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(54) **DUPLEX STAINLESS STEEL**

(57) A duplex stainless steel having excellent pitting resistance and weldability and particularly a duplex stainless steel which does not form minute intermetallic compounds even in a weld heat affected zone is provided.

It has a chemical composition comprising C: at most 0.03%, Si: at most 1.0%, Mn: at most 1.5%, P: at most 0.040%, S: at most 0.008%, Cr: 23.0 - 27.0%, Mo: 2.0 - 4.0%, Ni: 5.0 - 9.0%, W: greater than 1.5% up to 5.0%, N : 0.24 - 0.35%, and a remainder of Fe and impurities and satisfying the relationships

$$PREW = Cr + 3.3(Mo + 0.5W) + 16N \text{ is at least } 40 \text{ and}$$

$$Mo + 1.1Ni \leq 12.5$$

$$Mo - 0.8Ni \leq -1.6$$

wherein the number of coarse inclusions having the following definition observed in a cross section is at most 10 per mm².

Here, coarse inclusions are defined as inclusions containing at least 20 mass % of Al and having a major diameter of at least 5 micrometers.

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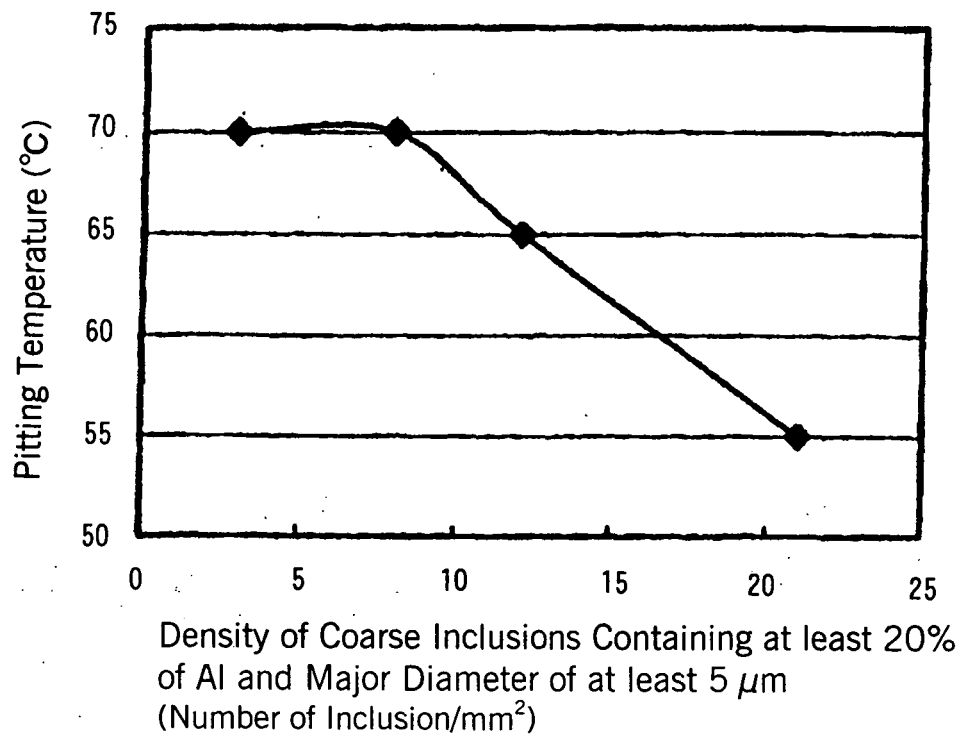


Fig. 1

Description

Technical Field

5 **[0001]** This invention relates to a duplex stainless steel and particularly to a duplex stainless steel having excellent weldability and pitting resistance.

Background Art

10 **[0002]** Duplex stainless steels have excellent strength and corrosion resistance and particularly resistance to corrosion in sea water, and they have long been used in a wide range of technical fields of steel pipes for use in heat exchangers and the like. In the past, there have been many proposals for compositions of duplex stainless steels having improved corrosion resistance, strength, workability, and the like.

15 **[0003]** For example, Japanese Published Unexamined Patent Application Hei 5-132741 discloses a high-strength duplex stainless steel including 1.5 - 5 mass % of W and in which PREW [PREW = Cr + 3.3(Mo + 0.5W) + 16N] is at least 40. Since a large amount of W is added, corrosion resistance is enormously increased, and deterioration of mechanical properties and corrosion resistance due to precipitation of intermetallic compounds (sigma phases and the like) are small.

20 Disclosure of the Invention

[0004] Today, various types of welded structures are being widely used. When a duplex stainless steel is subjected to welding in a heat exchanger, a pump, or the like for use in a high-temperature sea water environment, for example, corrosion resistance and particularly pitting resistance are becoming a problem.

25 **[0005]** It has been found that minute sigma phases which are formed in the heat affected zones of welds become the starting points of pitting or the starting points of metal fatigue. As a result, it has been recognized that it is necessary to prevent the formation of such sigma phases in duplex stainless steel.

30 **[0006]** In order to suppress such minute sigma phases, it is conceivable to improve welding techniques by decreasing the welding heat input, for example. Although reducing welding heat input is certainly effective, when the heat input decreases, welding performance decreases. Under present-day conditions in which there is a strong demand for cost reductions, this cannot be described as a desirable solution.

[0007] Accordingly, there is a desire for improvement of duplex stainless steels themselves.

35 **[0008]** The object of the present invention is to provide a duplex stainless steel having excellent pitting resistance and weldability and particularly a duplex stainless steel having excellent pitting resistance and weldability which does not form intermetallic compounds such as minute sigma phases even in a weld heat affected zone.

[0009] The present inventors performed various research with the goal of achieving the above described objects and they found the following.

[0010] Namely, there are two points to obtaining excellent corrosion resistance and particularly pitting resistance even in a weld heat affected zone.

40 1) Suppressing the formation of intermetallic compounds referred to as sigma phases in the weld heat affected zone, and

2) Suppressing the formation of coarse precipitates in the form of nitrides in the weld heat affected zone.

45 **[0011]** With a structure which is obtained by rapid heating and rapid cooling in a short length of time such as occur in welding (referred to below simply as a "rapid heating/rapid cooling structure"), formation of sigma phases is controlled by the formation of sigma phase nuclei and growth of the nuclei. The present inventors found that the formation of sigma phase nuclei is suppressed by addition of around 2% of W, and that under these conditions, it also depends on the amount of Ni and Mo. Ni and Mo are essential elements for guaranteeing ordinary corrosion resistance such as resistance to crevice corrosion and pitting resistance.

50 **[0012]** In addition, the present inventors quantitatively elucidated the conditions for suppressing formation of sigma phase nuclei taking into consideration the degree of influence of each element as shown by the following Equation (1).

55
$$\text{Mo} + 1.1\text{Ni} \leq 12.5 \quad (1)$$

[0013] The metallurgical meaning of Equation (1) is as follows.

[0014] A sigma phase is an intermetallic compound having a composition in which the ratio of Cr to Fe is approximately 1:1, and in order to form sigma phase nuclei by heating during welding, for example, it is necessary to increase the concentration of Cr. Mo is not necessarily a main constituent element of sigma phases. However, when Mo is present, the activation energy for forming nuclei is reduced, even smaller embryo (the appearance of nuclei) are not eliminated, and stable nuclei are formed. At the sigma phases precipitation temperature, when Ni is present, a ferrite phase becomes unstable. As a result, the driving force of a reaction for transformation of ferrite phase into sigma phase and austenite phase is increased.

[0015] In this manner, Mo and Ni increase the nucleus forming potential of sigma phases. According to the research of the present inventors, the impact of Ni is 1.1 times that of Mo. Based on this knowledge, they solved for the value of the left side of Equation (1). The left side of Equation (1) is a parameter which describes the relative level of the nucleus forming frequency.

[0016] According to the present invention, by prescribing the contents of Ni and Mo so that this parameter is at most 12.5, the formation of sigma phases can be suppressed to a level which does not affect pitting resistance.

[0017] The formation of sigma phase nuclei is greatly affected by the presence of oxide inclusions in the parent metal. Sigma phases easily precipitate in a low temperature HAZ heated to a temperature of 700 - 1000 °C, which is a temperature range at least 400 °C lower than the melting point of steel. Here, a portion which is heated to just below the melting point of steel will be referred to as a high temperature HAZ, while a HAZ which is heated to a relatively low temperature will be referred to as a low temperature HAZ. Since the form of an austenite phase does not change in the temperature range of a low temperature HAZ, the formation of sigma phase nuclei is greatly affected by the presence of inclusions in the parent metal. Namely, at the border between inclusions and a steel matrix, the free energy is high, so nuclei having a reduced energy due to precipitation form easily.

[0018] As a result of considering all of the above, it was found that oxide type inclusions including Al, Mg, or Ca and particularly inclusions including Al have a particularly high surface energy, that coarse inclusions thereof above a certain size are harmful inclusions which promote sigma phase precipitation, and that reducing their density is effective at suppressing precipitation of sigma phases in a HAZ.

[0019] Figure 1 shows the relationship between the density of coarse inclusions having a major diameter of at least 5 micrometers and containing at least 20 mass % of Al in a HAZ and the temperature for the occurrence of pitting. The higher the temperature for the occurrence of pitting, the greater the temperature difference from the temperature of the ordinary environment of use (namely, room temperature), and a steel having a high temperature for the occurrence of pitting can be said to have high pitting resistance. With a conventional duplex stainless steel, the number of such alumina type coarse inclusions is at least 20 2 per mm .

[0020] From the results shown in Figure 1, it can be seen that a steel for which the density of alumina type inclusions is at most 10 per mm² has good corrosion resistance, but if the density exceeds 10 per mm², the temperature for the occurrence of pitting abruptly decreases.

[0021] According to Equation (1), if the amounts of Mo and Ni are decreased, the formation of sigma phase nuclei in a HAZ is suppressed, and it should be possible to obtain good pitting resistance due to the absence of sigma phases. However, if the amount of Ni is excessively decreased, in a high temperature HAZ which is heated to just below the melting point, the formation of nitrides is promoted. The formation of such nitrides causes pitting in the same manner as with the formation of sigma phases.

[0022] According to the present invention, the requirements for suppressing this are quantitatively shown by Equation (2).

$$\text{Mo} - 0.8\text{Ni} \leq -1.6 \quad (2)$$

[0023] The driving force for precipitation of nitrides depends upon the solid solubility of N and the speed of diffusion in the parent metal in a temperature range of at least 500 °C in which N can diffuse in a short period of time. Addition of Ni increases the temperature for the start of precipitation of an austenite phase which precipitates in the course of cooling from a state in which it has been heated to just below the melting point of a purely ferrite phase. Precipitation of austenite phase at a high temperature means that N present in a supersaturated state in a ferrite phase moves towards an austenite phase in which N has a high solid solubility, in a shorter period of time. This also promotes formation of austenite phase, and it effectively contributes to alleviating the degree of supersaturation of N in ferrite phase, which increases as cooling progresses. As a result, the precipitation of nitrides is suppressed.

[0024] However, when Mo is present, Mo lowers the temperature for the start of precipitation of austenite phase. According to the results of research by the present inventors, the degree of contribution to this by Mo is 0.8 times that of Ni. Based on this knowledge, the value of the left side of Equation (2) was determined. The left side of Equation (2)

is a parameter which describes the relative degree of supersaturation of N in a ferrite phase due to a change in the temperature at which austenite phase forms.

[0025] According to the present invention, by making this parameter at most -1.6 and suppressing formation of nitrides, the occurrence of pitting caused thereby can be nearly entirely suppressed.

[0026] Based on each of the above findings, it was found that by designing the components so as to satisfy the above Equations (1) and (2) and controlling oxide inclusions, a duplex stainless steel is obtained which has excellent corrosion resistance and particularly pitting resistance even in a HAZ and which does not form minute sigma phases and nitrides in a HAZ without a decrease in welding performance.

[0027] In order to perform such control of oxide inclusions in a parent metal, a new method different from that used in the past is necessary. Control is made possible by optimally combining the basicity of slag and the number of desulfurizations at the time of steel melting, the temperature and length of killing in a ladle, and the total degree of working after casting.

[0028] In the present invention as well, PREW is at least 40.

[0029] Here, the present invention is as follows.

(1) A duplex stainless steel characterized by having a chemical composition comprising, in mass percent, C: at most 0.03%, Si: at most 1.0%, Mn: at most 1.5%, P: at most 0.040%, S: at most 0.008%, Cr: 23.0 - 27.0%, Mo: 2.0 - 4.0%, Ni: 5.0 - 9.0%, W: greater than 1.5% and at most 5.0%, N: 0.24 - 0.35%, and a remainder of Fe and impurities and satisfying the relationship

$$\text{PREW} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N} \text{ is at least } 40$$

$$\text{Mo} + 1.1\text{Ni} \leq 12.5$$

$$\text{Mo} - 0.8\text{Ni} \leq -1.6$$

wherein the number of coarse inclusions defined as inclusions containing at least 20% of Al and having a major diameter of at least 5 micrometers observed in a cross section is at most 10 per mm².

(2) A duplex stainless steel as described above in (1) wherein the chemical composition further includes one or both of 0.2 - 2.0 mass % of Cu and 0.05 - 1.5 mass % of V.

(3) A duplex stainless steel as described above in (1) or (2) wherein the chemical composition further includes one or more of 0.0005 - 0.005 mass % of B and 0.0005 - 0.2 mass % of a rare earth element.

(4) A duplex stainless steel as described above in any of (1) - (3) wherein the chemical composition further includes at most 0.040% of sol. Al.

Brief Description of the Drawings

[0030]

Figure 1 is a graph showing the relationship between the density of oxide inclusions containing at least 20% of Al and having a major diameter of at least 5 micrometers and the temperature for the occurrence of pitting.

Figure 2 is a schematic view of oxide inclusions defining the major diameter of oxide inclusions and the location for measuring the composition thereof.

Best Form for Carrying Out the Invention

[0031] Next, the reasons why the chemical composition of a duplex stainless steel is limited in the above manner in the present invention will be explained. In this specification, % with respect to the chemical compositions of steel and inclusions means mass % unless otherwise specified.

[0032] A duplex stainless steel according to the present invention exhibits excellent weldability (maintaining pitting resistance without decreasing welding performance) by the overall effect of the above-described plurality of types of alloying elements and by control of the structure. However, the most significant characteristic resides in the combination

of optimum amounts of Ni and Mo and control of coarse alumina type inclusions.

[0033] C: In the same manner as described below with respect to N, C is effective at stabilizing an austenite phase. However, if its content exceeds 0.03%, carbides easily precipitate and corrosion resistance worsens, so it is made at most 0.03%. Preferably it is at most 0.02%. The present invention includes the case in which C is included as an impurity.

[0034] Si: Si is effective as a deoxidizing component of steel, but it is an element which promotes formation of inter-metallic compounds (sigma phases and the like), so in the present invention it is limited to at most 1.0%. Preferably it is at most 0.5%. The present invention includes the case in which Si is present as an impurity.

[0035] Mn: Mn increases hot workability by a desulfurization and deoxidation effect during preparation of a duplex stainless steel. It also has the effect of increasing the solubility of N. In order to obtain these effects, its content is normally up to 2.0%. However, Mn is an element which decreases corrosion resistance. In the present invention it is limited to at most 1.5%. Preferably it is at most 1.0%. The present invention includes the case in which Mn is contained as an impurity.

[0036] P: P is an impurity element which is unavoidably mixed into steel. If its content exceeds 0.040%, corrosion resistance and toughness markedly deteriorate, so its upper limit is made 0.040%.

[0037] S: S is an impurity element which is unavoidably mixed into steel and worsens the hot workability of steel. In addition, sulfides become the starting points of pitting and worsen pitting resistance. In order to avoid these adverse effects, its content is suppressed to at most 0.008%. It is preferably as small as possible at or below this level, and at most 0.005% is particularly preferred.

[0038] Cr: Cr is a fundamental component which is effective for maintaining corrosion resistance. If its content is less than 23.0%, a parent metal having the corrosion resistance of a so-called super duplex stainless steel is not obtained. On the other hand, if the Cr content exceeds 27.0%, precipitation of intermetallic compounds (sigma phases and the like) becomes marked, and this leads to a decrease in hot workability and a worsening of weldability.

[0039] Mo: In the same manner as Cr, Mo contributes to an increase in PREW, and it is a component which is extremely effective at improving corrosion resistance. Particularly in order to increase pitting resistance and resistance to crevice corrosion, its content is made at least 2.0% in the present invention. On the other hand, excessive addition of Mo becomes a cause of embrittlement of a material during manufacture, and in the same manner as Cr, it has a strong effect of facilitating precipitation of intermetallic compounds. Accordingly, the content of Mo is limited to 4.0%.

[0040] Ni: Ni is a component which is essential for stabilizing austenite. However, if its content exceeds 9.0%, due to a decrease in the amount of ferrite, it becomes difficult to guarantee the basic properties of a duplex stainless steel, and it becomes easy for sigma phases and the like to precipitate. On the other hand, if the Ni content is smaller than 5.0%, the amount of ferrite becomes too large, and in the same manner, the properties of a duplex stainless steel are not obtained. In addition, the solid solubility of N in ferrite is small, so nitrides precipitate and corrosion resistance worsens.

[0041] It is not sufficient to prescribe only the above ranges for Ni and Mo. As stated above, they are limited so as to satisfy below-described Equations (1) and (2) which are characteristics of the present invention.

$$\text{Mo} + 1.1\text{Ni} \leq 12.5 \quad (1)$$

$$\text{Mo} - 0.8\text{Ni} \leq -1.6 \quad (2)$$

[0042] In the above equations, Mo and Ni indicate the respective content (in mass %) of these elements.

[0043] If the value of (Mo + 1.1Ni) exceeds 12.5, minute sigma phases precipitate in a low temperature HAZ, and if the value of (Mo - 0.8Ni) exceeds -1.6, nitride precipitation occurs in a high temperature HAZ, so they are restricted to the above-described ranges.

[0044] The below-described pitting resistance index (PREW), which is a parameter indicating the corrosion resistance and particularly the resistance to corrosion in sea water of a duplex stainless steel, is made at least 40.

PREW (Pitting Resistance Equivalent after Welding)

$$= \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N}$$

[0045] In general, the contents of Cr, Mo, and N are adjusted so that PREW is at least 35. However, in a super duplex stainless steel according to the present invention, Cr, Mo, and N are further increased and PREW is made at least 40,

so an exceptional resistance to corrosion in sea water is exhibited. An increase in Cr, Mo, and N contributes to a higher strength of steel, so a duplex stainless steel which already has a higher strength than a single-phase ferrite or austenite steel becomes a super duplex stainless steel having an even higher strength.

[0046] In the same manner as Mo, W is an element which increases corrosion resistance and particularly resistance to pitting and crevice corrosion. Above all, it is an element which forms stable oxides which increase corrosion resistance in a low pH environment. Accordingly, greater than 1.5% of W is added. If it is 1.5% or less, it becomes necessary to increase the added amounts of Cr, Mo, N, and the like in order to make PREW at least 40, so the effects of utilizing W decrease. The greater the content of W is, the smaller the contents of Cr and Mo can be made in order to make PREW at least 40, and damage caused by promotion of the formation of sigma phases and the like by these elements can be reduced. A preferred content of W is greater than 2.0%. However, if W is added in excess of 5.0%, an increase in effects commensurate therewith is not observed and costs merely increase accordingly, so its upper limit is made 5.0%.

[0047] N (nitrogen): N is a powerful austenite forming element. It is effective for improving the thermal stability and corrosion resistance of a duplex stainless steel. When large amounts of Cr and Mo, which are ferrite forming elements, are added as is the case with the steel of the present invention, at least 0.24% of N is added in order to obtain a suitable balance between ferrite and austenite phases.

[0048] N also contributes to an increase in PREW, and it increases the corrosion resistance of an alloy in the same manner as Cr, Mo, and W. However, in a duplex stainless steel like the steel of the present invention containing around 25% of Cr, if N is contained in excess of 0.35%, the toughness and corrosion resistance of the steel are worsened due to defects caused by the formation of blow holes or due to the formation of nitrides caused by thermal effects at the time of welding. Therefore, the upper limit on N is made 0.35%.

[0049] Sol. Al: Al is effective as a deoxidizing agent of steel, but when the amount of N in a steel is high, it precipitates as AlN (aluminum nitride), and it worsens toughness and corrosion resistance. In addition, it forms oxides, and these become sites of formation of nuclei of sigma phases. Accordingly, in the present invention, the Al content expressed as sol. Al is made at most 0.040%. In the present invention, addition of a large amount of Si is avoided, so Al is often used as a deoxidizing agent, but when vacuum melting is carried out, it is not always necessary to add Al.

[0050] A duplex stainless steel according to the present invention may if necessary include at least one element from the following Groups 1 and 2 in addition to the above-described components.

[0051] Element Group 1 (Cu, V): At least one of Cu and V can be contained in a duplex stainless steel of the present invention. They have equivalent effects from the standpoint of increasing corrosion resistance and particularly resistance to acids such as sulfuric acid.

[0052] Cu is particularly effective at improving resistance to acids in a reducing low-pH environment, such as a H_2SO_4 or hydrogen sulfide environment. In order to obtain this effect, its content is made at least 0.2%. However, addition of a large amount of Cu worsens the hot workability of steel, so its upper limit is made 2.0%.

[0053] If at least 0.05% of V is added, it increases resistance to acids such as sulfuric acid, and particularly when it is added together with W, it also increases resistance to crevice corrosion. However, if too much V is added, the amount of ferrite excessively increases, and this leads to a decrease in toughness and corrosion resistance, so its upper limit is made 1.5%.

[0054] Element Group 2 (B and rare earth elements): Each of these is an element which fixes S or O (oxygen) and increases hot workability.

[0055] In a steel of the present invention, S is suppressed to a low level. The formation of sigma phases and the like is not prompt, even though a large amount of W is added. Thus, hot workability is fundamentally good.

[0056] A duplex stainless steel according to the present invention can be in the form of a casting, and it can also be made into a pipe or the like by a powder metallurgy method including forming into a powder, pressing, sintering, and the like.

[0057] When employing such a manufacturing method, hot workability is not a problem. Accordingly, addition of an element of Element Group 2 is not always necessary. However, excellent hot workability is desired when forming a product by the steps of forging, rolling, extrusion, and the like, so in such cases, if necessary, one or more of B: at least 0.0005% and at least 0.0005% each of one or more rare earth element such as La and Ce may be added. However, if a large amount of these elements is added, non-metallic inclusions such as oxides and sulfides increase, they become sites of precipitation nuclei of sigma phases, and these become starting points of pitting and lead to a deterioration in corrosion resistance. Accordingly, the contents are preferably at most 0.005% for B and at most 0.2% for rare earth elements (primarily La and Ce).

[0058] The total of the lower limits of B and rare earth elements is preferably at least the sum of S and O as impurities ($\text{S} + \frac{1}{2} \text{O}$).

[0059] In the present invention, the number of coarse inclusions which are defined below and particularly coarse alumina inclusions observed in a cross section is limited to at most 10 per mm^2 .

[0060] In our invention, coarse inclusions are defined as "inclusions having a major diameter of at least 5 micrometers and containing at least 20% of Al or a total in mass percent of at least 20% of Ca and/or Mg together with Al when Ca

and/or Mg is contained in the inclusions." The reason for this is that inclusions including a total in mass percent of at least 20% of Al and Ca and Mg increase deviations of the crystal lattice from that of the parent phase (ferrite phase) and increase the surface energy. In the present specification, for convenience, such coarse inclusions are referred to as "inclusions containing at least 20 mass % of Al and having a major diameter of at least 5 micrometers".

[0061] Coarse inclusions in a duplex stainless steel according to the present invention are primarily oxide inclusions and particularly alumina inclusions. In the present specification, coarse inclusions will be referred to for convenience as alumina inclusions.

[0062] When the major diameter is less than 5 micrometers, the area of the interface between the parent phase and the inclusions is sufficiently large, so the probability of the interface becoming a site of precipitation of sigma phases becomes small.

[0063] As shown in Figures 2(a) and 2(b), the major diameter of an inclusion means the length of the longest straight line of the straight lines connecting two different points on the interface between the parent metal and the inclusion 1. These are a1 and a2 in Figures 2(a) and 2(b), respectively. The composition of an oxide type inclusion is determined by finding the content of alloying elements other than O (oxygen) using EDX (energy dispersion x-ray analysis) near the center of the inclusion 1 (b1 and b2 in the examples shown in Figures 2(a) and 2(b), respectively), i.e. near the center of gravity of the cross-sectional shape of the inclusion 1. Accordingly, in this specification, "including at least 20 mass % of Al" means the content of Al(+ Ca + Mg) with respect to all alloying elements other than O.

[0064] In actual practice, the effect of the density of these coarse alumina inclusions is large, and if the number observed in a cross section exceeds 10 per mm², the probability of the growth of precipitation of sigma phase increases not only in the interface of coarse inclusions and the mother phase but also in a ferrite/austenite interface having a high free energy. Therefore, the presence of such coarse inclusions has a harmful effect on precipitation of sigma phases in the HAZ, and making the density lower than this is effective at suppressing sigma phase precipitation in a HAZ.

[0065] In the present invention, the density of coarse alumina inclusions is limited to at most 10 per mm² as described above.

[0066] Such a duplex stainless steel according to the present invention can be manufactured by carrying out secondary refining by vacuum refining, for example, adjusting the slag basicity at this time to 0.3 - 3.0, for example, and performing adequate stirring of molten steel and refining with slag.

[0067] In a steel composition according to the present invention, inclusions which are formed are primarily alumina inclusions, and when Ca, Mg, and the like are mixed in as impurities, there is the possibility of there being inclusions including Ca and Mg.

[0068] In the present invention, when the Al content of coarse alumina type inclusions is at least 20% and Ca and Mg type inclusions are intermixed, the reason why the total of (Al + Ca + Mg) for coarse alumina type inclusions, coarse Ca type inclusions, and coarse Mg type inclusions is made at least 20% is in order to guarantee pitting resistance by making it difficult for dissolving out to occur in a corrosive environment. Such Mg and Ca type inclusions are in the form of oxides, and they are combined with alumina type inclusions.

[0069] Next, the operation and effects of the present invention will be explained more concretely by examples.

Examples

[0070] Steels having the chemical compositions shown in Table 1 were melted in an electric furnace, and then they were transferred to an AOD furnace for secondary refining. However, in the case of symbol B6, secondary refining was not carried out. In the secondary refining, the slag basicity defined as [weight of (CaO + MgO) in the slag]/[weight of (Al₂O₃ + SiO₂) in the slag] was set to different values in the range from 1 to 3, and molten steel was prepared containing inclusions of different compositions, shapes, and densities. After casting, heating was performed for 1200 °C, and plates with a thickness of 40 mm were obtained by forging.

[0071] The resulting plates were heated to 1250 °C and then rolled to a thickness of 10 mm. A portion of each of the resulting steel plates was cut out, it was mounted in a resin with a cross section perpendicular to the rolled surface facing upwards, and this cross section was polished to a mirror finish. Coarse inclusions were then observed with a SEM at a magnification of 200 times in 5 fields of view, and their size was evaluated.

[0072] The major diameter of the coarse alumina inclusions was measured in accordance with the definition in Figure 2, the composition of the coarse inclusions near their central portions (b1 and b2 in Figure 2) was analyzed by EPMA, the above-described coarse inclusions were identified, and their density was measured. The density was evaluated based on the average of the number of coarse inclusions per mm² in 5 fields of view.

[0073] The steel plates to be tested were machined to obtain test materials measuring 8 mm thick x 100 mm wide x 200 mm long and having a V-shaped bevel with an internal angle of 30° formed in a long side thereof. Using a welding rod with an outer diameter of 2 mm prepared from the steel of symbol A1, two test materials were abutted against each other, multi-layer welding by TIG welding from one side was carried out using a heat input of 10 kJ/cm (welding condition 1) used for highly corrosion resistance stainless steel which is a higher grade than ordinary stainless steel, or a heat

input of 20 kJ/cm (welding condition 2) which does not cause any particular performance problems in welding of ordinary stainless steel to prepare two types of welded joints.

[0074] A corrosion test piece which measured 3 mm thick, 10 mm wide, and 40 mm long with the 40 mm side extending perpendicular to the welding line and the 3 x 10 mm surface being parallel to the rolled surface was cut from the resulting welded joint, it was immersed for 24 hours in a 10% FeCl₃•6H₂O solution (65 °C), and the occurrence of pitting in the HAZ was evaluated at a magnification of 500.

[0075] A cross section perpendicular to the welding line and the rolled surface was etched for microscopic examination, image analysis was carried out at a magnification of 500, and the proportion of the area in the HAZ occupied by minute sigma phases was measured. If the proportion of area occupied by sigma phases was 1%, it was determined that there were minute sigma phases.

[0076] These results are compiled in Table 2. As is clear from the results shown in Table 2, with the test pieces for which the chemical composition and the density of coarse inclusions satisfied the ranges of the present invention, in spite of carrying out evaluation at a high heat input which does not cause any particular performance problem during welding of ordinary stainless steel, no precipitation of minute sigma phases was observed, and excellent pitting resistance was exhibited. In contrast, as was the case for symbols B1 and B2, even though the elements satisfied the range for the chemical composition, if the combined range of Ni and Mo did not satisfy the requirements of the present invention, minute sigma phases were formed as with symbol B1, or sigma phases were not formed but nitrides were formed as with symbol B2, and pitting resistance was inferior. For symbols B3 - B5, even though the steel composition was the same as for symbols A1 and A3, a minute amount of sigma phases was formed and pitting resistance was degraded for those for which the density of coarse inclusions was not in the range of the present invention.

Table 1

Symbol	C	Si	Mn	P	S	Ni	Cr	Mo	W	N	sol. Al	PREW	Element Group 1	Element Group 2
A1	0.020	0.30	0.51	0.016	0.001	7.02	25.20	2.97	2.16	0.30	0.005	43.365		
A2	0.020	0.31	0.49	0.016	0.001	6.32	25.47	2.92	2.17	0.26	0.006	42.8305		
A3	0.021	0.31	0.51	0.015	0.001	7.12	24.20	3.64	2.10	0.31	0.005	44.669		
A4	0.020	0.31	0.50	0.016	0.001	6.99	26.10	2.21	2.19	0.26	0.007	41.2305		
A5	0.019	0.12	0.49	0.016	0.001	7.06	25.26	2.34	3.15	0.27	0.006	42.5315	Cu=0.56	
A6	0.021	0.28	0.50	0.022	0.001	7.35	24.98	3.12	2.15	0.31	0.007	43.7995	V=0.65	
A7	0.021	0.45	0.50	0.016	0.001	6.85	24.98	2.87	2.32	0.31	0.008	43.255		B=0.006
A8	0.019	0.35	0.47	0.015	0.001	7.12	25.26	2.98	2.24	0.27	0.005	43.142		REM =0.01
A9	0.019	0.37	0.49	0.016	0.001	8.15	24.87	3.25	2.26	0.27	0.006	43.676		
A10	0.021	0.30	0.58	0.017	0.001	6.95	25.98	2.95	2.15	0.31	0.005	44.2385		
A11	0.021	0.30	0.50	0.016	0.001	7.23	24.98	3.12	2.64	0.31	0.007	44.608	Cu=0.46	B=0.006
A12	0.022	0.30	0.49	0.017	0.001	7.74	24.78	3.14	2.17	0.28	0.005	43.1865	Cu=1.25 V=0.87	
A13	0.021	0.30	0.50	0.016	0.001	6.58	25.12	3.30	2.37	0.27	0.006	44.2085	Cu=1.31 V=0.77	B=0.007
A14	0.021	0.32	0.50	0.014	0.001	7.11	25.17	2.99	3.16	0.26	0.005	44.411	Cu=1.31 V=0.77	REM =0.01
A15	0.021	0.29	0.10	0.015	0.001	7.00	25.25	2.98	2.18	0.27	0.005	43.049	Cu=1.31 V=0.77	
A16	-	0.32	0.49	0.015	0.001	7.01	25.1	2.97	2.17	0.37	0.004	44.4015		
A17	0.021	-	0.48	0.018	0.001	7.04	25.17	3.01	2.37	0.31	0.003	43.9735		
A18	0.022	0.3	-	0.017	0.001	6.89	24.87	3.11	2.26	0.28	0.005	43.342		
A19	0.022	0.32	0.49	0.018	0.001	7.1	24.89	3.08	2.26	0.26	-	42.943		
B1	0.021	0.30	0.30	0.016	0.001	8.56	24.88	3.61	2.16	0.28	0.005	44.805		
B2	0.021	0.30	0.50	0.015	0.001	6.12	24.95	3.52	2.15	0.28	0.006	44.5615		
B3	0.020	0.30	0.51	0.016	0.001	7.02	25.20	2.97	2.16	0.30	0.008	43.365		
B4	0.020	0.31	0.49	0.016	0.001	6.32	25.47	2.92	2.17	0.26	0.007	42.8305		
B5	0.021	0.31	0.51	0.015	0.001	7.12	24.20	3.64	2.10	0.31	0.007	44.669		
B6	0.020	0.30	0.51	0.016	0.001	7.02	25.20	2.97	2.16	0.30	0.005	43.365		

Table 2

Symbol	Density of harmful inclusions	Mo+1.1 Ni-12.5	Mo-0.8 Ni+1.6	Welding condition 1		Welding condition 2		Comments
				Minute sigma phases	Occurrence of pitting	Minute sigma phases	Occurrence of pitting	
A1	5	- 1.808	- 1.046	○	○	○	No	Present Invention
A2	7	- 2.628	- 0.536	○	○	○	No	
A3	4	- 1.028	- 0.456	○	○	○	No	
A4	8	- 2.601	- 1.782	○	○	○	No	
A5	4	- 2.394	- 1.708	○	○	○	No	
A6	6	- 1.295	- 1.16	○	○	○	No	
A7	7	- 2.095	- 1.01	○	○	○	No	
A8	6	- 1.688	- 1.116	○	○	○	No	
A9	5	- 0.285	- 1.67	○	○	○	No	
A10	5	- 1.905	- 1.01	○	○	○	No	
A11	3	- 1.427	- 1.064	○	○	○	No	
A12	6	- 0.846	- 1.452	○	○	○	No	
A13	6	- 1.962	- 0.364	○	○	○	No	
A14	5	- 1.689	- 1.098	○	○	○	No	
A15	3	- 1.82	- 1.02	○	○	○	No	
A16	4	- 1.819	- 1.038	○	○	○	No	
A17	5	- 1.746	- 1.022	○	○	○	No	
A18	5	- 1.811	- 0.802	○	○	○	No	
A19	3	- 1.61	- 1	○	○	○	No	
B1	6	0.526	- 1.638	○	○	×	Yes	Comparative
B2	7	- 2.248	0.224	○	○	×	Yes	
B3	13	- 1.808	- 1.046	○	○	×	Yes	
B4	12	- 2.628	- 0.536	○	○	×	Yes	
B5	15	- 1.028	- 0.456	○	○	×	Yes	
B6	30	- 1.808	- 1.046	○	○	×	*Yes	

○ : Area of sigma phase of 1 % or less

× : Area of sigma phase of more than 1 %

* No secondary refining

Effects of the Invention

[0077] According to the present invention, the formation of sigma phases in a weld heat affected zone can be prevented, and the amount of coarse inclusions which are formed can be greatly decreased, so the resulting duplex stainless steel

exhibits excellent pitting resistance, and an excellent duplex stainless steel is provided which can be applied to present-day uses.

5 Claims

1. A duplex stainless steel **characterized by** having a chemical composition comprising, in mass percent, C: at most 0.03%, Si: at most 1.0%, Mn: at most 1.5%, P: at most 0.040%, S: at most 0.008%, Cr: 23.0 - 27.0%, Mo: 2.0 - 4.0%, Ni: 5.0 - 9.0%, W: greater than 1.5% and at most 5.0%, N: 0.24 - 0.35%, and a remainder of Fe and impurities and satisfying the relationships

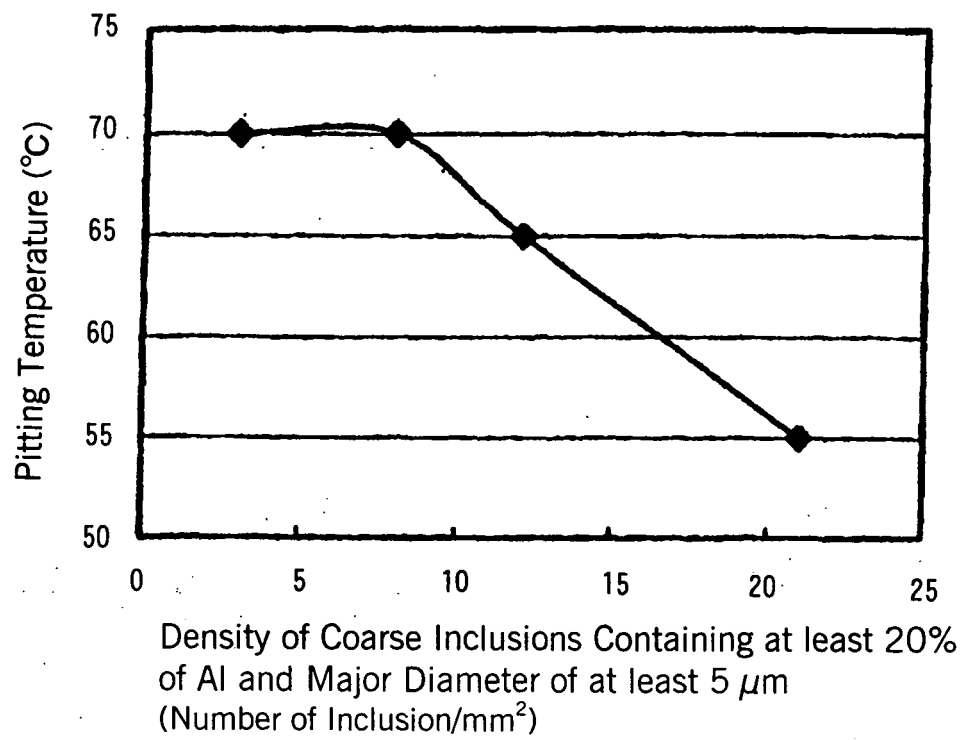
$$\text{PREW} = \text{Cr} + 3.3(\text{Mo} + 0.5\text{W}) + 16\text{N} \text{ is at least } 40$$

$$\text{Mo} + 1.1\text{Ni} \leq 12.5$$

$$\text{Mo} - 0.8\text{Ni} \leq -1.6$$

and with the number of coarse inclusions defined as inclusions containing at least 20 mass % of Al and having a major diameter of at least 5 micrometers which are observed in a cross section being at most 10 per mm².

2. A duplex stainless steel as set forth in claim 1 wherein the chemical composition further includes, in mass %, one or both of Cu: 0.2 - 2.0% and V: 0.05 - 1.5%.
3. A duplex stainless steel as set forth in claim 1 or claim 2 wherein the chemical composition further includes, in mass %, one or both of 0.0005 - 0.005% of B and 0.0005 - 0.2% of at least one rare earth element.
4. A duplex stainless steel as set forth in any of claims 1 - 3 wherein the chemical composition further includes, in mass %, sol. Al: at most 0.040%.

***Fig. 1***

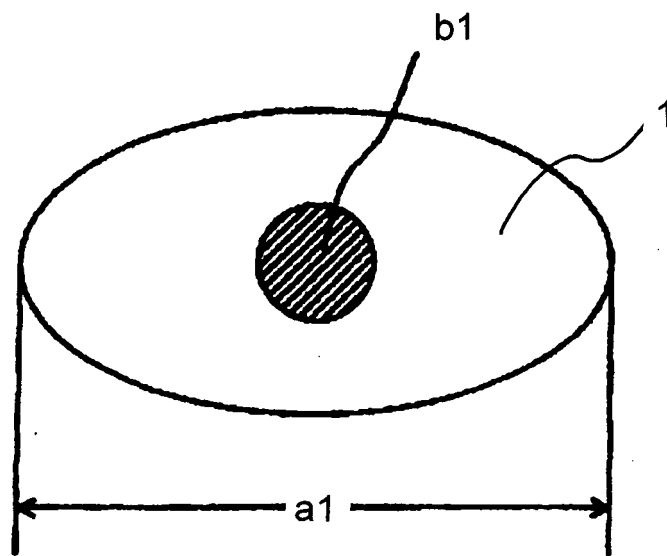


Fig. 2a

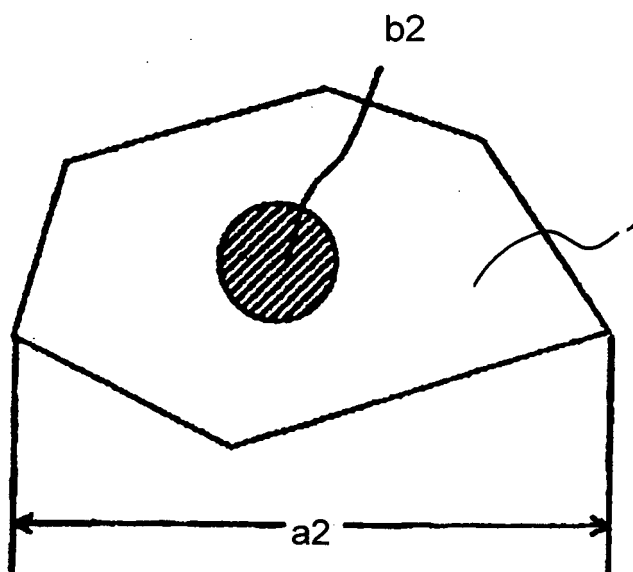


Fig. 2b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/009511

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C22C38/00, C22C38/44, C22C38/54		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C22C38/00, C22C38/44, C22C38/54		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2004 Kokai Jitsuyo Shinan Koho 1971-2004 Jitsuyo Shinan Toroku Koho 1996-2004		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2500162 B2 (Sumitomo Metal Industries, Ltd.), 29 May, 1996 (29.05.96), Full text & EP 545753 A1 & US 5298093 A	1-4
A	JP 2002-241838 A (Sumitomo Metal Industries, Ltd.), 28 August, 2002 (28.08.02), Full text (Family: none)	1-4
A	JP 3127822 B2 (Sumitomo Metal Industries, Ltd.), 29 January, 2001 (29.01.01), Full text (Family: none)	1-4
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 13 September, 2004 (13.09.04)		Date of mailing of the international search report 28 September, 2004 (28.09.04)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/009511

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 2001-220652 A (Sumitomo Metal Industries, Ltd.), 14 August, 2001 (14.08.01), Full text (Family: none)	1-4
A	JP 8-13094 A (Sumitomo Metal Mining Co., Ltd.), 16 January, 1996 (16.01.96), Full text (Family: none)	1-4
A	JP 10-88288 A (Sumitomo Metal Industries, Ltd.), 07 April, 1998 (07.04.98), Full text (Family: none)	1-4

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