.67	1.62	2.65	0.63	57.3	30.68	2.51	4.42	0.05	47.8	9.6	1.4	
×	46	22.58	4.88	0.08	0.53	54.7	24.16	7.56	0.14	0.05	50.8	3.8	-5.4	

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Classification ¹⁾	No.	PREW (γ)					PREW (α)					Corrosion Resistance Balances of Phases [PREW(γ)-PREW(α)]		
		Cr	Mo	W	N	PREW	Cr	Mo	W	N	PREW	30N	16N	
×	47	22.58	4.88	0.08	0.53	54.7	24.16	7.56	0.14	0.05	50.8	3.8	-2.9	
×	48	33.96	1.34	0.08	0.51	53.9	36.34	2.08	0.14	0.05	44.9	9.0	2.5	
×	49	28.93	3.28	0.17	0.57	57.2	30.96	5.09	0.29	0.05	49.7	7.4	0.2	
×	50	26.41	3.40	0.16	0.57	55.1	28.26	5.27	0.26	0.05	47.6	7.6	0.2	
UR 52N+		24.21	2.88	0	0.53	49.6	25.9	4.46	0	0.05	42.1	7.5	0.8	
SAF 2507		23.85	2.97	0	0.54	49.7	25.52	4.61	0	0.05	42.2	7.5	0.7	
ZERON 100		24.26	2.91	0.51	0.52	50.4	25.95	4.51	0.85	0.05	43.7	6.7	0.0	
SAF 2205		21.11	2.22	0	0.71	49.8	22.59	3.44	0	0.05	35.4	14.3	5.1	

(Notes) 1) Invention Steel ○; Comparative Steel ×

Table 5. Properties of Hot-Rolled Broad Plank of Invention Steel and Comparative Steel

	Classification ¹⁾		CPT(°C)	Mechanical Properties			Evaluation to Hot-Rolling ²⁾
				Yield Strength (MPa)	Tensile Strength (MPa)	Elongation (%)	
5	○	2	85	663	879	44	○
	○	5	90	681	877	37	○
10	○	8	90	721	894	38	○
	○	11	85	711	892	36	○
	○	14	90	673	833	35	○
15	○	17	85	682	851	34	○
	○	21	85	673	843	38	○
	○	23	90	693	887	36	○
20	○	24	85	716	902	34	○
	○	36	90	691	837	35	○
	×	39	95	620	632	36	×
	×	41	90	643	812	38	×
25	(Notes) 1) Invention Steel ○; Comparative Steel × 2) Evaluation: Good(No Crack) ○; Normal(Few Crack) Δ; Bad(Many Crack) ×						

INDUSTRIAL APPLICABILITY

[0085] As described above, the present invention removes brittleness and improves corrosion resistance by reducing the precipitation speed and amount of intermetallic phases having high brittleness, by delaying diffusion and precipitation of intermetallic phases by using an appropriate amount of Ba, Y, Ce, La, Nd, Pr, Ta, Zr and Ti atoms having a large atomic diameter, and additionally blocking diffusion of Cr, Mo, Si and W by using minute RE metallic compound mixtures or Ba oxides.

[0086] In addition, the present invention prevents individual formation of Al₂O₃ and MnS non-metallic inclusions which have detrimental effects on general properties of steel by performing proper preliminary deoxidation according to the common method using Ti, Mg, Ca, Al and Ca+Al, and adding MM and/or Y. For this, the present invention improves mechanical properties, physical properties and corrosion resistance by forming the rare-earth metallic compound mixture (RExO_y or (RE,Al)xO_y+RExO_yS+RExS_y) having a diameter below 5μm, supplying heterogeneous nucleation sites to make the solidified structure fine and minute during dendrite formation of the solidification, and controlling segregation of the solute elements such as Cr, Mo, W, Ni, Mn and Si, by using the solubility product equation '[MM and/or Y+Al]·[O+S]=0.001 × 10⁻⁵ to 30000 × 10⁻⁵[%]²'.

[0087] Accordingly, the present invention provides the method for remarkably suppressing formation of intermetallic phases such as sigma in duplex stainless steel by adding new alloying elements, and improving the production yield during mass production.

[0088] Moreover, the present invention increases the production yield in casting and hot working, by improving embrittlement resistance and preventing cracks by lowering a precipitation speed of intermetallic phases such as sigma.

[0089] Furthermore, the present invention considerably improves corrosion resistance and mechanical properties and upgrades durability of equipments, by suppressing precipitation of sigma and khi phases deteriorating corrosion resistance and mechanical properties in a casting state, and also controlling precipitation of such phases in a heat-affected zone when equipment components are necessarily welded in various application fields.

Claims

1. High-grade duplex stainless steel with high corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases, consisting of 21.0 to 38.0% of Cr, 3.0 to 12.0% of Ni, 1.5

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to 6.5% of Mo, 0 to 6.5% of W, 3.0% or less of Si, 8.0% or less of Mn, 0.2 to 0.7% of N, 0.1% or less of C, 0.0001 to 0.6% of Ba, and a balance of Fe and incidental impurities on a weight basis, a pitting resistance equivalent (PREW) defined by following formula (1) satisfying $40 \leq \text{PREW} \leq 67$:

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$$\text{PREW} = \text{wt}\% \text{Cr} + 3.3(\text{wt}\% \text{Mo} + 0.5\text{wt}\% \text{W}) + 30\text{wt}\% \text{N} \quad (1)$$

2. The high-grade duplex stainless steel of claim 1, further containing 0.0001 to 1.0% of MM and/ or Y in total.

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3. The high-grade duplex stainless steel of claim 2, wherein Ba is added within the range of 0.001 to 0.2%.

4. High-grade duplex stainless steel with high corrosion resistance, embrittlement resistance, castability and hot workability which suppresses formation of intermetallic phases, consisting of 21.0 to 38.0% of Cr, 3.0 to 12.0% of Ni, 1.5 to 6.5% of Mo, 0 to 6.5% of W, 3.0% or less of Si, 8.0% or less of Mn, 0.2 to 0.7% of N, 0.1% or less of C, 0.0001 to 1.0% of MM and/or Y in total, and a balance of Fe and incidental impurities on a weight basis, wherein MM is rare-earth metallic mixtures consisting of atoms with atomic numbers from 57 to 71, containing major elements of 51% of Ce, 26% of La, 15,5% of Nd and 5,5% of Pr, minute amounts of Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Sc, and 1% or less Fe, and a pitting resistance equivalent (PREW) defined by following formula (1) satisfying $40 \leq \text{PREW} \leq 67$:

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$$\text{PREW} = \text{wt}\% \text{Cr} + 3.3(\text{wt}\% \text{Mo} + 0.5\text{wt}\% \text{W}) + 30\text{wt}\% \text{N} \quad (1)$$

5. The high-grade duplex stainless steel of one of claims 2 to 4, wherein a value of [MM and/ or Y+Al] [O+S] which is an equation of solubility products of MM and/ or Y, and Al, O and S of steel ranges from 0.001×10^{-5} to $30000 \times 10^{-5} [\%]^2$.

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6. The high-grade duplex stainless steel of claim 5, wherein, in the case of a cast product, the value of the equation of the solubility products ranges from 1×10^{-5} to $5000 \times 10^{-5} [\%]^2$.

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7. The high-grade duplex stainless steel of claim 5, wherein, in the case of a hot working product, the value of the equation of the solubility products ranges from 0.1×10^{-5} to $2000 \times 10^{-5} [\%]^2$.

8. The high-grade duplex stainless steel of one of claims 2 to 4, wherein a total amount of MM and/or Y ranges from 0.01 to 0.6%.

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9. The high-grade duplex stainless steel of claim 8, wherein the total amount of MM and/or Y ranges from 0.2 to 0.5%.

10. The high-grade duplex stainless steel of one of claims 1 to 4, further containing at least one element selected from the group consisting of 0.5% or less of Ca, 0.5% or less of Mg, 1.0% or less of Al, 0.5% or less of Ta, 0.5% or less of Nb, 1.5% or less of Ti, 1.0% or less of Zr, 1.0% or less of Sn and 1.0% or less of In.

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11. The high-grade duplex stainless steel of one of claims 1 to 4 and 10, further containing 0.1 % or less of B.

12. The high-grade duplex stainless steel of one of claims 1 to 4, 10 and 11, further containing one or more among 3.0% or less of Cu and 3.0 % or less of Co.

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13. The high-grade duplex stainless steel of one of claims 1 to 4, wherein a value of [PREW(γ)-PREW(α)] which is a corrosion resistance balance of austenitic phase and ferritic phase ranges from -5 to 10.

14. The high-grade duplex stainless steel of one of claims 1 to 4, wherein a volume fraction of ferritic phase ranges from 20 to 70%, and a volume fraction of austenitic phase ranges from 30 to 80% on a volume basis.

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Patentansprüche

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1. Hochwertiger rostfreier Duplexstahl mit hoher Korrosionsbeständigkeit, Versprödungsbeständigkeit, Gießbarkeit und Warmumformbarkeit, der die Bildung intermetallischer Phasen unterdrückt, bestehend aus 21,0 bis 38,0% Cr,

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3,0 bis 12,0% Ni, 1,5 bis 6,5% Mo, 0 bis 6,5% W, 3,0% oder weniger Si, 8,0% oder weniger Mn, 0,2 bis 0,7% N, 0,1% oder weniger C, 0,0001 bis 0,6% Ba und dem Rest Fe und zufälligen Verunreinigungen auf Gewichtsbasis, mit einem Lochfraßwiderstandsäquivalent (PREW, pitting resistance equivalent), definiert durch die nachfolgende Formel (1), welches die Bedingung $40 \leq \text{PREW} \leq 67$ erfüllt:

$$\text{PREW} = \text{Gew.}\% \text{ Cr} + 3,3(\text{Gew.}\% \text{ Mo} + 0,5 \text{ Gew.}\% \text{ W}) + 30 \text{ Gew.}\% \text{ N} \quad (1).$$

2. Hochwertiger rostfreier Duplexstahl nach Anspruch 1, weiterhin insgesamt enthaltend 0,0001 bis 1,0% MM und/oder Y.
3. Hochwertiger rostfreier Duplexstahl nach Anspruch 2, worin Ba im Bereich von 0,001 bis 0,2% zugegeben wird.
4. Hochwertiger rostfreier Duplexstahl mit hoher Korrosionsbeständigkeit, Versprödungsbeständigkeit, Gießbarkeit und Warmumformbarkeit, der die Bildung intermetallischer Phasen unterdrückt, bestehend aus 21,0 bis 38,0% Cr, 3,0 bis 12,0% Ni, 1,5 bis 6,5% Mo, 0 bis 6,5% W, 3,0% oder weniger Si, 8,0% oder weniger Mn, 0,2 bis 0,7% N, 0,1% oder weniger C, insgesamt 0,0001 bis 1,0% MM und/oder Y und dem Rest Fe und zufälligen Verunreinigungen auf Gewichtsbasis, wobei MM eine Seltenerdmetallmischung darstellt, bestehend aus Atomen mit Atomordnungszahlen von 57 bis 71, enthaltend Hauptelemente von 51% Ce, 26% La, 15,5% Nd und 5,5% Pr, geringere Mengen an Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu und Sc, und 1% oder weniger Fe, und mit einem Lochfraßwiderstandsäquivalent (PREW, pitting resistance equivalent), definiert durch die nachfolgende Formel (1), welches die Bedingung $40 \leq \text{PREW} \leq 67$ erfüllt:

$$\text{PREW} = \text{Gew.}\% \text{ Cr} + 3,3(\text{Gew.}\% \text{ Mo} + 0,5 \text{ Gew.}\% \text{ W}) + 30 \text{ Gew.}\% \text{ N} \quad (1).$$

5. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 2 bis 4, worin der Wert von [MM und/oder Y+Al] [O+S], welches eine Gleichung der Löslichkeitsprodukte von MM und/oder Y und Al, O und S in Stahl darstellt, im Bereich von $0,001 \times 10^{-5}$ bis $30000 \times 10^{-5} [\%]^2$ liegt.
6. Hochwertiger rostfreier Duplexstahl nach Anspruch 5, worin, im Fall eines Gußprodukts, der Wert der Gleichung der Löslichkeitsprodukte im Bereich von 1×10^{-5} bis $5000 \times 10^{-5} [\%]^2$ liegt.
7. Hochwertiger rostfreier Duplexstahl nach Anspruch 5, worin, im Fall eines Warmumformungsprodukts, der Wert der Gleichung der Löslichkeitsprodukte im Bereich von $0,1 \times 10^{-5}$ bis $2000 \times 10^{-5} [\%]^2$ liegt.
8. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 2 bis 4, worin die Gesamtmenge von MM und/oder Y im Bereich von 0,01 bis 0,6% liegt.
9. Hochwertiger rostfreier Duplexstahl nach Anspruch 8, worin die Gesamtmenge von MM und/oder Y im Bereich von 0,2 bis 0,5% liegt.
10. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 1 bis 4, weiterhin enthaltend mindestens ein Element, ausgewählt aus der Gruppe, bestehend aus 0,5% oder weniger Ca, 0,5% oder weniger Mg, 1,0% oder weniger Al, 0,5% oder weniger Ta, 0,5% oder weniger Nb, 1,5% oder weniger Ti, 1,0% oder weniger Zr, 1,0% oder weniger Sn und 1,0% oder weniger In.
11. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 1 bis 4 und 10, weiterhin enthaltend 0,1% oder weniger B.
12. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 1 bis 4, 10 und 11, weiterhin enthaltend ein oder mehr von: 3,0% oder weniger Cu und 3,0% oder weniger Co.
13. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 1 bis 4, worin der Wert von $[\text{PREW}(\gamma) - \text{PREW}(\alpha)]$, was den Korrosionswiderstandsausgleich von austenitischen und ferritischen Phasen darstellt, im Bereich von -5 bis 10 liegt.

14. Hochwertiger rostfreier Duplexstahl nach einem der Ansprüche 1 bis 4, worin die Volumenfraktion der ferritischen Phase im Bereich von 20 bis 70% und die Volumenfraktion der austenitischen Phase von 30 bis 80% auf Volumenbasis liegt.

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Revendications

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1. Acier inoxydable duplex de qualité supérieure ayant une résistance à la corrosion, une résistance à la fragilisation, une coulabilité et une aptitude au façonnage à chaud élevées qui suppriment la formation de phases intermétalliques, constitué de 21,0 à 38,0 % de Cr, 3,0 à 12,0 % de Ni, 1,5 à 6,5 % de Mo, 0 à 6,5 % de W, 3,0 % ou moins de Si, 8,0 % ou moins de Mn, 0,2 à 0,7 % de N, 0,1 % ou moins de C, 0,0001 à 0,6 % de Ba, le reste étant du Fe et des impuretés fortuites sur une base en poids, un équivalent de résistance à la corrosion par piqûres (PREW) défini par la formule suivante (1) satisfaisant $40 \leq \text{PREW} \leq 67$:

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$$\text{PREW} = \% \text{ en poids de Cr} + 3,3(\% \text{ en poids de Mo} + 0,5 \% \text{ en poids de W}) + 30 \% \text{ en poids de N} \text{ --- (1)}$$

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2. Acier inoxydable duplex de qualité supérieure selon la revendication 1, contenant en outre 0,0001 à 1,0 % de MM et/ou de Y au total.

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3. Acier inoxydable duplex de qualité supérieure selon la revendication 2, dans lequel du Ba est ajouté dans la plage de 0,001 à 0,2 %.

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4. Acier inoxydable duplex de qualité supérieure ayant une résistance à la corrosion, une résistance à la fragilisation, une coulabilité et une aptitude au façonnage à chaud qui suppriment la formation de phases intermétalliques, constitué de 21,0 à 38,0 % de Cr, 3,0 à 12,0 % de Ni, 1,5 à 6,5 % de Mo, 0 à 6,5 % de W, 3,0 % ou moins de Si, 8,0 % ou moins de Mn, 0,2 à 0,7 % de N, 0,1 % ou moins de C, 0,0001 à 1,0 % de MM et/ou de Y au total, et le reste étant du Fe et des impuretés fortuites sur une base en poids, dans lequel MM est constitué de mélanges métalliques de terres rares constitués d'atomes ayant des numéros atomiques allant de 57 à 71, contenant des éléments majeurs constitués de 51 % de Ce, 26 % de La, 15,5 % de Nd et 5,5 % de Pr, d'infimes quantités de Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, et Sc, et 1 % ou moins de Fe, et un équivalent de résistance à la corrosion par piqûres (PREW) défini par la formule suivante (1) satisfaisant $40 \leq \text{PREW} \leq 67$:

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$$\text{PREW} = \% \text{ en poids de Cr} + 3,3(\% \text{ en poids de Mo} + 0,5 \% \text{ en poids de W}) + 30 \% \text{ en poids de N} \text{ --- (1)}$$

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5. Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 2 à 4, dans lequel la valeur $[\text{MM et/ou Y} + \text{Al}][\text{O} + \text{S}]$, qui est une équation de produits de solubilité de MM et/ou Y, et Al, O et S de l'acier, est dans la plage de $0,001 \times 10^{-5}$ à $30\,000 \times 10^{-5} [\%]^2$.

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6. Acier inoxydable duplex de qualité supérieure selon la revendication 5, dans lequel, dans le cas d'un produit coulé, la valeur de l'équation des produits de solubilité est dans la plage de 1×10^{-5} à $5000 \times 10^{-5} [\%]^2$.

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7. Acier inoxydable duplex de qualité supérieure selon la revendication 5, dans lequel, dans le cas d'un produit de façonnage à chaud, la valeur de l'équation des produits de solubilité est dans la plage de $0,1 \times 10^{-5}$ à $2000 \times 10^{-5} [\%]^2$.

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8. Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 2 à 4, dans lequel la quantité totale de MM et/ou de Y est dans la plage de 0,01 à 0,6 %.

9. Acier inoxydable duplex de qualité supérieure selon la revendication 8, dans lequel la quantité totale de MM et/ou de Y est dans la plage de 0,2 à 0,5 %.

10. Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 1 à 4, contenant en outre

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au moins un élément choisi dans le groupe constitué de 0,5 % ou moins de Ca, 0,5 % ou moins de Mg, 1,0 % ou moins de Al, 0,5 % ou moins de Ta, 0,5 % ou moins de Nb, 1,5 % ou moins de Ti, 1,0 % ou moins de Zr, 1,0 % ou moins de Sn et 1,0 % ou moins de In.

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- 11.** Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 1 à 4 et 10, contenant en outre 0,1 % ou moins de B.
- 12.** Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 1 à 4, 10 et 11, contenant en outre un ou plusieurs parmi 3,0 % ou moins de Cu et 3,0 % ou moins de Co.
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- 13.** Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 1 à 4, dans lequel la valeur $[\text{PREW}(\gamma) - \text{PREW}(\alpha)]$, qui est le solde entre la résistance à la corrosion de la phase austénitique et de la phase ferritique, est dans la plage de -5 à 10.
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- 14.** Acier inoxydable duplex de qualité supérieure selon l'une quelconque des revendications 1 à 4, dans lequel une fraction volumique de phase ferritique est dans la plage de 20 à 70 %, et une fraction volumique de phase austénitique est dans la plage de 30 à 80 %, sur une base en volume.

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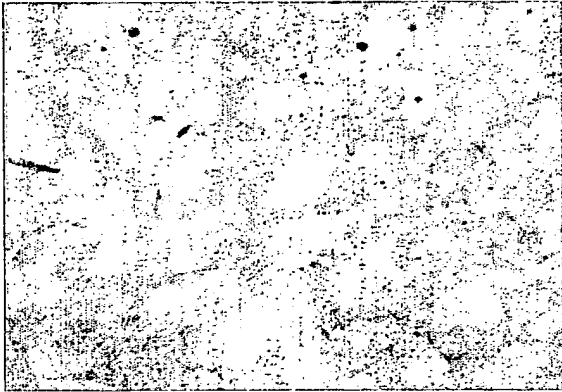


FIG. 1A

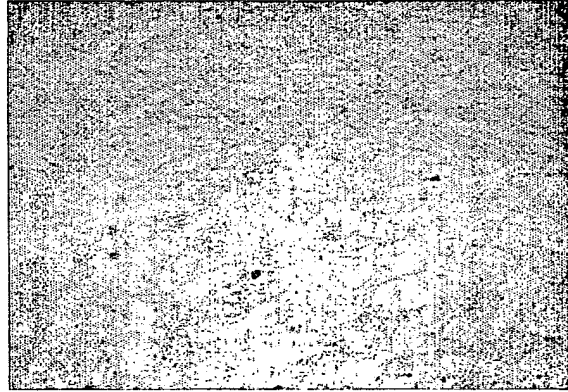


FIG. 1B

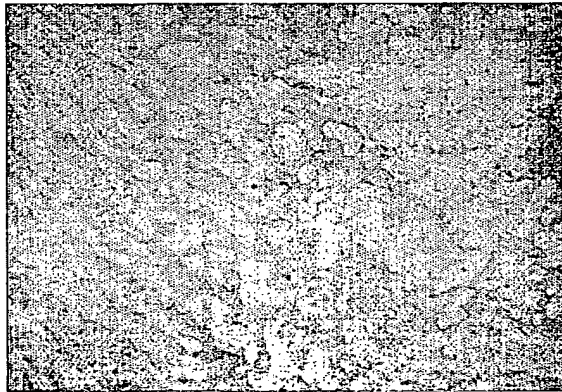


FIG. 1C

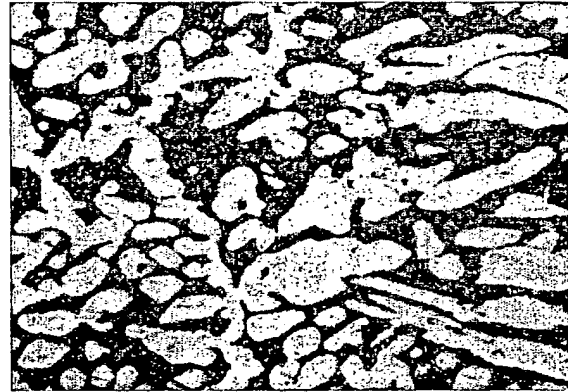


FIG. 1D



FIG. 1E



FIG. 1F

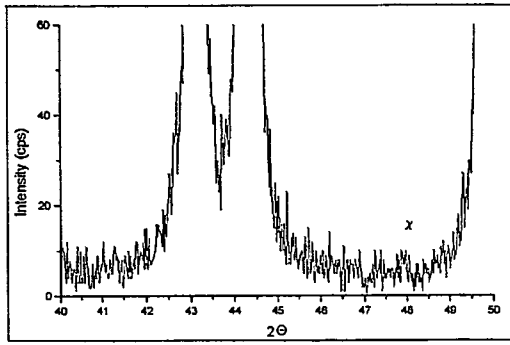


FIG. 2A

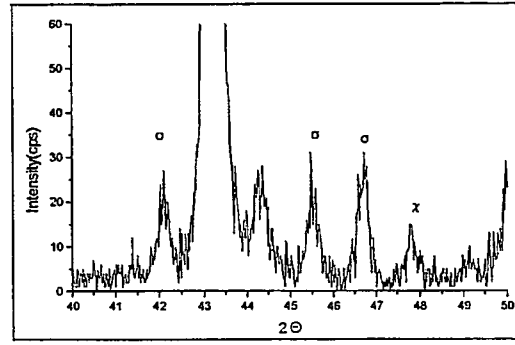


FIG. 2B

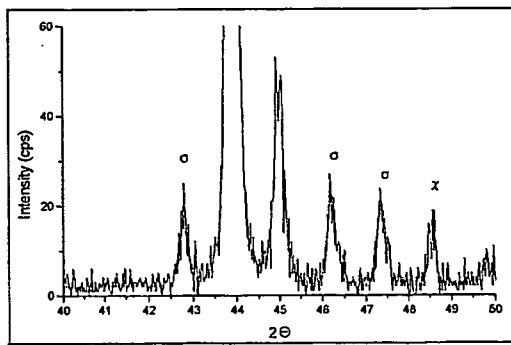


FIG. 2C

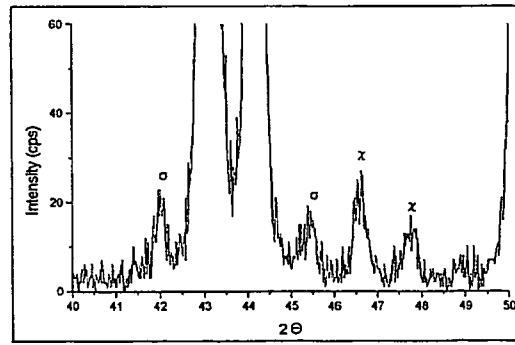


FIG. 2D



FIG. 3A

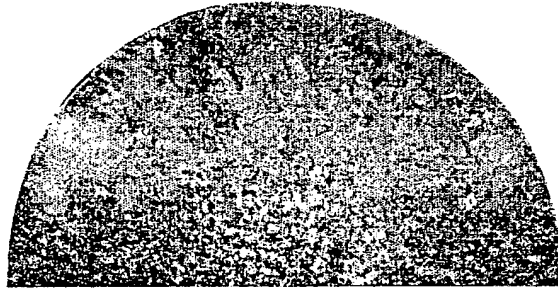


FIG. 3B

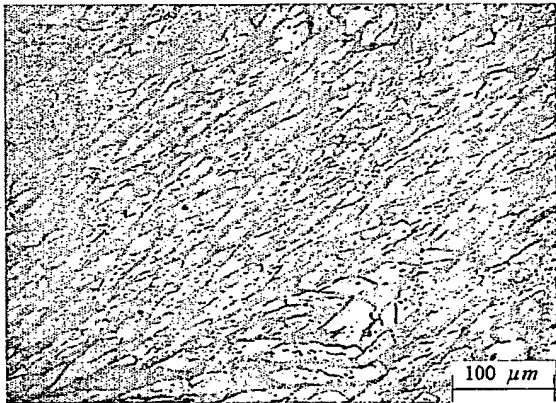


FIG. 3C

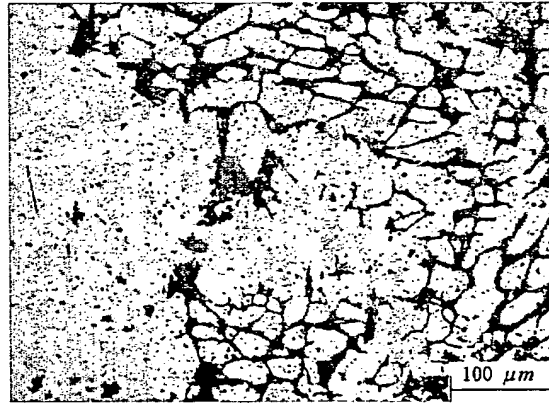


FIG. 3D

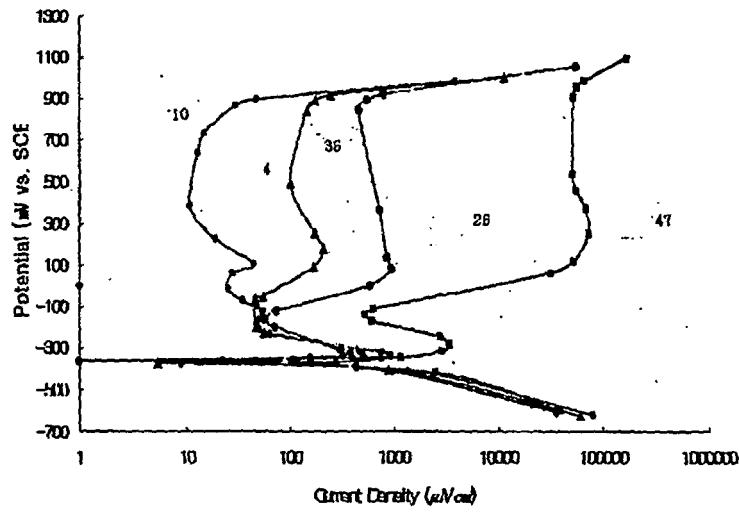


FIG. 4

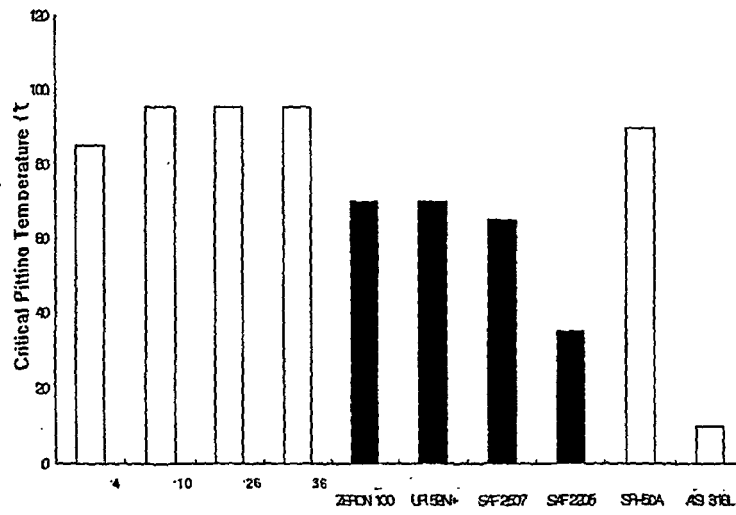


FIG. 5

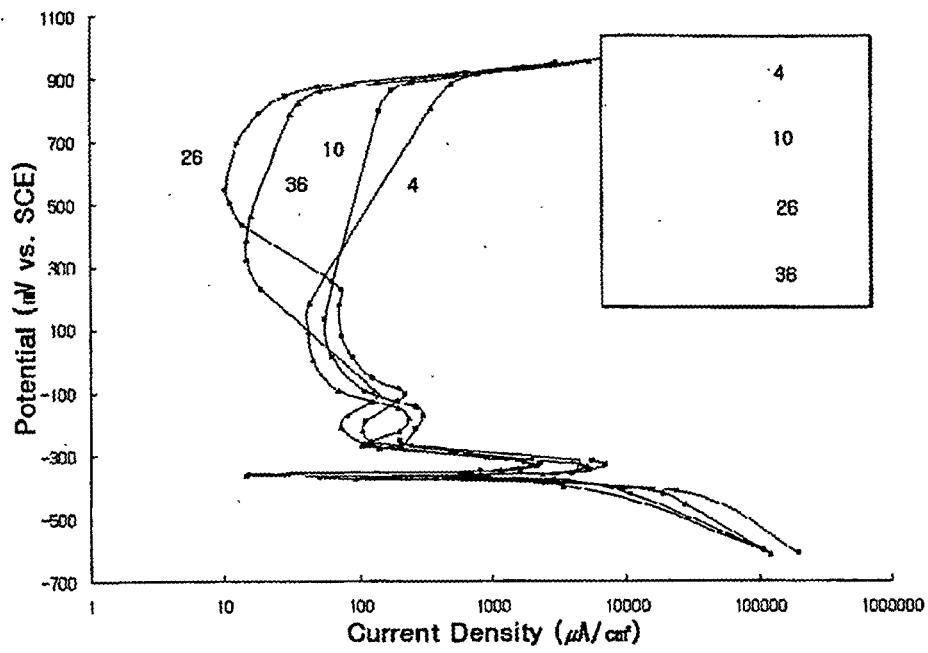


FIG. 6A

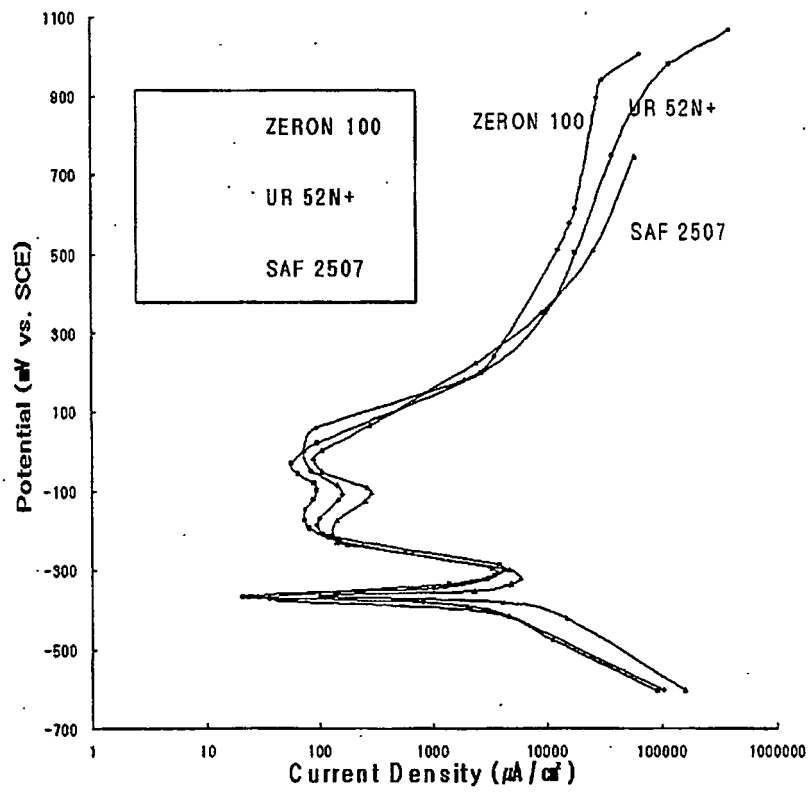


FIG. 6B

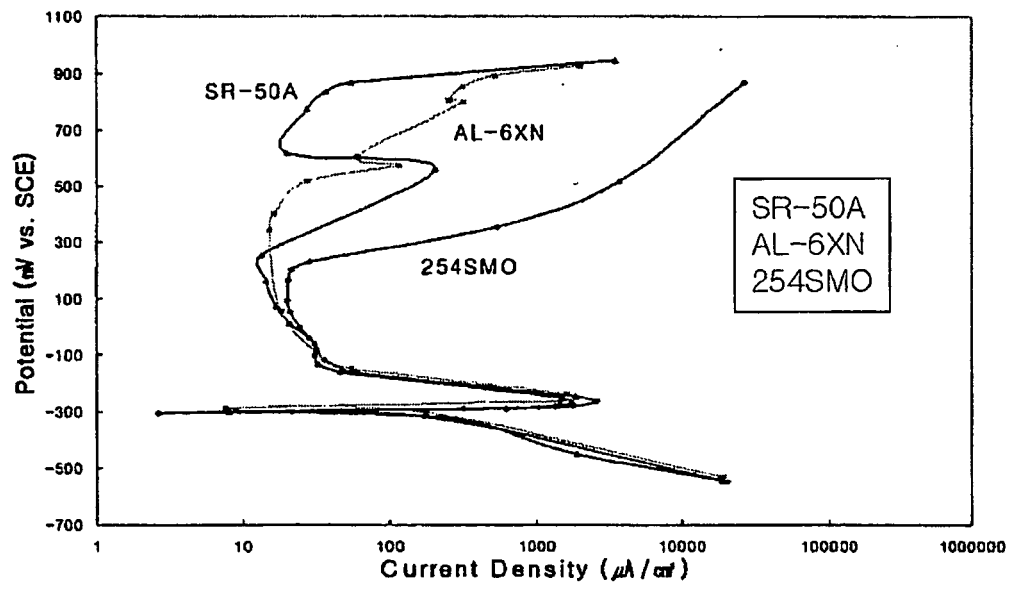


FIG. 6C

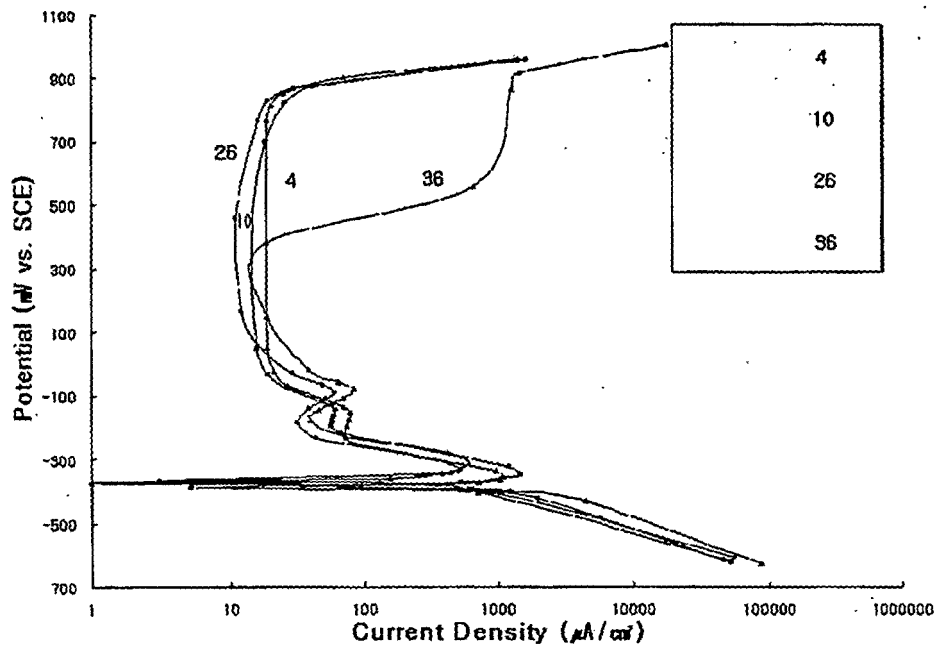


FIG. 7A

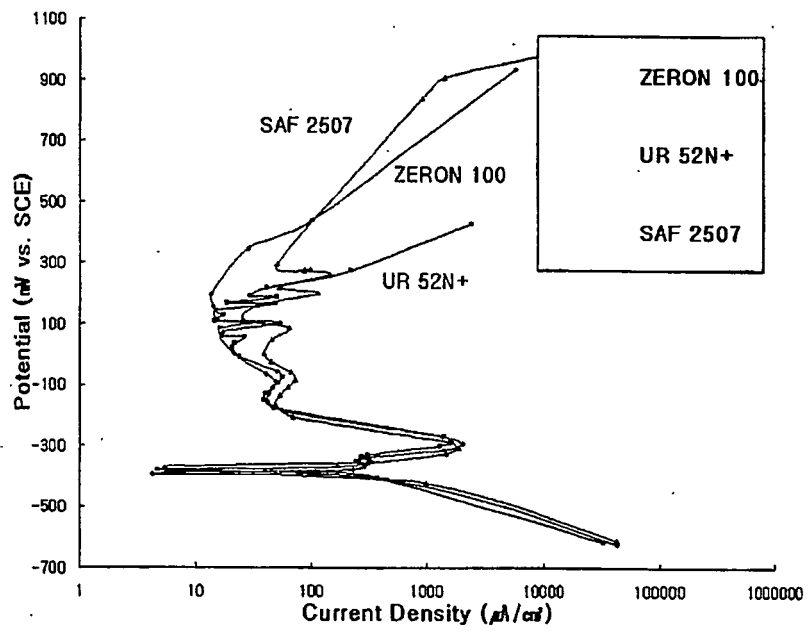


FIG. 7B

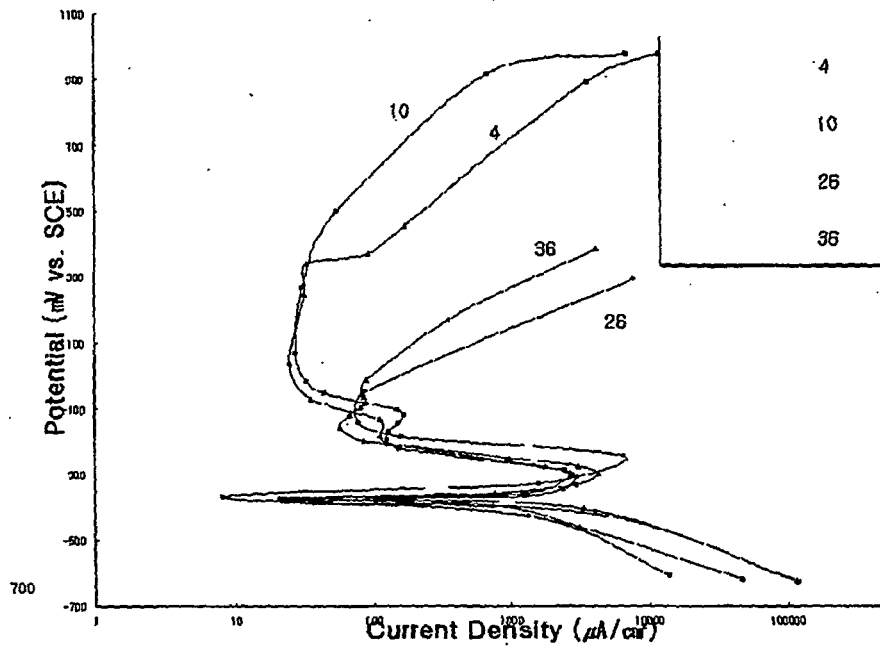


FIG. 8A

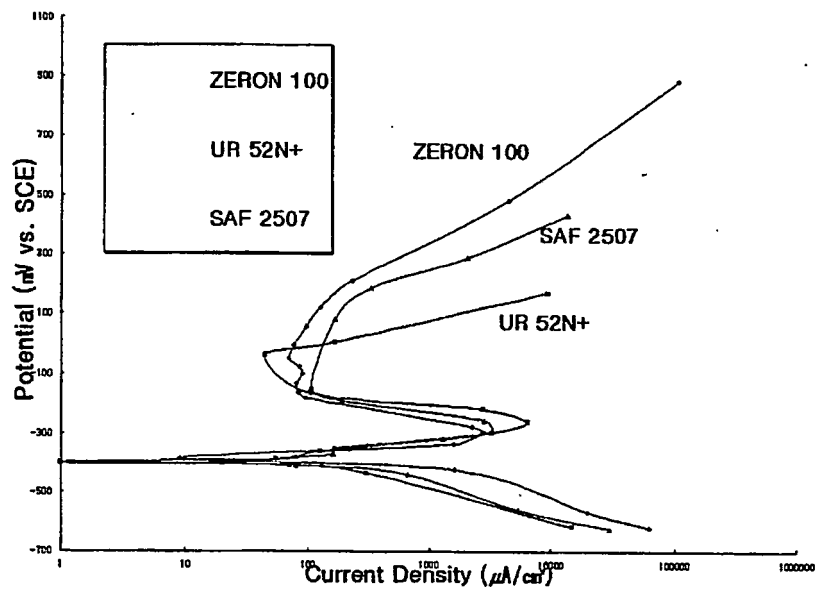


FIG. 8B