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(54) **DUPLEX STAINLESS STEEL, DUPLEX STAINLESS STEEL SLAB, AND DUPLEX STAINLESS STEEL MATERIAL**

(57) One aspect of this duplex stainless steel contains, in mass%, C: 0.03% or less, Si: 0.05% to 1.0%, Mn: 0.1% to 7.0%, P: 0.05% or less, S: 0.0001% to 0.0010%, Ni: 0.5% to 5.0%, Cr: 18.0% to 25.0%, N: 0.10% to 0.30%, Al: 0.05% or less, Ca: 0.0010% to 0.0040%, and Sn: 0.01% to 0.2%, with the remainder being Fe and inevitable impurities, wherein a ratio Ca/O of the amounts of Ca and O is in a range of 0.3 to 1.0, and a pitting index PI shown by formula (1) is in a range of less than 30,

$$PI=Cr+3.3Mo+16N \quad (1).$$

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**Description**

TECHNICAL FIELD

**[0001]** The present invention relates to an inexpensive Sn-containing duplex stainless steel. In addition, the present invention relates to an inexpensive duplex stainless steel which contains a combination of Cu and Sn and which is excellent in corrosion resistance. In detail, the present invention relates to a duplex stainless steel, a duplex stainless steel slab (a cast steel of a duplex stainless steel), and a duplex stainless steel material which are able to be used in a seawater desalination unit, tanks for a transport ship, various types of containers, or the like.

**[0002]** The present application claims priority on Japanese Patent Application No. 2011-231352 filed on October 21,2011 in Japan, and Japanese Patent Application No. 2011-266351 filed on December 6, 2011 in Japan, the contents of which are incorporated herein by reference.

BACKGROUND ART

**[0003]** A general-purpose duplex stainless steel contains a large amount of Cr, Mo, Ni, and N and has favorable corrosion resistance. However, as a result of containing Mo and Ni, which are expensive, the alloy cost is high and the manufacturability is not favorable. As a result, the price of steel material is not cheap and the duplex stainless steel is not widely used in place of 316 grade stainless steel or 317 grade stainless steel. Here, the general-purpose duplex stainless steel referred to in the present invention indicates duplex stainless steel having the pitting index PI (represented by the following formula which is the sum of the amounts of the alloy elements: PI=Cr+3.3Mo+16N) of approximately 30 or more to less than 40 (mass%). From the circumstances described above, in such steels, it is considered that there is a need for steels where the alloy cost is lower than that in the related art and the manufacturing costs are inexpensive and which have favorable hot manufacturability while exhibiting the same level of corrosion resistance as the general-purpose duplex stainless steel of the related art.

**[0004]** On the other hand, recently, an alloy-saving type duplex stainless steel in which amounts of Cr, Ni, Mo, and the like are reduced has been developed. Here, the alloy-saving type duplex stainless steel indicates a stainless steel which exhibits a pitting resistance equivalent to those of SUS 304 and 316L and where the pitting resistance index PI (=Cr+3.3Mo+16N), which is indexed by the amounts of the alloy elements, is approximately in a range of less than 30. In these steels where the amounts of alloy elements which are effective for pitting resistance and acid resistance are reduced, it is difficult to obtain the same level of corrosion resistance as that of the general-purpose duplex stainless steel. However, it is considered that it is possible to develop improved steels by using inexpensive alternative elements.

**[0005]** Various types of duplex stainless steels which contain Sn have been proposed in the related art. For example, duplex stainless steels are disclosed which contain 25% or more of Cr and contain 0.01% to 0.1% of Sn as a selected element (refer to Patent Documents 1 and 2 described below). In addition, alloy-saving type duplex stainless steels are disclosed which contain 1% or less or 0.1% of Sn (refer to Patent Documents 3 and 4 described below). In the Patent Documents, an object is to improve the corrosion resistance by means of the amount of Sn; however, the relationship between the hot manufacturability of the steel material and the amount of Sn was not investigated.

**[0006]** In addition, in the Patent Documents described above, the subject is a steel where the amount of N is in a range of 0.2% or less. N is an element which decreases the hot workability of the stainless steel. Ensuring a desired level of hot workability of a duplex stainless steel which contains 0.2% or more of N is more difficult than ensuring a desired level of hot workability of a duplex stainless steel which contains less than 0.2% of N. Technical literature which makes a disclosure regarding the hot workability of a duplex stainless steel which contains 0.20% or more ofN and further contains a combination of Sn and Cu is not to be found.

**[0007]** The present inventors focused on the possibility of improving the acid resistance and the pitting resistance using Sn in an alloy-saving type duplex stainless steel. Then, the present inventors investigated the relationship between the amount of Sn and the corrosion resistance and the hot manufacturability. As a result, it was found that it was possible to improve the corrosion resistance by 0.01% to 0.2% of Sn being contained. However, it was learned that the hot manufacturability decreased in duplex stainless steels which contained a large amount of Sn. For this reason, the frequency of decreases in the yield of the steel material will increase and a significant cost increase is predicted.

**[0008]** In addition, the present inventors focused on the possibility of improving the acid resistance and the pitting resistance using Sn and Cu in the general-purpose duplex stainless steel. Then, with regard to the duplex stainless steel where the amounts of Mo and Ni are reduced and which contains 0.20% or more of N, the present inventors investigated the relationship between the amounts of Sn and Cu, the corrosion resistance, and the hot manufacturability. As a result, it was found that it was possible to improve the corrosion resistance by 0.01% to 0.2% of Sn and 0.2% to 3.0% of Cu being contained. However, it was learned that the hot manufacturability decreased in duplex stainless steels which contained a large amount of Sn and Cu. For this reason, the frequency of decreases in the yield of the steel material will increase and a significant cost increase is predicted.

**[0009]** The present inventors investigated the knowledge of the related art relating to the manufacturing techniques for Sn-containing duplex stainless hot-rolled steel material of the related art starting with Patent Documents 1 to 4. As a result, it was found that there was little knowledge with regard to the relationship between the temperature range where hot embrittlement occurs due to Sn which is included in the duplex stainless steel and the amount of Sn and the relationship with the amounts of other elements.

PRIOR ART DOCUMENT

Patent Documents

**[0010]**

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. H3-158437
Patent Document 2: Japanese Unexamined Patent Application, First Publication No. H4-072013
Patent Document 3: Japanese Unexamined Patent Application, First Publication No. 2010-222593
Patent Document 4: PCT International Publication No. WO2009-11989
Patent Document 5: Japanese Unexamined Patent Application, First Publication No. 2002-69592
Patent Document 6: Japanese Unexamined Patent Application, First Publication No. H7-118805

Non-Patent Document

**[0011]** Non-Patent Document 1: "Effect of Cu and Ni on Hot Workability of Hot-rolled Mild Steel" ISIJ, Vol.37, p.217 to 223 (1997)

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

**[0012]** The present invention finds a measure for solving the problems described above by clarifying the relationship between the amount of Sn and hot manufacturability in an alloy-saving type duplex stainless steel. In addition, the present invention finds a measure for solving the problems described above by clarifying the relationship between the amounts of Sn and Cu and hot manufacturability in a general-purpose duplex stainless steel. Due to this, the object of the present invention is to provide an Sn-containing duplex stainless steel, a cast steel of a duplex stainless steel, and a duplex stainless steel material which are inexpensive and have favorable hot manufacturability. Such a duplex stainless steel is expected to have an excellent balance between corrosion resistance and cost. For this reason, it is considered that the possibility that the duplex stainless steel will be widely used in various fields is high.

**[0013]** In particular, an object of a second aspect (a second embodiment) of the invention is to develop an inexpensive general-purpose duplex stainless steel where the amounts of Ni and Mo, which are expensive elements, are reduced by increasing the amounts ofN and Mn and adding a combination of Cu and Sn.

Means for Solving the Problems

**[0014]** In order to solve the problems described above, for the alloy-saving type duplex stainless steel which is the subject of the present invention, the present inventors prepared melted materials where the amount of Sn and the amounts of Ca, B, rare earth elements (REM), or the like were changed and performed the following experiments. Here, the amounts of Ca, B, rare earth elements (REM), or the like are said to improve the hot manufacturability.

**[0015]** Tensile test pieces were collected from cast steels which were cast from the melted materials. High temperature tensile test was performed at a temperature of 1200 to 700°C with respect to the tensile test pieces, and the high temperature ductility was evaluated by measuring the reduction of area (cross-sectional reduction ratio of the fracture surface). In addition, a hot-rolled steel plate with a plate thickness of 12 mm was obtained by hot forging and hot rolling and the edge cracking resistance was evaluated. The edge cracking resistance was evaluated by changing the heating temperature and the rolling temperature of the hot rolling with respect to a part of the steel, and a correlation of the heating temperature and the rolling temperature of the hot rolling with the high temperature ductility was determined.

**[0016]** As disclosed in Patent Documents 5 and 6 described above, generally, in duplex stainless steels, it is known that significant edge cracking is generated in the hot rolling of the cast steel in most cases where the reduction of area of the cast steel, which is evaluated by high temperature tensile test, falls below 60%. For this reason, engineers in this field often subject steels to refining, casting, and hot working for the purpose of setting the reduction of area of the cast steel at high temperatures to be in a range of 60% or more. Here, when the present inventors evaluated the high temperature ductility of the alloy-saving type duplex stainless steel (base composition: 21% Cr - 2% Ni - 3% Mn-0.18% N) cast steel which contains around 0.1 % of Sn, it was clear that all the reductions of area fell below 60% in several melting experiments. The evaluation of high temperature ductility was performed as follows. First, a parallel section of a round bar of 8 mmϕ was heated to 1200°C using a high frequency. Next, the temperature was lowered to a temperature for performing a break test, and tensile rupture was performed at a rate of 20 mm/second at this temperature. Then, the shrinkage ratio of the cross section was determined. An example of the data is shown in FIG. 1. From these results, it was considered that there was almost no hope of obtaining an inexpensive alloy-saving type duplex stainless steel with added Sn in practice.

**[0017]** The present inventors observed an edge cracking length which was generated when a cast steel of an alloy-saving type Sn-containing duplex stainless steel, which was obtained by vacuum melting and casting, was subjected to hot rolling. As a result, it was found that there rarely exists a cast steel of an Sn-containing duplex stainless steel in which a number of edge cracks is small. Hot rolling experiments were performed as follows. First, a cast steel with a thickness of 90 to 44 mm was heated to 1200°C. Next, the thickness of the cast steel was reduced to a thickness of 12 to 6 mm by a plurality of rolling passes. The finishing rolling temperature was controlled to be approximately 900°C. Edge cracking was generated on the left and right sides and the maximum lengths on both sides were totaled to obtain the edge cracking length. Even when the edge cracking length of the steel material was looked upon as being related to the minimum value (the minimum value is obtained at approximately 900°C in FIG. 1) of the reduction of area of the high temperature ductility of the cast steel, it was not possible to obtain a clear correlation. However, when the edge cracking length was looked upon as being related to the reduction of area at 1000°C as shown in FIG. 2, it was clear that a good correlation is exhibited regardless of whether or not Sn is contained. Here, in FIG. 2, the points which are plotted by ○ (open circles) correspond to the results of Sn-A and Sn-B of FIG. 1, and the points which are plotted by ♦ (black diamonds) are the other experiment results (the experiment results examined regardless of whether or not Sn is contained).

**[0018]** The present inventors performed melting, casting, and rolling experiments while further changing the amounts of various elements in order to find the conditions for reliably obtaining a cast steel with little edge cracking as described above. Then, the evaluation of the high temperature ductility of the cast steel and the evaluation of edge cracking of the steel material after hot rolling were actively performed. The first aspect of the present invention where the inexpensive Sn-containing alloy-saving type duplex stainless steel is specified was completed on the basis of the findings which were obtained through the above experiments.

**[0019]** The requirements of the first aspect of the duplex stainless steel of the present invention are shown below.

(1) A duplex stainless steel which includes, in mass%: C: 0.03% or less; Si: 0.05% to 1.0%; Mn: 0.1% to 7.0%; P: 0.05% or less; S: 0.0001% to 0.0010%; Ni: 0.5% to 5.0%; Cr: 18.0% to 25.0%; N: 0.10% to 0.30%; Al: 0.05% or less; Ca: 0.0010% to 0.0040%; and Sn: 0.01% to 0.2%, with the remainder being Fe and inevitable impurities, wherein a ratio Ca/O of the amounts of Ca and O is in a range of 0.3 to 1.0, and a pitting index PI shown by formula (1) is in a range of less than 30.

$$PI=Cr+3.3Mo+16N \quad (1)$$

(The chemical symbols in the formula (1) indicate the amounts of the elements).

(2) The duplex stainless steel according to (1), which further includes one or more selected from Mo: 1.5% or less, Cu: 2.0% or less, W: 1.0% or less, and Co: 2.0% or less.

(3) The duplex stainless steel according to (1) or (2), which further includes one or more selected from V: 0.05% to 0.5%, Nb: 0.01% to 0.20%, and Ti: 0.003% to 0.05%.

(4) The duplex stainless steel according to any one of (1) to (3), which further includes one or more selected from B: 0.0050% or less, Mg: 0.0030% or less, and REM: 0.10% or less.

**[0020]** In addition, in order to solve the problems described above, with regard to the general-purpose duplex stainless steel which is the subject of the present invention, the present inventors prepared melted materials where the amount of Sn, the amounts of Ca, B, rare earth elements (REM), and the like and the amount of Ni were changed and where Co was further added, and they performed the following experiments. Here, it is said that the hot manufacturability is improved by containing Ca, B, rare earth elements (REM), and the like.

**[0021]** Tensile test pieces were collected from a cast steel which was cast from the melted materials. The tensile test pieces were subjected to high temperature tensile test at a temperature of 1200 to 700°C, and the high temperature ductility was evaluated by measuring the reduction of area (cross-sectional reduction ratio of the fracture surface). In addition, a hot-rolled steel plate with a plate thickness of 12 mm was obtained by hot forging and hot rolling, and the edge cracking resistance was evaluated. The edge cracking resistance was evaluated by changing the heating temperature and the rolling temperature of the hot rolling with respect to a part of the steel, and a correlation of the heating temperature and the rolling temperature of the hot rolling with the high temperature ductility was determined.

**[0022]** As disclosed in Patent Documents 5 and 6 described above, generally, in duplex stainless steels, it is known that significant edge cracking is generated in the hot rolling of the cast steel in most cases where the reduction of area of the cast steel, which is evaluated by high temperature tensile test, falls below 60%. For this reason, engineers in this field often subject steels to refining, casting, and hot working for the purpose of setting the reduction of area of the cast steel at high temperatures to be in a range of 60% or more. Here, when the present inventors evaluated the high temperature ductility of the general-purpose cast steel of a duplex stainless steel (base composition: 25% Cr - 4% Ni - 1.2% Mo - 1.5% Cu - 0.25% N) which contains around 0.1% of Sn, it was clear that the minimum values of all the reductions of area fell below 60% in several melting experiments. The evaluation of high temperature ductility was performed as follows. First, a parallel section of a round bar of 8 mmϕ was heated to 1200°C using a high frequency. Next, the temperature was lowered to a temperature for performing a break test, and tensile rupture was performed at a rate of 20 mm/second at this temperature. Then, the shrinkage ratio of the cross section was determined. An example of the data is shown in FIG. 3. From these results, it was considered that there was almost no hope of obtaining an inexpensive general-purpose duplex stainless steel with added Sn in practice.

**[0023]** The present inventors observed an edge cracking length which was generated when a cast steel of a general-purpose duplex stainless steel, which was obtained by vacuum melting and casting, was subjected to hot rolling. As a result, it was discovered that there rarely exists an Sn-containing duplex stainless steel material in which a number of edge cracks is small. Hot rolling experiments were performed as follows. First, a cast steel with a thickness of 90 to 44 mm was heated to 1200°C. Next, the thickness of the cast steel was reduced to a thickness of 12 to 6 mm by a plurality of rolling passes. The finishing rolling temperature was controlled to be approximately 900°C. Edge cracking was generated on the left and right sides and the maximum lengths on both sides were totaled to obtain the edge cracking length. Even when the edge cracking length of the steel material was looked upon as being related to the minimum value (the minimum value is obtained at approximately 900°C in FIG. 3) of the reduction of area of the high temperature ductility of the cast steel, it was not possible to obtain a clear correlation. However, when the edge cracking length was looked upon as being related to the reduction of area at 1000°C as shown in FIG. 4, it was clear that a good correlation is exhibited regardless of whether or not Sn is contained. Here, in FIG. 4, the points which are plotted by ○ (open circles) correspond to the results of Sn-A and Sn-B of FIG. 3, and the points which are plotted by ♦ (black diamonds) are the other experiment results (the experiment results examined regardless of whether or not Sn is contained).

**[0024]** The present inventors performed melting, casting, and rolling experiments while further changing the amounts of various elements in order to find the conditions for reliably obtaining a steel material with little edge cracking as described above. Then, the evaluation of the high temperature ductility of the cast steel and the evaluation of the edge cracking of the steel material after hot rolling were actively performed. The second aspect of the present invention where the inexpensive Sn-containing duplex stainless steel is specified was completed on the basis of the findings which were obtained through the above experiments.

**[0025]** The requirements of the second aspect of the duplex stainless steel of the present invention are shown below.

(5) A duplex stainless steel which includes, in mass%: C: 0.03% or less; Si: 0.05% to 1.0%; Mn: 0.1% to 4.0%; P: 0.05% or less; S: 0.0001% to 0.0010%; Cr: 23.0% to 28.0%; Ni: 2.0% to 6.0%; Co: 0% to 1.0%; Cu: 0.2% to 3.0%; Sn: 0.01% to 0.2%; N: 0.20% to 0.30%; Al: 0.05% or less; and Ca: 0.0010% to 0.0040%, with the remainder being Fe and inevitable impurities, wherein Ni+Co is in a range of 2.5% or more and a ratio Ca/O of the amounts of Ca and O is in a range of 0.3 to 1.0, and PI shown by formula (1) is in a range of 30 or more and less than 40.

$$PI=Cr+3.3Mo+16N \quad (1)$$

(The chemical symbols in the formula (1) indicate the amounts of the elements).

(6) The duplex stainless steel according to (5), which further includes either one or both of Mo: 2.0% or less, and W: 1.0% or less.

(7) The duplex stainless steel according to (5) or (6), which further includes one or more selected from V: 0.05% to 0.5%, Nb: 0.01% to 0.15%, and Ti: 0.003% to 0.05%.

(8) The duplex stainless steel according to any one of (5) to (7), which further includes one or more selected from B: 0.0050% or less, Mg: 0.0030% or less, and REM: 0.10% or less.

**[0026]** The requirements of one aspect of the cast steel of the duplex stainless steel and the duplex stainless steel material of the present invention are shown below.

(9) A cast steel of a duplex stainless steel which has a composition according to any one of (1) to (8), wherein a

fracture reduction of area at 1000°C is in a range of 70% or more.

(10) A duplex stainless steel material which is manufactured by hot working the cast steel of the duplex stainless steel according to (9).

Effects of the Invention

**[0027]** According to an aspect of the present invention, it is possible to provide a duplex stainless steel, a cast steel of a duplex stainless steel, and a duplex stainless steel material which have improved corrosion resistance compared to a steel used in the related art as the material for seawater desalination unit, tanks for a transport ship, various types of containers, or the like in addition to an excellent balance with cost. For this reason, the aspects of the present invention make a significant contribution to industrial development.

BRIEF DESCRIPTION OF THE DRAWINGS

**[0028]**

FIG. 1 is a diagram which illustrates the high temperature ductility of Sn-containing and Sn-free duplex stainless steels associated with the first aspect of the duplex stainless steel (an alloy-saving type duplex stainless steel).

FIG. 2 is a diagram which shows the relationship between the edge cracking length after hot rolling and the reduction of area at 1000°C associated with the first aspect of the duplex stainless steel (the alloy-saving type duplex stainless steel).

FIG. 3 is a diagram which illustrates the high temperature ductility of Sn-containing and cast steels of Sn-free duplex stainless steels associated with the second aspect of the duplex stainless steel (a general-purpose duplex stainless steel).

FIG. 4 is a diagram which shows the relationship between the edge cracking length after hot rolling and the reduction of area at 1000°C associated with the second aspect of the duplex stainless steel (the general-purpose duplex stainless steel).

EMBODIMENTS OF THE INVENTION

(First Embodiment)

**[0029]** Below, description will be given of the reasons for limiting the first aspect (the alloy-saving type duplex stainless steel) of the duplex stainless steel of the present invention. Here, the amounts of the respective components are shown in terms of mass%.

**[0030]** Here, in the present embodiment, the cast steel of the stainless steel indicates a steel in a state after casting and before processing such as hot working, forging, or the like is performed, and the stainless steel material indicates a semi-finished product, a hot-rolled steel plate, a cold-rolled steel plate, a steel wire, a steel pipe, or the like after processing the cast steel by various methods. In addition, the stainless steel indicates general forms for a steel such as a cast steel, a steel material, and the like. The processing described above includes hot and cold processings.

**[0031]** In order to ensure the corrosion resistance of the stainless steel, the amount of C is limited to be in a range of 0.03% or less. When more than 0.03% of C is contained, the corrosion resistance and toughness are degraded due to the generation of Cr carbides during hot rolling.

**[0032]** 0.05% or more of Si is added for deoxidation. However, when more than 1.0% of Si is added, the toughness is degraded. Therefore, the upper limit for the amount of Si is limited to 1.0%. The preferable range for the amount of Si is in a range of 0.2% to 0.7%.

**[0033]** Mn has the effect of improving the toughness by increasing the austenite phase. In addition, since Mn has the effect of decreasing the nitride precipitation temperature TN, it is preferable to actively add Mn to the steel material of the present embodiment. For the toughness of the base material and the welding sections, 0.1% or more of M is added. However, when more than 7.0% of Mn is added, the corrosion resistance and the toughness are degraded. Therefore, the upper limit for the amount of Mn is limited to 7.0%. The amount of Mn is preferably in a range of 1.0% to 6.0%, and more preferably in a range of 2.0% to 5.0%.

**[0034]** P is an element which is inevitably mixed in from raw materials and the amount of P is limited to be in a range of 0.05% or less since P degrades the hot workability and the toughness. The amount of P is preferably in a range of 0.03% or less.

**[0035]** S is an element which is inevitably mixed in from the raw materials and the amount of S is limited to be in a range of 0.0010% or less since S degrades the hot workability, the toughness, and the corrosion resistance. In addition, reducing the amount of S to less than 0.0001% increases the costs due to desulfurization refining. For this reason, the amount of S is set to be in a range of 0.0001% to 0.0010%. The amount of S is preferably in a range of 0.0002% to 0.0006%.

**[0036]** Since Ni stabilizes the austenitic structure and improves the toughness and the corrosion resistance with respect to various types of acid, 0.5% or more of Ni is contained. By increasing the amount of Ni, it is possible to decrease the precipitation temperature of nitrides. On the other hand, Ni is an expensive alloy, and from the point of view of costs, the amount of Ni is limited to be in a range of 5.0% or less in the steel of the present embodiment where the subject is an alloy-saving type duplex stainless steel. The amount of Ni is preferably in a range of 1.0% to 4.0%, and more preferably in a range of 1.5% to 3%.

**[0037]** In order to ensure the basic corrosion resistance, 18.0% or more of Cr is contained. On the other hand, when more than 25.0% of Cr is contained, the ferrite phase fraction increases and the toughness and the corrosion resistance of the welding sections are inhibited. For this reason, the amount of Cr is set to be in a range of 18.0% or more and 25.0% or less. The amount of Cr is preferably in a range of 19.0% to 23.0%.

**[0038]** N is an element which is effective for increasing the strength and the corrosion resistance by being solid-solubilized in the austenite phase. For this reason, 0.10% or more of N is contained. On the other hand, the solid solubility limit is increased according to the amounts of Cr and Mn; however, when more than 0.30% of N is contained in the steel of the present embodiment, Cr nitrides are precipitated such that the toughness and the corrosion resistance are inhibited and the hot manufacturability is inhibited. For this reason, the upper limit of the amount of N is set to 0.30%. The amount of N is preferably in a range of 0.10% to 0.25%.

**[0039]** Al is an element which deoxidizes a steel and reduces the oxygen in the steel according to necessity. For this reason, Al is contained together with 0.05% or more of Si. In an Sn-containing steel, the reduction of the oxygen amount is essential in order to ensure the hot manufacturability, and for this reason, it is necessary that 0.003% or more of Al be contained according to necessity. On the other hand, Al is an element having comparatively large affinity with N, and when an excessive amount of Al is added, the toughness of the stainless steel is inhibited due to the generation of AlN. The degree also depends on the amount of N; however, when the amount of Al exceeds 0.05%, the toughness is greatly decreased. For this reason, the upper limit of the amount of Al is set to 0.05%. The amount of Al is preferably in a range of 0.04% or less.

**[0040]** Ca is an important element for the hot manufacturability of the steel, and it is necessary that Ca be contained in order to fix S and O in the steel as inclusions and to improve the hot manufacturability. In the steel of the present embodiment, 0.0010% or more of Ca is contained for this purpose. In addition, addition of an excessive amount thereof decreases the pitting resistance. For this reason, the upper limit of the amount of Ca is set to 0.0040%.

**[0041]** Sn is contained in order to improve the corrosion resistance of the steel of the present embodiment. For this reason, it is necessary that at least 0.01% of Sn be contained. Furthermore, it is preferable that 0.02% or more of Sn be contained. On the other hand, Sn is an element which inhibits the hot manufacturability of the steel, and decreases the hot strength of the interface between the ferrite phase and the austenite phase, particularly at a temperature of 900°C or less in the alloy element saving type duplex stainless steel which is the subject of the present embodiment. The degree of the decrease depends on the amounts of S, Ca, and O; however, when more than 0.2% of Sn is contained, it is not possible to prevent the decrease in the hot manufacturability even by restricting other limits in the present embodiment. Therefore, the upper limit of the amount of Sn is set to 0.2%.

**[0042]** The ratio Ca/O of the amounts of O and Ca is an important component index in order to improve the hot manufacturability and the corrosion resistance of the steel of the present embodiment. The lower limit of Ca/O is limited in order to improve the hot manufacturability of the Sn-containing steel. The high temperature ductility of the Sn-containing steel is decreased, particularly at a temperature of 900°C or less. When the value of Ca/O is in a range of less than 0.3, the high temperature ductility at 1000°C is also decreased and the hot manufacturability is greatly impaired. For this reason, Ca/O is limited to be in a range of 0.3 or more in the steel of the present embodiment. On the other hand, when an excessive amount of Ca is added and Ca/O exceeds 1.0, the pitting resistance is impaired. In addition, when the amount of Ca is excessive, the high temperature ductility at a temperature of 1000 to 1100°C is also impaired. For this reason, the upper limit of Ca/O is set to be in a range of 1.0. Ca/O is preferably in a range of 0.4 to 0.8.

**[0043]** O is an inevitable impurity and an upper limit thereof is not particularly set; however, O is an important element which configures oxides which are the representative of non-metallic inclusions. Composition control of the oxides is extremely important for the improvement of the hot manufacturability. In addition, surface defects are caused when coarse cluster-shaped oxides are generated. For this reason, it is necessary to limit the amount of O so as to be low. In the present embodiment, as described above, by setting the ratio of the amount of Ca and the amount of O to be in a range of 0.3 or more, the amount of O is limited. The upper limit of the amount of O is preferably in a range of 0.005% or less.

**[0044]** In order to incrementally increase the corrosion resistance, one or more selected from Mo: 1.5% or less, Cu: 2.0% or less, W: 1.0% or less, and Co: 2.0% or less may be contained according to necessity. Description will be given of the reasons for these limits.

**[0045]** Mo is an element which is extremely effective at incrementally increasing the corrosion resistance of the stainless steel, and Mo can be contained according to necessity. In order to improve the corrosion resistance, it is preferable that 0.2% or more of Mo be contained. On the other hand, Mo is an element which promotes precipitation of intermetallic compounds, and the upper limit of the amount of Mo is set to 1.5% from the point of view of suppressing precipitation in the steel of the present embodiment during hot rolling.

**[0046]** Cu is an element which incrementally increase the corrosion resistance of the stainless steel with respect to acid, and Cu has an effect of improving the toughness; and therefore, it is recommended that 0.3% or more be contained according to necessity. When more than 2.0% of Cu is contained, the amount of Cu exceeds the solid solubility; and thereby, ε-Cu is precipitated during hot rolling to cause embrittlement. For this reason, the upper limit of the amount of Cu is set to 2.0%. In a case where Cu is contained, the amount is preferably in a range of 0.3% to 1.5%.

**[0047]** W is an element which incrementally increases the corrosion resistance of the stainless steel in the same manner as Mo, and W can be added according to necessity. For the purpose of increasing the corrosion resistance in the steel of the present embodiment, the upper limit of the amount of W is set to 1.0%. The amount of W is preferably in a range of 0.05% to 0.5%.

**[0048]** Co is an element which is effective for increasing the toughness and the corrosion resistance of the steel and which is selectively added. The amount of Co is preferably in a range of 0.03% or more. When more than 2.0% of Co is contained, an effect which is commensurate with the cost is not exhibited as Co is an expensive element. For this reason, the upper limit of the amount of Co is set to 2.0%. In a case where Co is added, the amount is preferably in a range of 0.03% to 1.0%.

**[0049]** Furthermore, one or more selected from V: 0.05% to 0.5%, Nb: 0.01% to 0.20%, and Ti: 0.003% to 0.05% may be contained. These are elements which are more likely to generate nitrides rather than Cr. V, Nb, and Ti can be added according to necessity, and there is a tendency for the corrosion resistance to be improved in cases where these are contained in trace amounts.

**[0050]** Nitrides and carbides which are formed by V are generated in the hot working and the cooling process of the steel material, and these have the effect of increasing the corrosion resistance. The reasons therefor are not sufficiently confirmed; however, it is considered that there is a probability of suppressing the generation speed of the chromium nitrides at a temperature of 700°C or less. 0.05% or more of V is contained in order to improve the corrosion resistance. When more than 0.5% of V is contained, coarse V carbonitrides are generated, and toughness is degraded. Therefore, the upper limit of the amount of V is limited to 0.5%. In a case where V is added, the amount is preferably in a range of 0.1 % to 0.3%.

**[0051]** Nitrides and carbides which are formed by Nb are generated in the hot working and the cooling process of the steel material, and these have the effect of increasing the corrosion resistance. The reasons therefor are not sufficiently confirmed; however, it is considered that there is a probability of suppressing the generation speed of the chromium nitrides at a temperature of 700°C or less. 0.01 % or more of Nb is contained in order to improve the corrosion resistance. On the other hand, in the case where an excessive amount ofNb is added, Nb is precipitated as non-solid-solubilized precipitates during heating before the hot rolling; and thereby, the toughness is inhibited. For this reason, the upper limit of the amount of Nb is set to 0.20%. In a case where Nb is added, the range of the amount is preferably in a range of 0.03% to 0.10%.

**[0052]** Ti is an element which forms oxides, nitrides, and sulfides in very small amounts and Ti refines crystal grains in the solidified structure and the structure heated at a high temperature of the steel. In addition, in the same manner as V and Nb, Ti also has the property of replacing a part of the chromium in the chromium nitrides. With an amount of Ti of 0.003% or more, Ti precipitates are formed. On the other hand, when more than 0.05% of Ti is contained in the duplex stainless steel, the toughness of the steel is impaired due to the generation of coarse TiN. For this reason, the upper limit of the amount of Ti is set to 0.05%. A suitable amount of Ti is in a range of 0.005% to 0.020%.

**[0053]** Furthermore, one or more selected from B: 0.0050% or less, Mg: 0.0030% or less, and REM: 0.10% or less may be contained. In order to achieve further improvement of the hot workability, the B, Mg, and REM to be contained according to necessity are limited as follows.

**[0054]** B, Mg, and REM are all elements which improve the hot workability of the steel, and one or more thereof is added for this purpose. The addition of an excessive amount of any one of B, Mg, and REM has the opposite effect of decreasing the hot workability and the toughness. For this reason, the upper limits of the above amounts are set as follows. The upper limit of the amount of B is 0.0050%. The upper limit of the amount of Mg is 0.0030%. The upper limit of the amount of REM is 0.10%. Preferable amounts of respective elements are B: 0.0005% to 0.0030%, Mg: 0.0001% to 0.0015%, and REM 0.005% to 0.05%. Here, REM is the sum of the amounts of lanthanoid rare earth elements such as Ce, La, and the like.

**[0055]** By having the characteristics of the duplex stainless steel of the present embodiment described above, it is possible to greatly improve the hot manufacturability of the alloy-saving duplex stainless steel which contains Sn.

**[0056]** In the cast steel stage, a fracture reduction of area at 1000°C is in a range of 70% or more. In addition, by subjecting the cast steel to the processes which include the hot working, it is possible to obtain a duplex stainless steel material with a high yield and few surface defects.

(Second Embodiment)

**[0057]** Below, description will be given of the reasons for the limits of the second aspect (a general-purpose duplex stainless steel) of the duplex stainless steel of the present invention. Here, the amounts of the respective components are shown in terms of mass%.

**[0058]** Here, in the present embodiment, the cast steel of the stainless steel indicates a steel in a state after casting and before processing such as hot working, forging, or the like is performed, and the stainless steel material indicates a semi-finished product, a hot-rolled steel plate, a cold-rolled steel plate, a steel wire, a steel pipe, or the like after processing the cast steel by various methods. In addition, the stainless steel indicates the general forms for a steel such as a cast steel, a steel material, and the like. The processing described above includes hot and cold processings.

**[0059]** In order to ensure the corrosion resistance of the stainless steel, the amount of C is limited to be in a range of 0.03% or less. When more than 0.03% of C is contained, the corrosion resistance and toughness are degraded due to the generation of Cr carbides during hot rolling.

**[0060]** 0.05% or more of Si is added for deoxidation. However, when more than 1.0% of Si is added, the toughness is degraded. Therefore, the upper limit for the amount of Si is limited to 1.0%. The preferable range for the amount of Si is in a range of 0.2% to 0.7%.

**[0061]** Mn has the effect of improving the toughness by increasing the austenite phase. In addition, since Mn has the effect of suppressing the precipitation of nitrides, it is preferable to actively add Mn to the steel material of the present embodiment. For the toughness of the base material and the welding sections, 0.1% or more of Mn is added. However, when more than 4.0% of Mn is added, the corrosion resistance and the toughness are degraded. Therefore, the upper limit for the amount of Mn is limited to 4.0%. The amount of Mn is preferably in a range of 1.0% to 3.5%, and more preferably in a range of 2.0% to 3.0%.

**[0062]** P is an element which is inevitably mixed in from raw materials and the amount of P is limited to be in a range of 0.05% or less since P degrades the hot workability and the toughness. The amount of P is preferably in a range of 0.03% or less.

**[0063]** S is an element which is inevitably mixed in from the raw materials and the amount of S is limited to in a range of 0.0010% or less since S degrades the hot workability, the toughness, and the corrosion resistance. In addition, reducing the amount of S to less than 0.0001% increases the costs due to desulfurization refining. For this reason, the amount of S is set to be in a range of 0.0001% to 0.0010%. The amount of S is preferably in a range of 0.0002% to 0.0006%.

**[0064]** 23.0% or more of Cr is contained in order to ensure basic corrosion resistance. On the other hand, when more than 28.0% of Cr is contained, the ferrite phase fraction increases and the toughness and the corrosion resistance of the welding sections are inhibited. For this reason, the amount of Cr is set to be in a range of 23.0% or more to 28.0% or less. The amount of Cr is preferably in a range of 24.0% to 27.5%.

**[0065]** Ni stabilizes the austenitic structure and improves the toughness and the corrosion resistance with respect to various types of acid. Furthermore, Ni suppresses a decrease in hot workability due to the addition of Sn and Cu. For this reason, 2.0% or more of Ni is contained. By increasing the amount of Ni, it is possible to decrease the nitride precipitation temperature. On the other hand, since Ni is an expensive alloy, the amount of Ni is limited to be in a range of 6.0% or less. The amount of Ni is preferably in a range of 2.5% to 5.5%, and more preferably in a range of 3.0% to 5.0%.

**[0066]** Co is an element which is effective for increasing the toughness and the corrosion resistance of the steel and which suppresses a decrease in the hot workability due to the addition of Sn and Cu, and it is desirable that Co be contained together with Ni. In addition, in a case where Co is added, it is preferable that 0.1% or more of Co be contained. When more than 1.0% of Co is contained, an effect which is commensurate with the cost is not exhibited as Co is an expensive element. For this reason, the upper limit of the amount of Co is set to 1.0%. In a case where Co is added, the amount is preferably in a range of 0.1% to 0.5%.

**[0067]** It is known from Non-Patent Document 1 that Ni increases the solid solubility of Cu and has an effect of suppressing the generation of a liquid phase having a low melting point due to the addition of Cu and Sn. In addition, Co is an element which belongs to the same group as Ni. For this reason, it is considered that the decrease in the hot workability due to Cu and Sn is suppressed by increasing the sum of the amounts of Ni and Co. The present inventors learned that the edge cracking of the steel material increases in the case where the total amount of Ni and Co is in a range of less than 2.5% when the hot workability of the steel which is the subject of the present embodiment is arranged on the sum of the amounts of Ni and Co. For this reason, the range of Ni+Co is set to be in a range of 2.5% or more.

**[0068]** Cu is an element which increases the corrosion resistance of the stainless steel with respect to acid and has an effect of improving the toughness. In the present embodiment, in order to increase the corrosion resistance, 0.2% or more of Cu is contained together with 0.01% or more of Sn. When more than 3.0% of Cu is contained, the amount of Cu exceeds the solid solubility; and thereby, $\varepsilon$-Cu is precipitated during hot rolling to cause embrittlement. For this reason, the upper limit of the amount of Cu is set to 3.0%. In the case where Cu is contained, the amount is preferably in a range of 0.5% to 2.0%.

**[0069]** Sn is contained in order to improve the corrosion resistance of the steel of the present embodiment. For this reason, it is necessary that at least 0.01% of Sn be contained. Furthermore, it is preferable that 0.02% or more of Sn be contained. On the other hand, Sn is an element which inhibits the hot manufacturability of the steel, and decreases the hot strength of the interface between the ferrite phase and the austenite phase, particularly at a temperature of 900°C or less in the alloy element saving type duplex stainless steel which is the subject of the present embodiment. The degree of the decrease depends on the amounts of S, Ca, and O; however, when more than 0.2% of Sn is contained, it is not possible to prevent the decrease in the hot manufacturability even by restricting other limits in the present embodiment. Therefore, the upper limit of the amount of Sn is set to 0.2%.

**[0070]** N is an element which is effective for increasing the strength and the corrosion resistance by being solid-solubilized in the austenite phase. For this reason, 0.20% or more ofN is contained. Since it is possible to decrease the amount ofNi by increasing the amount of N, N is an element which it is desirable to actively add. On the other hand, it is necessary to limit the upper limit of the amount of N to be within the solubility limit of N. The solubility limit of N is increased according to the amounts of Cr and Mn. When more than 0.30% of N is contained in the steel of the present embodiment, Cr nitrides are precipitated such that the toughness and the corrosion resistance are inhibited and the hot manufacturability is inhibited. For this reason, the upper limit of the amount of N is set to 0.30%. The amount of N is preferably in a range of 0.20% to 0.28%.

**[0071]** Al is an element which deoxidizes a steel and Al is contained together with 0.05% or more of Si in order to reduce the oxygen in the steel according to necessity. In an Sn-containing steel, the reduction of the oxygen amount is essential in order to ensure the hot manufacturability, and for this reason, it is necessary that 0.003% or more of Al be contained according to necessity. On the other hand, Al is an element having comparatively large affinity with N, and when an excessive amount of Al is added, the toughness of the stainless steel is inhibited due to the generation of AlN. The degree also depends on the amount ofN; however, when the amount of Al exceeds 0.05%, the toughness is greatly decreased. For this reason, the upper limit of the amount of Al is set to 0.05%. The amount of Al is preferably in a range of 0.04% or less.

**[0072]** Ca is an important element for the hot manufacturability of the steel, and it is necessary that Ca be contained in order to fix the S and O in the steel as inclusions and to improve the hot manufacturability. In the steel of the present embodiment, 0.0010% or more of Ca is contained for this purpose. In addition, addition of an excessive amount thereof decreases the pitting resistance. For this reason, the upper limit of the amount of Ca was set to 0.0040%.

**[0073]** The ratio Ca/O of the amounts of O and Ca is an important component index in order to improve the hot manufacturability and the corrosion resistance of the steel of the present embodiment. The lower limit of Ca/O is limited in order to improve the hot manufacturability of the Sn-containing steel. The high temperature ductility of the Sn-containing steel is decreased, particularly at a temperature of 900°C or less. When the value of Ca/O is in a range of less than 0.3, the high temperature ductility at 1000°C is also decreased and the hot manufacturability is greatly impaired. For this reason, in the steel of the present embodiment, Ca/O is limited to be in a range of 0.3 or more. On the other hand, when an excessive amount of Ca is added and Ca/O exceeds 1.0, the pitting resistance is impaired. In addition, when the amount of Ca is excessive, the high temperature ductility at a temperature of 1000 to 1100°C is also impaired. For this reason, the upper limit of Ca/O is set to be in a range of 1.0. Ca/O is preferably in a range of 0.4 to 0.8.

**[0074]** O is an inevitable impurity and an upper limit thereof is not particularly set; however, O is an important element which configures oxides which are representatives of non-metallic inclusions. Composition control of the oxides is extremely important for the improvement of the hot manufacturability. In addition, surface defects are caused when coarse cluster-shaped oxides are generated. For this reason, it is necessary to limit the amount of O so as to be low. In the present embodiment, as described above, by setting the ratio of the amount of Ca and the amount of O to be in a range of 0.3 or more, the amount of O is limited. The upper limit of the amount of O is preferably in a range of 0.005% or less.

**[0075]** Furthermore, either one or both of Mo: 2.0% or less, and W: 1.0% or less may be contained. These are elements which incrementally increase the corrosion resistance. Description will be given of the reasons for these limits.

**[0076]** Mo is an element which is extremely effective at incrementally increasing the corrosion resistance of the stainless steel, and Mo can be contained according to necessity. In order to improve the corrosion resistance, it is preferable that 0.2% or more of Mo be contained. On the other hand, Mo is an expensive element, and from the point of view of suppressing the cost of the alloy in the steel of the present embodiment, the upper limit of the amount of Mo is set to 2.0%.

**[0077]** W is an element which incrementally increases the corrosion resistance of the stainless steel in the same manner as Mo, and it is possible to add W according to necessity. For the purpose of increasing the corrosion resistance in the steel of the present embodiment, the upper limit of the amount of W is set to 1.0%. The amount of W is preferably in a range of 0.1% to 0.8%.

**[0078]** Furthermore, one or more selected from V: 0.05% to 0.5%, Nb: 0.01% to 0.15%, and Ti: 0.003% to 0.05% may be contained. These are elements which are more likely to generate nitrides rather than Cr. It is possible to add any of V, Nb, and Ti according to necessity, and there is a tendency for the corrosion resistance to be improved in cases where these are contained in trace amounts.

**[0079]** Nitrides and carbides which are formed by V are generated in the hot working and the cooling process of the steel material, and these have the effect of increasing the corrosion resistance. The reasons therefor are not sufficiently confirmed; however, it is considered that there is a probability of suppressing the generation speed of the chromium nitrides at a temperature of 700°C or less. It is desirable that 0.05% or more of V be contained in order to improve the corrosion resistance. When more than 0.5% of V is contained, coarse V carbonitrides are generated and the toughness is degraded. Therefore, the upper limit of the amount of V is limited to 0.5%. In a case where V is added, the amount is preferably in a range of 0.1% to 0.3%.

**[0080]** Nitrides and carbides which are formed of Nb are generated in the hot working and the cooling process of the steel material, and these have the effect of increasing the corrosion resistance. The reasons therefor are not sufficiently confirmed; however, it is considered that there is a probability of suppressing the generation speed of the chromium nitrides at a temperature of 700°C or less. It is desirable that 0.01% or more of Nb be contained in order to improve the corrosion resistance. On the other hand, in the case where an excessive amount of Nb is added, Nb is precipitated as non-solid-solubilized precipitates during heating before the hot rolling; and thereby, the toughness is inhibited. For this reason, the upper limit of the amount of Nb is set to 0.15%. In a case where Nb is added, the range of the amount is preferably in a range of 0.03% to 0.10%.

**[0081]** Ti is an element which forms oxides, nitrides, and sulfides in very small amounts and Ti refines crystal grains in the solidified structure and the structure heated at a high temperature of the steel. In addition, in the same manner as V and Nb, Ti also has the property of replacing a part of the chromium in the chromium nitrides. With an amount of Ti of 0.003% or more, Ti precipitates are formed. On the other hand, when more than 0.05% of Ti is contained in the duplex stainless steel, the toughness of the steel is impaired due to the generation of coarse TiN. For this reason, the upper limit of the amount of Ti is set to 0.05%. A suitable amount of Ti is in a range of 0.005% to 0.020%.

**[0082]** Furthermore, one or more selected from B: 0.0050% or less, Mg: 0.0030% or less, and REM: 0.10% or less may be contained. In order to achieve further improvement of the hot workability, the B, Mg, and REM to be contained according to necessity are limited as follows.

**[0083]** B, Mg, and REM are all elements which improve the hot workability of the steel, and it is desirable that one or more be added for this purpose. The addition of an excessive amount of any of B, Mg, and REM has the opposite effect of decreasing the hot workability and the toughness. For this reason, the upper limits of the above amounts are set as follows. The upper limit of the amount of B is 0.0050%. The upper limit of the amount of Mg is 0.0030%. The upper limit of the amount of REM is 0.10%. Preferable amounts of respective elements are B: 0.0005% to 0.0030%, Mg: 0.0001% to 0.0015%, and REM 0.005% to 0.05%. Here, REM is the sum of the amounts of lanthanoid rare earth elements such as Ce, La, and the like.

**[0084]** Above, by having the characteristics of the duplex stainless steel of the present embodiment described above, it is possible to greatly improve the hot manufacturability of the general-purpose duplex stainless steel which contains Sn.

**[0085]** In the cast steel stage, a fracture reduction of area at 1000°C is in a range of 70% or more. In addition, by subjecting the cast steel to the processes which include the hot working, it is possible to obtain a duplex stainless steel material with a high yield and few surface defects.

## EXAMPLES

### (Example 1)

**[0086]** Description will be given of examples of the alloy-saving type duplex stainless steel below. The chemical compositions of test steels are shown in Tables 1 to 4. Here, the remainder other than the components which are described in Table 1 is Fe and inevitable impurity elements. In addition, for the components which are shown in Tables 1 to 4, portions where the amounts are not described show the impurity levels. REM indicates lanthanoid rare earth elements, and the amount of REM shows the total of these elements. The numbers which are underlined in the tables indicate values outside of the ranges which are defined in the first embodiment.

Table 1

| Steel No. | | C | Si | Mn | P | S | Ni | Cr | N | Al | Ca | Sn | Other | O | PI | Ca/O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-1 | Invention Examples | 0.015 | 0.39 | 3.21 | 0.022 | 0.0005 | 2.15 | 20.9 | 0.173 | 0.015 | 0.0013 | 0.05 | | 0.0038 | 23.7 | 0.34 |
| 1-2 | | 0.020 | 0.34 | 3.01 | 0.024 | 0.0004 | 2.08 | 21.0 | 0.165 | 0.042 | 0.0022 | 0.09 | | 0.0024 | 23.6 | 0.92 |
| 1-3 | | 0.018 | 0.42 | 4.93 | 0.021 | 0.0006 | 2.13 | 20.9 | 0.186 | 0.025 | 0.0019 | 0.06 | | 0.0032 | 23.9 | 0.59 |
| 1-4 | | 0.018 | 0.35 | 3.02 | 0.023 | 0.0007 | 2.35 | 20.8 | 0.178 | 0.023 | 0.0022 | 0.13 | Mo:0.32 | 0.0030 | 24.7 | 0.73 |
| 1-5 | | 0.018 | 0.35 | 3.05 | 0.023 | 0.0007 | 2.35 | 20.9 | 0.168 | 0.013 | 0.0028 | 0.02 | Cu:1.05 | 0.0048 | 23.6 | 0.58 |
| 1-6 | | 0.018 | 0.35 | 3.02 | 0.024 | 0.0007 | 2.35 | 20.8 | 0.181 | 0.015 | 0.0018 | 0.07 | W:0.25 | 0.0039 | 23.7 | 0.46 |
| 1-7 | | 0.018 | 0.35 | 3.05 | 0.023 | 0.0007 | 2.35 | 20.9 | 0.176 | 0.012 | 0.0019 | 0.03 | Co:0.23 | 0.0048 | 23.7 | 0.40 |
| 1-8 | | 0.021 | 0.42 | 2.56 | 0.031 | 0.0005 | 1.53 | 18.5 | 0.125 | 0.043 | 0.0013 | 0.05 | Mo:1.22, Cu:0.95 | 0.0026 | 24.5 | 0.50 |
| 1-9 | | 0.021 | 0.42 | 2.54 | 0.031 | 0.0005 | 1.42 | 18.5 | 0.132 | 0.047 | 0.0012 | 0.05 | Mo:1.38, Cu:1.03, Co:0.02 | 0.0024 | 25.2 | 0.50 |
| 1-10 | | 0.021 | 0.42 | 2.53 | 0.031 | 0.0005 | 1.44 | 18.5 | 0.115 | 0.049 | 0.0015 | 0.05 | Mo:0.12, Cu:1.23, W:0.23 | 0.0028 | 20.7 | 0.54 |
| 1-11 | | 0.025 | 0.64 | 4.89 | 0.026 | 0.0006 | 1.52 | 21.3 | 0.215 | 0.023 | 0.0023 | 0.06 | V:0.12 | 0.0034 | 24.7 | 0.68 |
| 1-12 | | 0.025 | 0.64 | 5.12 | 0.026 | 0.0006 | 1.52 | 21.5 | 0.205 | 0.021 | 0.0015 | 0.06 | Nb:0.052 | 0.0034 | 24.8 | 0.44 |
| 1-13 | | 0.025 | 0.64 | 4.96 | 0.026 | 0.0006 | 1.51 | 21.7 | 0.218 | 0.015 | 0.0018 | 0.06 | Ti:0.012 | 0.0038 | 25.2 | 0.47 |
| 1-14 | | 0.025 | 0.64 | 5.32 | 0.026 | 0.0006 | 1.53 | 21.5 | 0.232 | 0.019 | 0.0022 | 0.06 | V:0.11, Nb:0.035 | 0.0036 | 25.2 | 0.61 |
| 1-15 | | 0.028 | 0.56 | 1.74 | 0.023 | 0.0006 | 4.53 | 23.4 | 0.106 | 0.035 | 0.0023 | 0.17 | Mo:0.34, V:0.35, Ti:0.032 | 0.0027 | 26.2 | 0.85 |

Table 2

| Steel No. | | C | Si | Mn | P | S | Ni | Cr | N | Al | Ca | Sn | Other | O | PI | Ca/O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-16 | Invention Examples | 0.014 | 0.45 | 2.95 | 0.015 | 0.0003 | 1.95 | 20.7 | 0.175 | 0.023 | 0.0013 | 0.06 | Mo:0.35, Cu:1.04, V:0.12, Ti:0.007 | 0.0026 | 24.7 | 0.50 |
| 1-17 | | 0.007 | 0.44 | 2.98 | 0.014 | 0.0003 | 1.97 | 20.7 | 0.175 | 0.012 | 0.0036 | 0.07 | W:0.35, Co:0.03, V:0.11, Ti:0.006 | 0.0046 | 23.5 | 0.78 |
| 1-18 | | 0.005 | 0.46 | 2.96 | 0.013 | 0.0003 | 1.96 | 20.6 | 0.173 | 0.025 | 0.0021 | 0.08 | Mo:0.28, Cu:1.05, V:0.14, Nb:0.048, Ti:0.011 | 0.0027 | 24.3 | 0.78 |
| 1-19 | | 0.022 | 0.15 | 4.03 | 0.033 | 0.0002 | 2.03 | 21.3 | 0.155 | 0.023 | 0.0011 | 0.10 | B:0.0026 | 0.0033 | 23.8 | 0.33 |
| 1-20 | | 0.023 | 0.14 | 3.26 | 0.036 | 0.0010 | 2.00 | 21.2 | 0.165 | 0.023 | 0.0031 | 0.10 | Mg:0.0012 | 0.0032 | 23.8 | 0.97 |
| 1-21 | | 0.024 | 0.16 | 3.33 | 0.023 | 0.0009 | 2.04 | 20.9 | 0.166 | 0.022 | 0.0023 | 0.10 | REM:0.065 | 0.0034 | 23.6 | 0.68 |
| 1-22 | | 0.023 | 0.13 | 3.12 | 0.021 | 0.0008 | 2.03 | 20.0 | 0.164 | 0.024 | 0.0022 | 0.10 | B:0.0032, Mg:0.0006 | 0.0035 | 22.6 | 0.63 |
| 1-23 | | 0.021 | 0.07 | 2.86 | 0.019 | 0.0001 | 2.05 | 21.1 | 0.175 | 0.021 | 0.0016 | 0.10 | B:0.0023, REM:0.032 | 0.0023 | 23.9 | 0.70 |
| 1-24 | | 0.022 | 0.12 | 2.75 | 0.016 | 0.0002 | 2.01 | 20.9 | 0.177 | 0.023 | 0.0024 | 0.05 | Mo:0.56, Cu:1.45, B:0.0028 | 0.0036 | 25.6 | 0.67 |

Table 3

| Steel No. | | C | Si | Mn | P | S | Ni | Cr | N | Al | Ca | Sn | Other | O | PI | Ca/O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-25 | Invention Examples | 0.026 | 0.76 | 2.89 | 0.018 | 0.0005 | 2.45 | 20.8 | 0.172 | 0.022 | 0.0028 | 0.05 | Mo:0.38, Cu:1.06, Co:0.04, V:0.13, Ti:0.006, B:0.0024 | 0.0032 | 24.8 | 0.88 |
| 1-26 | | 0.024 | 0.78 | 3.01 | 0.015 | 0.0003 | 2.56 | 21.9 | 0.179 | 0.021 | 0.0023 | 0.05 | Mo:0.35, Cu:1.01, W:0.12, Co:0.03, V:0.16, Nb:0.015, Ti:0.004, B:0.0016, Mg:0.0003 | 0.0033 | 25.9 | 0.70 |
| 1-27 | | 0.016 | 0.43 | 6.53 | 0.021 | 0.0004 | 0.75 | 18.3 | 0.182 | 0.016 | 0.0016 | 0.04 | Mo:1.35, Cu:1.23 | 0.0034 | 25.7 | 0.47 |
| 1-28 | | 0.024 | 0.37 | 2.43 | 0.023 | 0.0006 | 4.58 | 24.4 | 0.245 | 0.023 | 0.0019 | 0.06 | V:0.13 | 0.0036 | 28.3 | 0.53 |
| 1-29 | | 0.013 | 0.42 | 3.15 | 0.022 | 0.0004 | 4.13 | 24.5 | 0.235 | 0.016 | 0.0022 | 0.07 | | 0.0046 | 28.3 | 0.48 |
| 1-30 | | 0.025 | 0.36 | 0.23 | 0.012 | 0.0003 | 3.02 | 21.1 | 0.165 | 0.005 | 0.0023 | 0.04 | Co:1.52 | 0.0047 | 23.7 | 0.49 |
| 1-31 | | 0.018 | 0.26 | 0.85 | 0.031 | 0.0002 | 4.23 | 21.3 | 0.201 | | 0.0021 | 0.08 | W:0.75 | 0.0052 | 24.5 | 0.40 |
| 1-32 | | 0.023 | 0.32 | 2.45 | 0.024 | 0.0005 | 3.24 | 18.2 | 0.112 | 0.003 | 0.0016 | 0.12 | Mo:1.43 | 0.0042 | 24.7 | 0.38 |
| 1-33 | | 0.019 | 0.39 | 0.31 | 0.021 | 0.0006 | 1.68 | 21.3 | 0.164 | 0.013 | 0.0014 | 0.06 | Cu:1.83 | 0.0038 | 23.9 | 0.37 |

Table 4

| Steel No. | | C | Si | Mn | P | S | Ni | Cr | N | Al | Ca | Sn | Other | O | PI | Ca/O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-A | Comparative Examples | 0.016 | 0.38 | 2.96 | 0.022 | 0.0006 | 1.96 | 20.9 | 0.174 | 0.026 | 0.0006 | 0.08 | | 0.0036 | 23.7 | 0.17 |
| 1-B | | 0.016 | 0.38 | 2.98 | 0.022 | 0.0006 | 1.96 | 20.9 | 0.174 | | 0.0012 | 0.08 | | 0.0052 | 23.7 | 0.23 |
| 1-C | | 0.015 | 0.39 | 2.96 | 0.023 | 0.0006 | 1.98 | 21.0 | 0.172 | 0.023 | 0.0016 | <0.01 | | 0.0032 | 23.8 | 0.50 |
| 1-D | | 0.016 | 0.38 | 2.98 | 0.022 | 0.0006 | 1.97 | 21.0 | 0.172 | 0.023 | 0.0018 | 0.26 | | 0.0032 | 23.8 | 0.56 |
| 1-E | | 0.021 | 0.42 | 3.12 | 0.023 | 0.0005 | 2.02 | 21.1 | 0.175 | 0.021 | 0.0045 | 0.08 | | 0.0021 | 23.9 | 2.14 |
| 1-F | | 0.043 | 0.54 | 2.86 | 0.025 | 0.0006 | 2.01 | 21.0 | 0.182 | 0.017 | 0.0020 | 0.08 | | 0.0036 | 23.9 | 0.56 |
| 1-G | | 0.025 | 1.54 | 3.13 | 0.029 | 0.0006 | 2.00 | 21.0 | 0.183 | 0.017 | 0.0020 | 0.07 | | 0.0036 | 23.9 | 0.56 |
| 1-H | | 0.024 | 0.39 | 7.85 | 0.028 | 0.0006 | 2.03 | 21.0 | 0.175 | 0.017 | 0.0020 | 0.07 | | 0.0032 | 23.8 | 0.63 |
| 1-I | | 0.023 | 0.46 | 3.24 | 0.065 | 0.0005 | 2.00 | 21.0 | 0.186 | 0.018 | 0.0020 | 0.06 | | 0.0033 | 24.0 | 0.61 |
| 1-J | | 0.026 | 0.48 | 3.16 | 0.022 | 0.0012 | 1.99 | 21.0 | 0.165 | 0.019 | 0.0018 | 0.07 | | 0.0041 | 23.6 | 0.44 |
| 1-K | | 0.025 | 0.42 | 3.08 | 0.031 | 0.0006 | 0.32 | 21.0 | 0.159 | 0.017 | 0.0007 | 0.07 | | 0.0035 | 23.5 | 0.20 |
| 1-L | | 0.024 | 0.41 | 2.56 | 0.022 | 0.0007 | 2.23 | 17.2 | 0.184 | 0.016 | 0.0018 | 0.12 | | 0.0038 | 20.1 | 0.47 |
| 1-M | | 0.025 | 0.43 | 2.66 | 0.023 | 0.0006 | 1.85 | 20.9 | 0.330 | 0.015 | 0.0018 | 0.08 | | 0.0033 | 26.2 | 0.55 |
| 1-N | | 0.016 | 0.44 | 2.36 | 0.021 | 0.0007 | 1.96 | 21.0 | 0.174 | 0.021 | 0.0019 | 0.07 | V:0.63 | 0.0035 | 23.8 | 0.54 |
| 1-O | | 0.017 | 0.42 | 2.86 | 0.025 | 0.0007 | 1.94 | 21.0 | 0.175 | 0.019 | 0.0019 | 0.07 | Nb:0.24 | 0.0036 | 23.8 | 0.53 |
| 1-P | | 0.016 | 0.38 | 2.94 | 0.024 | 0.0007 | 1.95 | 21.0 | 0.173 | 0.023 | 0.0019 | 0.07 | Ti:0.062 | 0.0034 | 23.8 | 0.56 |
| 1-Q | | 0.018 | 0.39 | 3.11 | 0.024 | 0.0007 | 1.93 | 21.1 | 0.172 | 0.022 | 0.0019 | 0.07 | B:0.0076 | 0.0036 | 23.9 | 0.53 |
| 1-R | | 0.015 | 0.41 | 3.13 | 0.023 | 0.0007 | 1.92 | 20.9 | 0.170 | 0.021 | 0.0019 | 0.07 | Mg:0.0041 | 0.0037 | 23.6 | 0.51 |
| 1-S | | 0.015 | 0.42 | 3.06 | 0.022 | 0.0007 | 1.94 | 21.0 | 0.169 | 0.020 | 0.0019 | 0.30 | REM:0.150 | 0.0042 | 23.7 | 0.45 |
| 1-T | | 0.023 | 0.38 | 2.98 | 0.024 | 0.0006 | 2.15 | 21.3 | 0.165 | 0.072 | 0.0022 | 0.05 | | 0.0018 | 23.9 | 1.22 |
| 1-U | | 0.023 | 0.39 | 2.99 | 0.023 | 0.0006 | 2.18 | 21.1 | 0.078 | 0.024 | 0.0021 | 0.06 | | 0.0036 | 22.3 | 0.58 |

**[0087]** For all the steels, firstly, a cast steel with a thickness of 100 mm was prepared, and the fracture reduction of area was evaluated. The evaluation was performed as follows. First, a parallel section of a round bar of 8 mmϕ was heated to 1200°C using a high frequency. Next, the temperature was lowered to a temperature (1000°C) at which a break test was performed. Tensile rupture was performed at a speed of 20 mm/second at this temperature, and the shrinkage of the cross section was measured. Steels where the fracture reduction of area was in a range of 70% or more were evaluated as A (good), steels where the reduction of area was in a range of 60% or more to less than 70% were evaluated as B (fair), steels where the reduction of area was in a range of less than 60% were evaluated as C (bad), and the results are given in Tables 5 and 6.

**[0088]** The cast steel was subjected to hot forging to obtain a semi-finished product with a thickness of 60 mm, and this semi-finished product was used as a hot-rolled material. The semi-finished product was heated to a predetermined temperature of 1150 to 1250°C, and then the hot rolling was performed using a two stage rolling machine in a laboratory under the following conditions. First, reduction was repeatedly performed so as to adjust the plate thickness to be 25 mm. Then, finishing rolling was performed from 1000°C, and the final finishing rolling was carried out at 900°C. This rolling was performed such that the final plate thickness became 12 mm and the plate width became 120 mm to obtain a hot-rolled steel plate. The maximum lengths of the edge crackings which were generated in the left and right edge sections of the obtained hot-rolled steel plate were measured, and the sum of the maximum lengths of the edge crackings in the left and right edge sections was determined. Steels where the sum of the edge crackings was in a range of less than 5 mm were evaluated as A (good), steels where the sum of the edge crackings was in a range of 5 to 10 mm were evaluated as B (fair), steels where the sum of the edge crackings exceeds 10 mm were evaluated as C (bad), and the results are given in Tables 5 and 6.

**[0089]** Furthermore, the steel plates were subjected to a solutionizing heat treatment in the following manner. The steel plate was inserted into a heat treatment furnace at 1000°C and heated for approximately 5 minutes. Next, the steel plate was taken out, and then was subjected to water cooling to room temperature.

**[0090]** The corrosion resistance of the steel plate was evaluated by the corrosion rate in sulfuric acid.

**[0091]** The corrosion rate in the sulfuric acid was measured as follows. Test pieces of 3 mm thick × 25 mm wide × 25 mm long were subjected to an immersion test for 6 hours in boiling 5% sulfuric acid. The weight before and after immersion was measured, and the rate of decrease in weight was calculated. Steels where the corrosion rate in the sulfuric acid was in a range of less than 0.3 g/m$^2$ per hour were evaluated as A (good), steels where the corrosion rate in the sulfuric acid was in a range of 0.3 to 1 g/m$^2$ per hour were evaluated as B (fair), steels where the corrosion rate in the sulfuric acid was in a range of 1 g/m$^2$ per hour or more were evaluated as C (bad), and the evaluation results are given in Tables 5 and 6.

**[0092]** The impact characteristics were measured using Charpy test pieces which were taken a long in the width direction. The test pieces were prepared by processing 2 mm V notches at full size in the rolling direction. Testing was carried out at -20°C using two test pieces for each of the steels, and the impact characteristics were evaluated by the average values of the obtained impact values. Steels where the impact value was in a range of more than 100 J/cm$^2$ were evaluated as A (good), steels where the impact value was in a range of 50 to 100 J/cm$^2$ were evaluated as B (fair), steels where the impact value was less than 50 J/cm$^2$ were evaluated as C (bad), and the evaluation results are given in Tables 5 and 6.

Table 5

| | Steel No. | Reduction of Area of Cast Steel | Edge Cracking Resistance of Steel Material | Sulfuric Acid Resistance of Steel Material | Impact Characteristics of Steel Material |
|---|---|---|---|---|---|
| Invention Examples | 1-1 | A | A | A | A |
| | 1-2 | A | A | A | A |
| | 1-3 | A | A | A | A |
| | 1-4 | A | A | A | A |
| | 1-5 | A | A | A | A |
| | 1-6 | A | A | A | A |
| | 1-7 | A | A | A | A |
| | 1-8 | A | A | A | A |
| | 1-9 | A | A | A | A |
| | 1-10 | A | A | A | A |
| | 1-11 | A | A | A | A |
| | 1-12 | A | A | A | A |
| | 1-13 | A | A | A | A |
| | 1-14 | A | A | A | A |
| | 1-15 | A | A | A | A |
| | 1-16 | A | A | A | A |
| | 1-17 | A | A | A | A |
| | 1-18 | A | A | A | A |
| | 1-19 | A | A | A | A |
| | 1-20 | A | A | A | A |
| | 1-21 | A | A | A | A |
| | 1-22 | A | A | A | A |
| | 1-23 | A | A | A | A |
| | 1-24 | A | A | A | A |
| | 1-25 | A | A | A | A |
| | 1-26 | A | A | A | A |
| | 1-27 | A | A | A | A |
| | 1-28 | A | A | A | A |
| | 1-29 | A | A | A | A |
| | 1-30 | A | A | A | A |
| | 1-31 | A | A | A | A |
| | 1-32 | A | A | A | A |
| | 1-33 | A | A | A | A |

Table 6

| | Steel No. | Reduction of Area of Cast Steel | Edge Cracking Resistance of Steel Material | Sulfuric Acid Resistance of Steel Material | Impact Characteristics of Steel Material |
|---|---|---|---|---|---|
| Comparative Examples | 1-A | C | C | A | A |
| | 1-B | B | C | A | A |
| | 1-C | A | A | B | A |
| | 1-D | C | C | A | B |
| | 1-E | C | C | A | A |
| | 1-F | B | B | A | B |
| | 1-G | A | A | A | B |
| | 1-H | B | C | B | A |
| | 1-I | C | C | A | B |
| | 1-J | C | C | A | A |
| | 1-K | C | C | C | C |
| | 1-L | C | C | C | A |
| | 1-M | C | C | A | A |
| | 1-N | C | B | A | C |
| | 1-O | B | B | A | C |
| | 1-P | B | B | A | C |
| | 1-Q | B | B | A | C |
| | 1-R | B | B | A | B |
| | 1-S | C | C | A | B |
| | 1-T | B | B | A | C |
| | 1-U | A | A | A | C |

**[0093]** From the examples which are shown in Table 5 and 6, steels No. 1-1 to 1-33 which satisfy the conditions of the first embodiment have favorable hot manufacturability, corrosion resistance, and impact characteristics. On the other hand, the steels No. 1-A to 1-U which do not satisfy the conditions of the first embodiment were inferior in all of hot manufacturability, corrosion resistance, and impact characteristics.

**[0094]** As seen from the above examples, it is clear that it is possible to obtain an inexpensive alloy-saving type duplex stainless steel with favorable hot manufacturability where the corrosion resistance is improved by the addition of Sn according to the first embodiment.

(Example 2)

**[0095]** Description will be given of examples of the general-purpose duplex stainless steel below. The chemical compositions of the test steels are shown in Tables 7 to 10. Here, the remainder other than the components which are described in Tables 7 to 10 is Fe and inevitable impurity elements. In addition, for the components which are shown in Tables 7 to 10, portions where the amounts are not described show the impurity levels. REM indicates lanthanoid rare earth elements and the amount of REM shows the total of these elements. The numbers which are underlined in the table indicate values outside of the ranges which are defined in the second embodiment.

Table 7

| Steel No. | | C | Si | Mn | P | S | Cr | Ni | Co | N | Al | Ca | Cu | Sn | Other | O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-1 | Invention Examples | 0.015 | 0.39 | 2.45 | 0.022 | 0.0005 | 26.5 | 4.48 | | 0.254 | 0.015 | 0.0021 | 1.43 | 0.07 | | 0.0038 |
| 2-2 | | 0.012 | 0.35 | 3.25 | 0.021 | 0.0007 | 27.3 | 4.83 | 0.65 | 0.235 | 0.023 | 0.0016 | 1.52 | 0.08 | | 0.0032 |
| 2-3 | | 0.021 | 0.42 | 3.45 | 0.023 | 0.0004 | 25.3 | 4.05 | 0.12 | 0.253 | 0.018 | 0.0018 | 1.03 | 0.05 | Mo:1.23 | 0.0034 |
| 2-4 | | 0.024 | 0.22 | 3.65 | 0.023 | 0.0005 | 23.5 | 2.35 | 0.32 | 0.245 | 0.025 | 0.0023 | 1.53 | 0.13 | Mo:1.75 | 0.0028 |
| 2-5 | | 0.023 | 0.53 | 1.52 | 0.024 | 0.0002 | 26.4 | 4.52 | 0.01 | 0.265 | 0.003 | 0.0021 | 0.52 | 0.14 | W:0.35 | 0.0038 |
| 2-6 | | 0.016 | 0.65 | 2.43 | 0.025 | 0.0006 | 25.1 | 3.85 | 0.23 | 0.245 | 0.016 | 0.0015 | 1.53 | 0.06 | Mo:1.25, W:0.24 | 0.0042 |
| 2-7 | | 0.007 | 0.24 | 0.25 | 0.021 | 0.0005 | 26.5 | 4.03 | 0.53 | 0.246 | 0.012 | 0.0016 | 1.45 | 0.07 | V:0.12 | 0.0043 |
| 2-8 | | 0.026 | 0.74 | 3.35 | 0.023 | 0.0006 | 26.5 | 4.53 | 0.24 | 0.224 | 0.017 | 0.0017 | 1.23 | 0.08 | Nb:0.034 | 0.0038 |
| 2-9 | | 0.015 | 0.44 | 2.56 | 0.031 | 0.0005 | 26.4 | 4.52 | 0.21 | 0.236 | 0.021 | 0.0023 | 1.52 | 0.13 | Ti:0.007 | 0.0032 |
| 2-10 | | 0.014 | 0.42 | 2.75 | 0.033 | 0.0005 | 26.6 | 4.51 | 0.23 | 0.245 | 0.022 | 0.0021 | 1.48 | 0.09 | V:0.07, Nb:0.024 | 0.0037 |
| 2-11 | | 0.023 | 0.39 | 3.21 | 0.015 | 0.0004 | 26.4 | 4.36 | 0.85 | 0.234 | 0.028 | 0.0013 | 1.03 | 0.10 | Nb:0.047, Ti:0.011 | 0.0028 |
| 2-12 | | 0.022 | 0.36 | 2.35 | 0.034 | 0.0006 | 26.3 | 4.42 | 0.03 | 0.253 | 0.013 | 0.0024 | 0.95 | 0.08 | V:0.13, Nb:0.015, Ti:0.005 | 0.0034 |
| 2-13 | | 0.025 | 0.35 | 2.64 | 0.026 | 0.0005 | 23.8 | 3.85 | 0.15 | 0.238 | 0.024 | 0.0023 | 1.05 | 0.12 | Mo:1.52, V:0.12 | 0.0040 |
| 2-14 | | 0.018 | 0.31 | 2.48 | 0.024 | 0.0009 | 25.6 | 4.15 | 0.19 | 0.247 | 0.018 | 0.0019 | 1.12 | 0.08 | Mo:0.52, V:0.07, Nb:0.034 | 0.0042 |
| 2-15 | | 0.019 | 0.28 | 2.54 | 0.026 | 0.0007 | 26.4 | 4.62 | 0.06 | 0.265 | 0.023 | 0.0022 | 1.33 | 0.06 | B:0.0023 | 0.0044 |
| 2-16 | | 0.013 | 0.33 | 2.53 | 0.024 | 0.0006 | 26.6 | 4.58 | 0.14 | 0.267 | 0.021 | 0.0024 | 1.22 | 0.07 | Mg:0.0012 | 0.0031 |

Table 8

| Steel No. | | C | Si | Mn | P | S | Cr | Ni | Co | N | Al | Ca | Cu | Sn | Other | O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-17 | Invention Examples | 0.024 | 0.37 | 2.54 | 0.025 | 0.0005 | 26.4 | 4.05 | 0.51 | 0.258 | 0.028 | 0.0023 | 1.45 | 0.06 | REM:0.035 | 0.0034 |
| 2-18 | | 0.025 | 0.45 | 2.56 | 0.023 | 0.0005 | 26.5 | 4.45 | 0.25 | 0.265 | | 0.0021 | 1.03 | 0.07 | B:0.0026, Mg:0.0007 | 0.0048 |
| 2-19 | | 0.027 | 0.51 | 2.51 | 0.025 | 0.0005 | 24.8 | 4.01 | 0.15 | 0.244 | 0.016 | 0.0025 | 1.49 | 0.05 | Mo:1.23, V:0.12, B:0.0031, Mg:0.0005 | 0.0036 |
| 2-20 | | 0.022 | 0.23 | 2.58 | 0.024 | 0.0005 | 23.3 | 3.52 | 0.36 | 0.228 | 0.026 | 0.0017 | 0.99 | 0.07 | Mo:1.36, W:0.75, V:0.06, Ti:0.004, B:0.0026 | 0.0035 |
| 2-21 | | 0.011 | 0.26 | 2.48 | 0.023 | 0.0004 | 25.0 | 4.49 | 0.13 | 0.240 | 0.018 | 0.0022 | 1.05 | 0.06 | Mo:1.22, V:0.13, Nb:0.045, Ti:0.004, B:0.0024, Mg:0.0001 | 0.0034 |
| 2-22 | | 0.016 | 0.12 | 2.36 | 0.025 | 0.0006 | 25.0 | 4.00 | 0.12 | 0.242 | 0.024 | 0.0023 | 1.48 | 0.02 | Mo:1.35, V:0.12, Nb:0.015, Ti:0.006, B:0.0023, Mg:0.0003 | 0.0035 |

Table 9

| Steel No. | | C | Si | Mn | P | S | Cr | Ni | Co | N | Al | Ca | Cu | Sn | Other | O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-23 | Invention Examples | 0.024 | 0.46 | 2.44 | 0.026 | 0.0005 | 25.3 | 4.23 | 0.16 | 0.248 | 0.023 | 0.0025 | 1.46 | 0.05 | Mo:1.02, W:0.32, V:0.10, Nb:0.021, Ti:0.005, B:0.0024, Mg:0.002 | 0.0042 |
| 2-A | Comparative Examples | 0.016 | 0.37 | 2.13 | 0.022 | 0.0006 | 25.6 | 3.25 | | 0.246 | 0.023 | 0.0008 | 2.85 | 0.12 | | 0.0042 |
| 2-B | | 0.013 | 0.41 | 2.65 | 0.027 | 0.0008 | 25.4 | 3.24 | 0.05 | 0.273 | 0.021 | 0.0014 | 2.23 | 0.24 | | 0.0035 |
| 2-C | | 0.015 | 0.40 | 3.01 | 0.025 | 0.0006 | 25.1 | 4.00 | 0.10 | 0.251 | 0.016 | 0.0021 | 0.05 | 0.10 | | 0.0037 |
| 2-D | | 0.014 | 0.40 | 2.99 | 0.025 | 0.0006 | 25.0 | 4.02 | 0.10 | 0.249 | 0.017 | 0.0020 | 0.50 | | | 0.0036 |
| 2-E | | 0.036 | 0.39 | 2.98 | 0.024 | 0.0005 | 24.8 | 3.98 | 0.10 | 0.248 | 0.026 | 0.0021 | 0.47 | 0.04 | | 0.0033 |
| 2-F | | 0.015 | 1.26 | 3.02 | 0.024 | 0.0007 | 26.8 | 3.88 | 0.10 | 0.233 | 0.026 | 0.0017 | 0.49 | 0.06 | | 0.0028 |
| 2-G | | 0.014 | 0.42 | 5.12 | 0.025 | 0.0005 | 25.1 | 3.87 | 0.11 | 0.256 | 0.020 | 0.0020 | 0.48 | 0.05 | | 0.0043 |
| 2-H | | 0.016 | 0.41 | 2.97 | 0.062 | 0.0005 | 26.5 | 3.76 | 0.09 | 0.232 | 0.014 | 0.0015 | 0.48 | 0.08 | | 0.0040 |
| 2-I | | 0.016 | 0.43 | 2.98 | 0.024 | 0.0013 | 26.3 | 4.04 | 0.12 | 0.255 | 0.013 | 0.0015 | 0.52 | 0.07 | | 0.0041 |
| 2-J | | 0.012 | 0.45 | 2.42 | 0.026 | 0.0006 | 29.1 | 4.53 | 0.08 | 0.262 | 0.018 | 0.0020 | 0.53 | 0.09 | | 0.0051 |
| 2-K | | 0.013 | 0.39 | 2.89 | 0.024 | 0.0007 | 24.9 | 1.78 | 0.35 | 0.249 | 0.019 | 0.0018 | 0.55 | 0.06 | | 0.0038 |
| 2-L | | 0.016 | 0.42 | 2.51 | 0.025 | 0.0008 | 24.9 | 3.98 | 1.35 | 0.244 | 0.018 | 0.0023 | 1.02 | 0.08 | | 0.0045 |
| 2-M | | 0.014 | 0.38 | 2.47 | 0.025 | 0.0006 | 25.0 | 3.42 | 0.06 | 0.321 | 0.015 | 0.0016 | 0.49 | 0.05 | | 0.0052 |
| 2-N | | 0.015 | 0.42 | 2.42 | 0.023 | 0.0007 | 24.8 | 4.02 | 0.07 | 0.253 | 0.062 | 0.0022 | 0.52 | 0.06 | | 0.0042 |
| 2-O | | 0.015 | 0.39 | 2.52 | 0.024 | 0.0007 | 24.9 | 4.01 | 0.09 | 0.245 | 0.008 | 0.0012 | 0.50 | 0.06 | | 0.0053 |
| 2-P | | 0.014 | 0.40 | 2.46 | 0.023 | 0.0006 | 25.0 | 3.99 | 0.10 | 0.246 | 0.007 | 0.0021 | 3.53 | 0.11 | | 0.0044 |

Table 10

| Steel No. | | C | Si | Mn | P | S | Cr | Ni | Co | N | Al | Ca | Cu | Sn | Other | O |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Q | Comparative Examples | 0.015 | 0.40 | 2.50 | 0.025 | 0.0007 | 25.0 | 4.00 | 0.09 | 0.251 | 0.021 | 0.0021 | 0.04 | | Mo:1.02 | 0.0038 |
| 2-R | | 0.014 | 0.39 | 2.48 | 0.026 | 0.0006 | 24.8 | 4.02 | 0.12 | 0.246 | 0.019 | 0.0017 | 0.03 | 0.02 | Mo:0.52, V:0.06, B:0.0021 | 0.0043 |
| 2-S | | 0.016 | 0.41 | 2.52 | 0.025 | 0.0005 | 25.1 | 2.35 | 0.01 | 0.265 | 0.018 | 0.0023 | 1.83 | 0.16 | Mo:0.48, W:0.12, Nb:0.012, Ti:0.006, B:0.0023 | 0.0033 |
| 2-T | | 0.014 | 0.42 | 2.49 | 0.026 | 0.0006 | 25.1 | 4.03 | 0.03 | 0.262 | 0.023 | 0.0048 | 1.02 | 0.07 | Mo:0.32 | 0.0032 |
| 2-U | | 0.013 | 0.48 | 1.65 | 0.024 | 0.0006 | 22.5 | 5.83 | | 0.178 | 0.013 | 0.0023 | 0.05 | | Mo:3.03 | 0.0035 |

**[0096]** Under the same conditions as Example 1, the manufacturing of the cast steel, the evaluation of the fracture reduction of area of the cast steel, the manufacturing of the hot-rolled material, the performing of the hot rolling with respect to the hot-rolled material, and the evaluation of the edge cracking were performed. The obtained evaluation results are given in Tables 11 and 12.

**[0097]** Furthermore, the steel plates were subjected to a solutionizing heat treatment in the following manner. The steel plate was inserted into a heat treatment furnace at 1050°C and heated for approximately 5 minutes. Next, the steel plate was taken out, and then was subjected to water cooling to room temperature.

**[0098]** The corrosion resistance of the steel plate was evaluated by the corrosion rate in the sulfuric acid.

**[0099]** The corrosion rate in the sulfuric acid was measured as follows. Test pieces of 3 mm thick × 25 mm wide × 25 mm long, were subjected to an immersion test for 6 hours in sulfuric acid including 2000 ppm of Cl ions, where the concentration was 15% and the temperature was 40%. The weight before and after immersion was measured, and the rate of decrease in weight was calculated. Steels where the corrosion rate in the sulfuric acid was in a range of less than 0.1 g/m$^2$ per hour were evaluated as A (good), steels where the corrosion rate in the sulfuric acid was in a range of 0.1 to 0.3 g/m$^2$ per hour were evaluated as B (fair), steels where the corrosion rate in the sulfuric acid was in a range of more than 0.3 g/m$^2$ per hour were evaluated as C (bad), and the evaluation results are given in Tables 11 and 12.

**[0100]** Under the same conditions as Example 1, the impact characteristics were measured. The obtained evaluation results are given in Tables 11 and 12.

Table 11

| | Steel No. | Ni+ Co | Ca/O | PI | Reduction of Area of Cast Steel | Edge Cracking Resistance of Steel Material | Sulfuric Acid Resistance of Steel Material | Impact Characteristics of Steel Material |
|---|---|---|---|---|---|---|---|---|
| Invention Examples | 2-1 | 4.48 | 0.55 | 30.6 | A | A | A | A |
| | 2-2 | 5.48 | 0.50 | 31.1 | A | A | A | A |
| | 2-3 | 4.17 | 0.53 | 33.4 | A | A | A | A |
| | 2-4 | 2.67 | 0.82 | 33.2 | A | A | A | A |
| | 2-5 | 4.53 | 0.55 | 30.6 | A | A | A | A |
| | 2-6 | 4.08 | 0.36 | 33.1 | A | A | A | A |
| | 2-7 | 4.56 | 0.37 | 30.4 | A | A | A | A |
| | 2-8 | 4.77 | 0.45 | 30.1 | A | A | A | A |
| | 2-9 | 4.73 | 0.72 | 30.2 | A | A | A | A |
| | 2-10 | 4.74 | 0.57 | 30.5 | A | A | A | A |
| | 2-11 | 5.21 | 0.46 | 30.1 | A | A | A | A |
| | 2-12 | 4.45 | 0.71 | 30.3 | A | A | A | A |
| | 2-13 | 4.00 | 0.58 | 32.6 | A | A | A | A |
| | 2-14 | 4.34 | 0.45 | 31.3 | A | A | A | A |
| | 2-15 | 4.68 | 0.50 | 30.6 | A | A | A | A |
| | 2-16 | 4.72 | 0.77 | 30.9 | A | A | A | A |
| | 2-17 | 4.56 | 0.68 | 30.5 | A | A | A | A |
| | 2-18 | 4.70 | 0.44 | 30.7 | A | A | A | A |
| | 2-19 | 4.16 | 0.69 | 32.8 | A | A | A | A |
| | 2-20 | 3.88 | 0.49 | 31.4 | A | A | A | A |
| | 2-21 | 4.62 | 0.65 | 32.9 | A | A | A | A |
| | 2-22 | 4.12 | 0.66 | 33.3 | A | A | A | A |
| | 2-23 | 4.39 | 0.60 | 32.6 | A | A | A | A |

Table 12

| | Steel No. | Ni+Co | Ca/O | PI | Reduction of Area of Cast Steel | Edge Cracking Resistance of Steel Material | Sulfuric Acid Resistance of Steel Material | Impact Characteristics of Steel Material |
|---|---|---|---|---|---|---|---|---|
| Comparative Examples | 2-A | 3.25 | 0.19 | 29.5 | C | C | A | A |
| | 2-B | 3.29 | 0.40 | 29.8 | C | C | A | A |
| | 2-C | 4.10 | 0.57 | 29.1 | A | A | C | A |
| | 2-D | 4.12 | 0.56 | 29.0 | A | A | C | A |
| | 2-E | 4.08 | 0.64 | 28.8 | A | A | B | B |
| | 2-F | 3.98 | 0.61 | 30.5 | A | A | A | C |
| | 2-G | 3.98 | 0.47 | 29.2 | A | A | C | A |
| | 2-H | 3.85 | 0.38 | 30.2 | A | A | B | B |
| | 2-I | 4.16 | 0.37 | 30.4 | C | C | B | A |
| | 2-J | 4.61 | 0.39 | 33.3 | A | A | A | C |
| | 2-K | 2.13 | 0.47 | 28.9 | C | C | B | C |
| | 2-L | 5.33 | 0.51 | 28.8 | A | A | A | A |
| | 2-M | 3.48 | 0.31 | 30.1 | C | C | A | B |
| | 2-N | 4.09 | 0.52 | 28.8 | A | A | A | C |
| | 2-O | 4.10 | 0.23 | 28.8 | C | C | A | B |
| | 2-P | 4.09 | 0.48 | 28.9 | C | C | A | B |
| | 2-Q | 4.09 | 0.55 | 32.4 | A | A | C | A |
| | 2-R | 4.14 | 0.40 | 30.5 | A | A | C | A |
| | 2-S | 2.36 | 0.70 | 30.9 | C | C | A | A |
| | 2-T | 4.06 | 1.50 | 30.3 | B | B | B | B |
| | 2-U | 5.83 | 0.66 | 35.4 | A | A | A | A |

**[0101]** From the examples which are shown in Table 11 and 12, the general-purpose duplex stainless steels No. 2-1 to 2-23 which satisfy the conditions of the second embodiment have favorable hot manufacturability, corrosion resistance, and impact characteristics. On the other hand, steels No. 2-A to 2-K and 2-M to 2-T which do not satisfy the conditions of the second embodiment were inferior in hot manufacturability, corrosion resistance, and impact characteristics. In addition, comparative example 2-L satisfied the characteristics; however, since a large amount of Co was contained, comparative example 2-L was inferior in terms of cost. In addition, comparative example 2-U is S31803 steel and is favorable in all of hot manufacturability, corrosion resistance, and manufacturability. However, the amounts of Ni and Mo are high and comparative example 2-U is inferior in terms of cost for the purpose of the second embodiment.

**[0102]** As seen from the above examples, it is clear that it is possible to obtain an inexpensive general-purpose duplex stainless steel with favorable hot manufacturability where the corrosion resistance is improved due to the addition of Sn and Cu according to the second embodiment.

Industrial Applicability

**[0103]** According to the first and second embodiments, it is possible to provide an alloy-saving type duplex stainless steel and a general-purpose duplex stainless steel which are inexpensive and where the corrosion resistance is improved. These duplex stainless steel materials make an extremely significant contribution to industries because it is possible to use the duplex stainless steel materials in seawater desalination unit, tanks for a transport ship, various types of containers, or the like.

## Claims

**1.** A duplex stainless steel comprising, in mass%:

C: 0.03% or less;
Si: 0.05% to 1.0%;
Mn: 0.1% to 7.0%;
P: 0.05% or less;
S: 0.0001% to 0.0010%;
Ni: 0.5% to 5.0%;
Cr: 18.0% to 25.0%;
N: 0.10% to 0.30%;
Al: 0.05% or less;
Ca: 0.0010% to 0.0040%; and
Sn: 0.01% to 0.2%,
with the remainder being Fe and inevitable impurities,
wherein a ratio Ca/O of the amounts of Ca and O is in a range of 0.3 to 1.0, and
a pitting index PI shown by formula (1) is in a range of less than 30,
PI=Cr+3.3Mo+16N (1),
(the chemical symbols in the formula (1) indicate the amounts of the elements).

**2.** The duplex stainless steel according to Claim 1 further comprising:

one or more selected from
Mo: 1.5% or less,
Cu: 2.0% or less,
W: 1.0% or less, and
Co: 2.0% or less.

**3.** The duplex stainless steel according to Claim 1 or 2, further comprising:

one or more selected from V: 0.05% to 0.5%,
Nb: 0.01% to 0.20%, and
Ti: 0.003% to 0.05%.

**4.** The duplex stainless steel according to any one of Claims 1 to 3, further comprising:

one or more selected from
B: 0.0050% or less,
Mg: 0.0030% or less, and
REM: 0.10% or less.

**5.** A duplex stainless steel comprising, in mass%:

C: 0.03% or less;
Si: 0.05% to 1.0%;
Mn: 0.1 % to 4.0%;
P: 0.05% or less;
S: 0.0001% to 0.0010%;
Cr: 23.0% to 28.0%;
Ni: 2.0% to 6.0%;
Co: 0% to 1.0%;
Cu: 0.2% to 3.0%;
Sn: 0.01% to 0.2%;
N: 0.20% to 0.30%;
Al: 0.05% or less; and
Ca: 0.0010% to 0.0040%,
with the remainder being Fe and inevitable impurities,

wherein Ni+Co is in a range of 2.5% or more and a ratio Ca/O of the amounts of Ca and O is in a range of 0.3 to 1.0, and
PI shown by formula (1) is in a range of 30 or more to less than 40,

$$PI=Cr+3.3Mo+16N \quad (1),$$

(the chemical symbols in the formula (1) indicate the amounts of the elements).

**6.** The duplex stainless steel according to Claim 5, further comprising:

either one or both of
Mo: 2.0% or less, and
W: 1.0% or less.

**7.** The duplex stainless steel according to Claim 5 or 6, further comprising:

one or more selected from
V: 0.05% to 0.5%,
Nb: 0.01% to 0.15%, and
Ti: 0.003% to 0.05%.

**8.** The duplex stainless steel according to any one of Claims 5 to 7, further comprising:

one or more selected from
B: 0.0050% or less,
Mg: 0.0030% or less, and
REM: 0.10% or less.

**9.** A cast steel of a duplex stainless steel which has a composition according to any one of Claims I to 8, wherein a fracture reduction of area at 1000°C is in a range of 70% or more.

**10.** A duplex stainless steel material which is manufactured by hot working the cast steel of the duplex stainless steel according to Claim 9.

FIG. 1

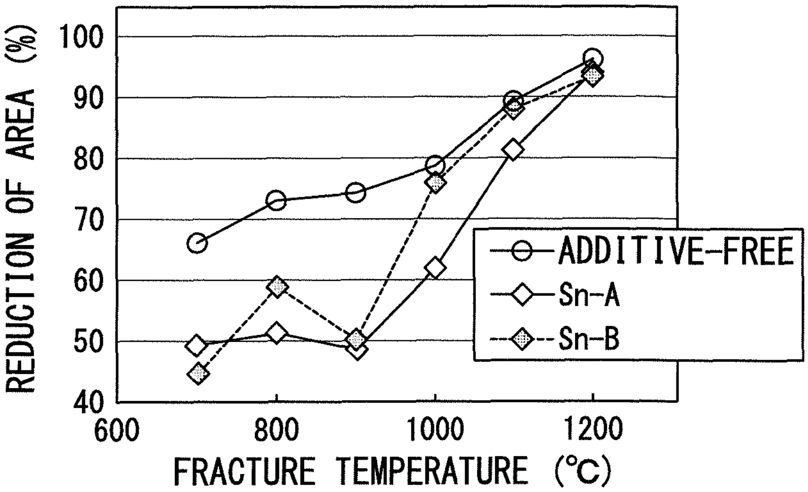

REDUCTION OF AREA (%)
100
90
80
70
60
50
40
600
800
1000
1200
FRACTURE TEMPERATURE (°C)
ADDITIVE-FREE
Sn-A
Sn-B

FIG. 2

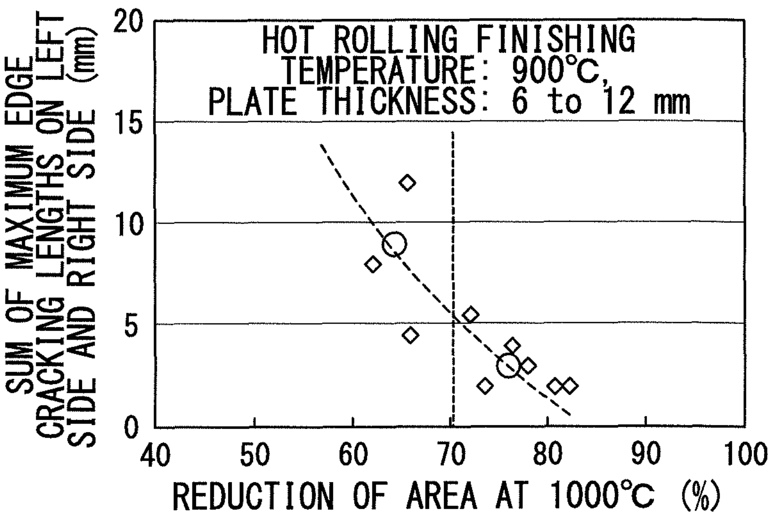
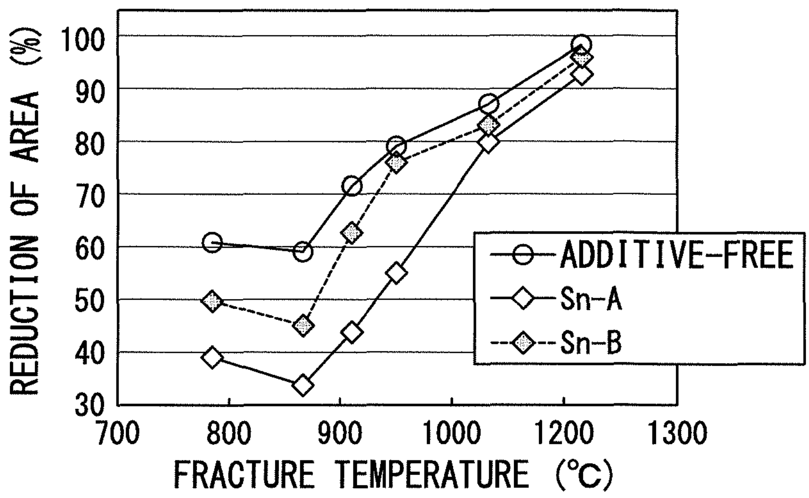
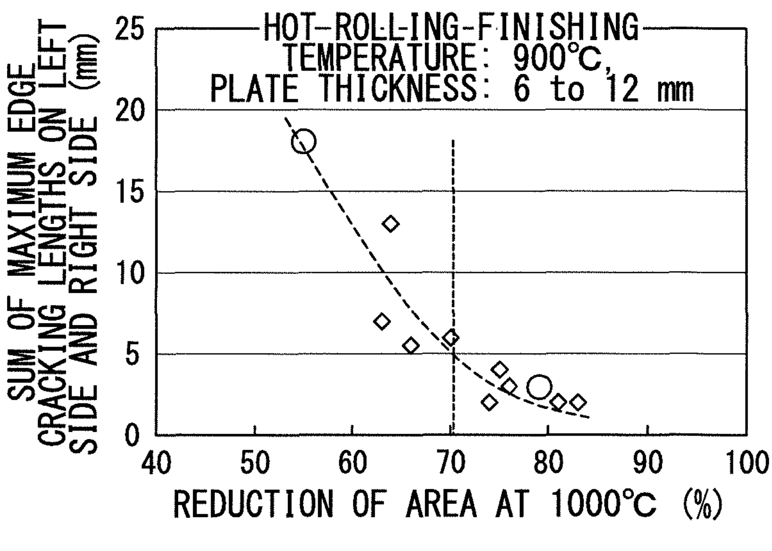

SUM OF MAXIMUM EDGE CRACKING LENGTHS ON LEFT SIDE AND RIGHT SIDE (mm)
20
15
10
5
0
40
50
60
70
80
90
100
REDUCTION OF AREA AT 1000°C (%)
HOT ROLLING FINISHING
TEMPERATURE: 900°C,
PLATE THICKNESS: 6 to 12 mm

FIG. 3



REDUCTION OF AREA (%)
100
90
80
70
60
50
40
30
700
800
900
1000
1200
1300
FRACTURE TEMPERATURE (°C)
ADDITIVE-FREE
Sn-A
Sn-B


FIG. 4



HOT-ROLLING-FINISHING TEMPERATURE: 900°C,
PLATE THICKNESS: 6 to 12 mm
SUM OF MAXIMUM EDGE CRACKING LENGTHS ON LEFT SIDE AND RIGHT SIDE (mm)
25
20
15
10
5
0
40
50
60
70
80
90
100
REDUCTION OF AREA AT 1000°C (%)

## INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2012/076821

A. CLASSIFICATION OF SUBJECT MATTER
*C22C38/00*(2006.01)i, *C22C38/58*(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C22C38/58

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 | 1996-2012 |
| Kokai Jitsuyo Shinan Koho | 1971-2012 | Toroku Jitsuyo Shinan Koho | 1994-2012 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 2009/119895 A1 (Nippon Steel & Sumikin Stainless Steel Corp.), 01 October 2009 (01.10.2009), claims; tables 1 to 4 & US 2011/0097234 A1 & EP 2258885 A1 & CN 101981216 A & KR 10-2010-0113642 A | 1-10 |
| A | WO 2003/080886 A1 (PARK, Yong-Soo), 02 October 2003 (02.10.2003), claims; table 1 & JP 2005-520934 A & US 2005/0158201 A1 & EP 1495150 B1 & EP 1803832 A1 & DE 60313763 T2 & CN 1643176 A & KR 10-2003-0077239 A & AU 2003221202 A1 | 1-10 |

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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 25 December, 2012 (25.12.12) | 08 January, 2013 (08.01.13) |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Japanese Patent Office | |
| Facsimile No. | Telephone No. |

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2012/076821

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 6-200353 A (Nippon Steel Corp.), 19 July 1994 (19.07.1994), claims; tables 1 to 2 (Family: none) | 1-10 |
| P,A | WO 2012/121380 A1 (Nippon Steel & Sumikin Stainless Steel Corp.), 13 September 2012 (13.09.2012), claims; table 1 & JP 2012-197509 A | 1-10 |

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## REFERENCES CITED IN THE DESCRIPTION

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- Effect of Cu and Ni on Hot Workability of Hot-rolled Mild Steel. *ISIJ,* 1997, vol. 37, 217-223 **[0011]**