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(54) **FERRITIC STAINLESS STEEL HAVING
EXCELLENT CORROSION RESISTANCE OF
WELD ZONE**

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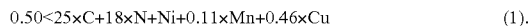
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ABSTRACT

Ferritic stainless steel that is excellent in terms of corrosion resistance of a weld zone. The ferritic stainless steel includes, by mass %, C: 0.001% or more and 0.025% or less, Si: 0.05% or more and 0.30% or less, Mn: 0.35% or more and 2.0% or less, P: 0.05% or less, S: 0.01% or less, Al: 0.05% or more and 0.80% or less, N: 0.001% or more and 0.025% or less, Cr: 16.0% or more and 20.0% or less, Ti: 0.12% or more and 0.50% or less, Nb: 0.002% or more and 0.050% or less, Cu: 0.30% or more and 0.80% or less, Ni: 0.05% or more and less than 0.50%, V: 0.01% or more and 0.50% or less, and Fe and inevitable impurities such that Expression (1) is satisfied:



FERRITIC STAINLESS STEEL HAVING EXCELLENT CORROSION RESISTANCE OF WELD ZONE

TECHNICAL FIELD

[0001] This application is directed to ferritic stainless steel that hardly has deterioration in corrosion resistance due to carbon and nitrogen, which enter a weld bead from an opposite material to be welded, or due to nitrogen, which enters a weld bead from atmospheric air when welding is performed.

BACKGROUND

[0002] In the case of ferritic stainless steel, satisfactory corrosion resistance can be achieved with smaller Ni content than in the case of austenite stainless steel. Since Ni is an expensive element, it is possible to manufacture ferritic stainless steel at lower cost than austenite stainless steel. In addition, ferritic stainless steel has some characteristics superior to those of austenite stainless steel, for example, higher thermal conductivity, lower thermal expansion coefficient, and excellent stress corrosion cracking resistance. Therefore, ferritic stainless steel has been widely used for automobile exhaust system members, architectural materials such as roofs and fittings, and materials for plumbing products such as kitchen appliances, water storage tanks and hot water storage tanks.

[0003] When manufacturing such structures, austenite stainless steel, in particular, for example, SUS304 (18% Cr-8% Ni) (JIS G 4305) and ferritic stainless steel are used in combination in many cases. As a method for welding such kinds of stainless steel, TIG welding is generally used. Also, in this case, a weld zone is required to have corrosion resistance as high as that of a base material zone.

[0004] In order to solve the problem described above, methods for achieving satisfactory corrosion resistance have been proposed in which the occurrence of sensitization is suppressed by suppressing the formation of Cr carbonitrides as a result of fixing C and N in the form of carbonitrides of Ti and Nb by adding Ti and Nb which have higher affinity for C and N than Cr has. For example, Patent Literature 1 discloses ferritic stainless steel having improved intergranular corrosion resistance by adding Ti and Nb in combination. In addition, Patent Literature 2 discloses steel having improved intergranular corrosion resistance by adding Nb.

[0005] However, in both Patent Literature 1 and 2, it is necessary to add Mo in an amount of 0.3 mass % or more. Although Mo is an element which improves the corrosion resistance of a base material, since Mo is a strong ferrite-forming element, the formation of a ferrite phase is promoted in a weld zone in the case where Mo is added in an amount as much as 0.3 mass %, which makes it impossible to achieve sufficient corrosion resistance for a weld zone because the sensitization of a weld zone is promoted. In addition, in both Patent Literature 1 and 2, it is necessary to add Nb in an amount of 0.1 mass % or more. However, in the case where steel having a large Nb content is welded, since a solid solute Nb precipitates in the form of coarse Nb precipitates in a weld zone, there is a case where problems such as a welding crack occur. It cannot be said that it is the most appropriate method to achieve satisfactory corrosion resistance for a weld zone only by adding carbonitride-forming elements such as Nb and Ti in consideration of manufacturability and practical utility.

PATENT LITERATURE

[0006] PTL 1: Japanese Unexamined Patent Application Publication No. 2007-270290

[0007] PTL 2: Japanese Unexamined Patent Application Publication No. 2010-202916 SUMMARY

Technical Problem

[0008] Therefore, an object of the present disclosure is to provide ferritic stainless steel excellent in terms of the corrosion resistance of a weld zone which does not require excessive amounts of Ti or Nb to be added.

Solution to Problem

[0009] In order to solve the problem described above, the present inventors diligently conducted investigations regarding techniques with which it is possible to inhibit a deterioration in the corrosion resistance of a weld zone better than ever. First, the present inventors conducted systematic investigations regarding acceptable degree of sensitization with which it is possible to achieve sufficient corrosion resistance for a weld zone using steel containing Cr in an amount of 16 to 20 mass %, and as a result, found that a deterioration in the corrosion resistance of a weld zone due to sensitization becomes noticeable in the case where a grain boundary coverage factor of a ferrite phase by Cr carbonitrides (refer to a measurement method for determining a grain boundary coverage factor in the EXAMPLE) is more than 40%.

[0010] Subsequently, the present inventors conducted investigations regarding a method for decreasing the grain boundary coverage factor of a ferrite phase by Cr carbonitrides, and as a result, found that, in order to improve the corrosion resistance of a weld zone, it is very effective to stabilize an austenite phase by adding Mn and Cu, which are austenite-forming elements.

[0011] That is, it was found that, in the case where an austenite phase is stabilized by adding Mn and Cu, since it is possible to inhibit the formation of a ferrite phase when welding is performed, and since it is possible to prevent sensitization due to the formation of Cr carbonitrides by stabilizing C and N, which are added in amounts equal to or more than solid solubility limits of a ferrite phase, in the form of solid solutions in an austenite phase which has a solid solubility limit much higher than that of a ferrite phase, there is a significant improvement in the corrosion resistance of a weld zone.

[0012] Moreover, it was clarified that, since a solid solute C and a solid solute N are formed in an austenite phase, it is possible to prevent sensitization even in the case where C content and N content are larger than those which are acceptable in the case where C and N are fixed using conventional methods such as one adding only Ti and Nb. The present inventors conducted systematic investigations regarding the chemical composition of steel with which the effects described above are realized, and found that the effects described above are realized in the case where the contents of C, N, Ni, Mn, and Cu, which stabilize an austenite phase, satisfy relational expression (1) below.

$$0.50 < 25 \times C + 18 \times N + Ni + 0.11 \times Mn + 0.46 \times Cu \quad (1)$$

[0013] Here, atomic symbols in the relational expression respectively represent the contents (mass %) of the corresponding elements.

[0014] Moreover, since the present effects can be utilized in combination with conventional technique in which C and N are fixed by adding Ti and Nb, it is possible to achieve significantly improved corrosion resistance for a weld zone compared with that of conventional steel without adding excessive amounts of Ti and Nb.

[0015] The disclosed embodiments include:

[0016] [1] Ferritic stainless steel having excellent corrosion resistance of a weld zone, the steel having a chemical composition containing, by mass %, C: 0.001% or more and 0.025% or less, Si: 0.05% or more and 0.30% or less, Mn: 0.35% or more and 2.0% or less, P: 0.05% or less, S: 0.01% or less, Al: 0.05% or more and 0.80% or less, N: 0.001% or more and 0.025% or less, Cr: 16.0% or more and 20.0% or less, Ti: 0.12% or more and 0.50% or less, Nb: 0.002% or more and 0.050% or less, Cu: 0.30% or more and 0.80% or less, Ni: 0.05% or more and less than 0.50%, V: 0.01% or more and 0.50% or less, and the balance being Fe and inevitable impurities, in which relational expression (1) below is satisfied:

$$0.50 < 25 \times C + 18 \times N + Ni + 0.11 \times Mn + 0.46 \times Cu \quad (1),$$

where, atomic symbols in the relational expression respectively represent the contents (mass %) of the corresponding elements.

[0017] [2] The ferritic stainless steel having excellent corrosion resistance of a weld zone according to item [1], the steel having the chemical composition further containing, by mass %, one or more selected from among Zr: 0.01% or more and 0.50% or less, W: 0.01% or more and 0.20% or less, REM: 0.001% or more and 0.10% or less, Co: 0.01% or more and 0.20% or less, B: 0.0002% or more and 0.010% or less, and Sb: 0.05% or more and 0.30% or less.

Advantageous Effects

[0018] According to the present disclosure, it is possible to obtain ferritic stainless steel having excellent corrosion resistance of a weld zone even under the welding conditions which C and N enter a base material from an opposite material to be welded.

DETAILED DESCRIPTION

[0019] The reasons for the limitations on the constituent aspects will be described hereafter.

[0020] 1. Regarding Chemical Composition and Metallographic Structure

[0021] First, the reasons for the limitation on the chemical composition of the steel according to the disclosed embodiments will be described. Here, % used when describing a chemical composition always represents mass %.

[0022] C: 0.001% or More and 0.025% or Less

[0023] C is an element which is inevitably contained. The larger the C content, the higher the strength, and the smaller the C content, the higher the workability. It is necessary that the C content be 0.001% or more in order to achieve sufficient strength. However, in the case where the C content is more than 0.025%, a significant deterioration in workability occurs and a deterioration in corrosion resistance (sensitization) due to local Cr depletion as a result of Cr carbides being precipitated is more likely to occur. Therefore, the C content is set to be 0.001% or more and 0.025% or less. However, although it is preferable that the C content be as small as possible from the viewpoint of corrosion resistance and workability, it is not preferable from the viewpoint of productivity that C content be extremely decreased, because there is an increase in the

time taken for refining. Therefore, it is preferable that the C content be 0.003% or more and 0.018% or less, or more preferably 0.005% or more and 0.012% or less.

[0024] Si: 0.05% or More and 0.30% or Less

[0025] Si is an element which is effective for improving the corrosion resistance of a weld zone. It is necessary that the Si content be 0.05% or more in order to realize such an effect, and, the larger the Si content, the larger the effect. However, it is not desirable that the Si content be more than 0.30%, because there is a deterioration in the formability and toughness of a weld zone. Therefore, the Si content is set to be 0.05% or more and 0.30% or less, preferably 0.05% or more and 0.25% or less, or more preferably 0.08% or more and 0.20% or less.

[0026] Mn: 0.35% or More and 2.0% or Less

[0027] Mn is a particularly important element in the present disclosure. Mn is an element which is effective as a deoxidizing agent and which is effective for stabilizing an austenite phase. By adding Mn in a specified amount, since it is possible to inhibit the formation of a ferrite phase when welding is performed, and since it is possible to realize the effect of preventing sensitization due to the formation of Cr carbonitrides by stabilizing C and N, which are added in amounts equal to or more than solid solubility limits of a ferrite phase, in the form of solid solutions in an austenite phase which has a solid solubility limit higher than that of a ferrite phase, there is an improvement in the corrosion resistance of a weld zone. It is necessary that the Mn content be 0.35% or more in order to realize such effects. However, it is not desirable that the Mn content be more than 2.0%, because there is a deterioration in ductility due to an excessive increase in the hardness of a base material, and because there is a deterioration in toughness due to an increase in the hardness of a weld zone. Therefore, the Mn content is set to be 0.35% or more and 2.0% or less, preferably 0.50% or more and 1.5% or less, or more preferably 0.75% or more and 1.25% or less.

[0028] P: 0.05% or Less

[0029] P is an element which is inevitably contained in steel and, in the case where the P content is excessively large, there is a deterioration in weldability and intergranular corrosion tends to occur. These tendencies become noticeable in the case where the P content is more than 0.05%. Therefore, the P content is set to be 0.05% or less, or preferably 0.03% or less.

[0030] S: 0.01% or Less

[0031] S is, like P, an element which is inevitably contained in steel, and there is a deterioration in corrosion resistance in the case where the S content is more than 0.01%. Therefore, the S content is set to be 0.01% or less, or preferably 0.008% or less.

[0032] Al: 0.05% or More and 0.80% or Less

[0033] Al is, like Si, an element which improves the corrosion resistance of a weld zone. Since Al has higher affinity for N than Cr has, N is precipitated in the form of Al nitrides instead of Cr nitrides in the case where N is mixed into a weld zone, which results in the effect of inhibiting sensitization. In addition, Al is a chemical element which is also effective for deoxidization in a steel-making process. Such effects are realized in the case where the Al content is 0.05% or more. However, in the case where the Al content is more than 0.80%, since there is coarsening of the ferrite crystal grain, there is a deterioration in workability and manufacturability. Therefore, the Al content is set to be 0.05% or more and

0.80% or less, preferably 0.10% or more and 0.60% or less, or more preferably 0.15% or more and 0.50% or less.

[0034] N: 0.001% or More and 0.025% or Less

[0035] N is, like C, an element which is inevitably contained in steel. There is an increase in strength in the case where the N content is large, and there is an improvement in workability as the N content becomes small. It is appropriate that the N content be 0.001% or more in order to achieve sufficient strength. However, it is not desirable that the N content be more than 0.025%, because there is a significant deterioration in ductility, and because there is a deterioration in corrosion resistance due to promoting the precipitation of Cr nitrides. Therefore, the N content is set to be 0.001% or more and 0.025% or less. It is preferable that the N content be as small as possible from the viewpoint of corrosion resistance. However, since it is necessary to increase refining time in order to decrease the N content, there is a decrease in productivity. Therefore, it is preferable that the N content be 0.003% or more and 0.025% or less, more preferably 0.003% or more and 0.015% or less, or even more preferably 0.003% or more and 0.010% or less.

[0036] Cr: 16.0% or More and 20.0% or Less

[0037] Cr is an element which is the most important for achieving the corrosion resistance for stainless steel. It is not desirable that the Cr content be less than 16.0%, because it is not possible to achieve sufficient corrosion resistance in a weld bead and in the vicinity of the weld bead, in which there is a decrease in the amount of Cr in a surface layer due to oxidation as a result of performing welding, and because sensitization, which is caused by N which is mixed in from an opposite material to be welded or from atmospheric air when welding is performed, is promoted to a higher degree. On the other hand, it is not desirable that the Cr content be more than 20.0%, because there is a deterioration in toughness, and because there is a deterioration in descaling performance after annealing. Therefore, the Cr content is set to be 16.0% or more and 20.0% or less, preferably 16.5% or more and 19.0% or less, or more preferably 17.0% or more and 18.5% or less.

[0038] Ti: 0.12% or More and 0.50% or Less

[0039] Ti is an element which is effective for inhibiting a deterioration in corrosion resistance due to sensitization due to the precipitation of Cr carbonitrides as a result of being more readily to combine with C and N than other elements are. Such an effect is realized in the case where the Ti content is 0.12% or more. However, it is not desirable that the Ti content be more than 0.50%, because surface defects occur due to the formation of coarse Ti carbonitrides. Therefore, the Ti content is set to be 0.12% or more and 0.50% or less, preferably 0.15% or more and 0.40% or less, or more preferably 0.20% or more and 0.35% or less.

[0040] Nb: 0.002% or More and 0.050% or Less

[0041] Nb is an element which is effective for inhibiting a deterioration in corrosion resistance due to sensitization due to the precipitation of Cr carbonitrides as a result of being more readily to combine with C and N than other elements are. In addition, Nb is effective for improving the toughness and bendability of a weld zone as a result of refining the crystal grain in a weld zone. Such effects are realized in the case where the Nb content is 0.002% or more. On the other hand, since Nb is also an element which increases the recrystallization temperature, it is not desirable that the Nb content be more than 0.050%, because there is an insufficient degree of annealing in an annealing process using a high speed annealing line for a cold-rolled steel sheet due to an increase

in an annealing temperature required for recrystallization, which results in a deterioration in workability due to the coexistence of non-recrystallized grains and recrystallized grains. Therefore, the Nb content is set to be 0.002% or more and 0.050% or less, preferably 0.010% or more and 0.045% or less, or more preferably 0.015% or more and 0.040% or less.

[0042] Cu: 0.30% or More and 0.80% or Less

[0043] Cu is an element which improves corrosion resistance and which is effective particularly for improving the corrosion resistance of a base material and a weld zone which are placed in an aqueous solution or to which slightly acidic water drops adhere. In addition, since Cu is, like Ni, a strong austenite-forming element, Cu is effective for inhibiting sensitization due to the precipitation of Cr carbonitrides as a result of inhibiting the formation of a ferrite phase in a weld zone. Such effects are realized in the case where the Cu content is 0.30% or more. On the other hand, it is not desirable that the Cu content be more than 0.80%, because there is a deterioration in hot workability. Therefore, the Cu content is set to be 0.30% or more and 0.80% or less, preferably 0.30% or more and 0.60% or less, or more preferably 0.35% or more and 0.50% or less.

[0044] Ni: 0.05% or More and Less than 0.50%

[0045] Ni is an element which improves the corrosion resistance of stainless steel and which inhibits the progress of corrosion in a corrosive environment in which active dissolution occurs because a passivation film cannot be formed. In addition, since Ni is a strong austenite-forming element, Ni is effective for inhibiting sensitization due to the precipitation of Cr carbonitrides as a result of inhibiting the formation of a ferrite in a weld zone. Such effects are realized in the case where the Ni content is 0.05% or more. However, it is not desirable that the Ni content be 0.50% or more, because there is a deterioration in workability, because there is an improvement in stress corrosion cracking sensitivity, and because there is an increase in manufacturing costs since Ni is an expensive element. Therefore, the Ni content is set to be 0.05% or less and less than 0.50%, preferably 0.10% or more and 0.30% or less, or more preferably 0.15% or more and 0.25% or less.

[0046] V: 0.01% or More and 0.50% or Less

[0047] V is an element which improves corrosion resistance and workability and which is effective for deteriorating the degree of the sensitization of a weld zone by inhibiting the formation of Cr nitrides as a result of combining with N when N is mixed into a weld zone. Such effects are realized in the case where the V content is 0.01% or more. However, it is not desirable that the V content be more than 0.50%, because there is a deterioration in workability. Therefore, the V content is set to be 0.01% or more and 0.50% or less, preferably 0.05% or more and 0.30% or less, or more preferably 0.08% or more and 0.20% or less.

$$0.50 < 25 \times C + 18 \times N + Ni + 0.11 \times Mn + 0.46 \times Cu \quad (1)$$

[0048] Here, atomic symbols in the relational expression respectively represent the contents (mass %) of the corresponding elements.

[0049] In order to fix C and N in a weld zone in the form of solid solutions in an austenite phase, it is necessary that an austenite phase be formed in a cooled microstructure after welding has been performed. In order to form an austenite phase in a cooling process after welding has been performed, it is necessary that relational expression (1) above be satisfied.

In the case where the right-hand side value of relational expression (1) is 0.50 or less, since an austenite phase is not sufficiently stabilized, it is not possible to form an austenite phase, which the present disclosure provides, in an amount sufficient to effectively fix a solid solute C and a solid solute N in a weld zone. Therefore, the right-hand side value of relational expression (1) is set to be more than 0.5, preferably 0.60 or more, or more preferably 0.70 or more.

[0050] The chemical composition described above is the basic chemical composition of the disclosed embodiments, and the balance of the chemical composition consists of Fe and inevitable impurities. Here, as an example of the inevitable impurities, Ca: 0.0020% or less is acceptable.

[0051] Moreover, in addition to the basic chemical composition described above, the elements below may be added to meet objectives such as inhibition of the sensitization of a weld bead and improvement of the corrosion resistance.

[0052] Zr: 0.01% or More and 0.50% or Less

[0053] Zr is effective for inhibiting sensitization by combining with C and N. Such an effect is realized in the case where the Zr content is 0.01% or more. However, in the case where the Zr content is more than 0.50%, there is a deterioration in workability. An excessive Zr content is not preferable also because there is an increase in manufacturing costs since Zr is an expensive element. Therefore, in the case where Zr is added, it is preferable that the Zr content be 0.01% or more and 0.50% or less, or more preferably 0.10% or more and 0.35% or less.

[0054] W: 0.01% or More and 0.20% or Less

[0055] W is, like Mo, effective for improving corrosion resistance. Such an effect is realized in the case where the W content is 0.01% or more. However, it is not preferable that the W content be more than 0.20%, because there is a deterioration in manufacturability due to, for example, an increase in rolling load since there is an increase in strength. Therefore, in the case where W is added, it is preferable that the W content be 0.01% or more and 0.20% or less, or more preferably 0.05% or more and 0.15% or less.

[0056] REM: 0.001% or More and 0.10% or Less

[0057] Since REM is effective for improving oxidation resistance, REM is effective for inhibiting the formation of a Cr depletion zone immediately behind welding temper color by inhibiting the formation of oxidized scale. In order to realize such an effect, it is necessary that REM content be 0.001% or more. However, in the case where REM content is more than 0.10%, there is a deterioration in manufacturability such as pickling performance. Excessive REM content is not preferable also because there is an increase in manufacturing costs since REM is, like Zr, an expensive element. Therefore, in the case where REM is added, it is preferable that the REM content be 0.001% or more and 0.10% or less, or more preferably 0.010% or more and 0.08% or less.

[0058] Co: 0.01% or More and 0.20% or Less

[0059] Co is an element which improves toughness. Such an effect is realized in the case where the Co content is 0.01% or more. On the other hand, in the case where the Co content is more than 0.20%, there is a deterioration in manufacturability. Therefore, in the case where Co is added, it is preferable that the Co content be 0.01% or more and 0.20% or less, or more preferably 0.05% or more and 0.15% or less.

[0060] B: 0.0002% or More and 0.010% or Less

[0061] B is an element which improves secondary working embrittlement, and such an effect is realized in the case where the B content is 0.0002% or more. However, in the case where

the B content is more than 0.010%, a deterioration in ductility may be caused due to excessive solid solution hardening. Therefore, in the case where B is added, it is preferable that the B content be 0.0002% or more and 0.010% or less, or more preferably 0.0010% or more and 0.0075% or less.

[0062] Sb: 0.05% or More and 0.30% or Less

[0063] Since Sb is, like Al, an element which is effective for capturing N which is mixed in from atmospheric air when a gas shield is insufficiently effective when TIG welding is performed, Sb is an element which is effective particularly in the case where stainless steel is used for a structure having a complex shape for which it is difficult to provide a sufficient gas shield. Such an effect is realized in the case where the Sb content is 0.05% or more. However, in the case where the Sb content is more than 0.30%, there is a deterioration in surface quality due to the formation of nonmetallic inclusions in a steel-making process, and there is a deterioration in the toughness of a hot-rolled steel sheet. Therefore, in the case where Sb is added, it is preferable that the Sb content be 0.05% or more and 0.30% or less, or more preferably 0.05% or more and 0.15% or less.

[0064] 2. Regarding Manufacturing Conditions

[0065] Hereafter, the method for manufacturing steel of the present disclosure will be described. Molten steel having the chemical composition described above is prepared by using a known method such as one using a converter, an electric furnace, or a vacuum melting furnace, and a steel material (slab) is manufactured by using a method such as a continuous casting method or an ingot casting-slabbing method. This slab is made into a hot-rolled steel sheet by performing hot rolling after heating the slab at a temperature of 1100° C. to 1250° C. for 1 to 24 hours or by performing hot rolling directly on the slab as cast without heating.

[0066] Usually, the hot-rolled steel sheet is subjected to hot-rolled steel sheet annealing at a temperature of 800° C. to 1100° C. for 1 to 10 minutes. Here, hot-rolled steel sheet annealing may be omitted for some purposes of use. Subsequently, after hot-rolled steel sheet pickling has been performed, a cold-rolled steel sheet is manufactured by performing cold rolling, and a product is completed by performing recrystallization annealing and pickling.

[0067] It is preferable that cold rolling be performed with a rolling reduction of 50% or more from the viewpoint of elongation, bendability, press formability, and shape. It is generally preferable that the recrystallization annealing of a cold-rolled steel sheet be performed at a temperature of 800° C. to 950° C. from the viewpoint of obtaining satisfactory mechanical properties and pickling performance in the case of a product having a surface finishing No. 2B in accordance with JIS G 0203. In addition, it is effective to perform BA annealing (bright annealing) as a finishing process on a member which is used for a part where luster is required. Here, for example, polishing may be performed after cold rolling has been performed and after forming has been performed in order to improve surface quality.

Example 1

[0068] Hereafter, the disclosed embodiments will be described more in detail based on examples.

[0069] Stainless steels having the chemical compositions given in Table 1 were prepared by using a small-size vacuum melting furnace having a capacity of 50 kg. These ingots were

heated at a temperature of 1150° C. for 1 hour and then made into hot-rolled steel sheets having a thickness of 3.5 mm by performing hot rolling. Subsequently, these hot-rolled steel sheets were subjected to hot rolled steel sheet annealing at a temperature of 950° C. for one minute, then subjected to shot blasting of surface, and then subjected to descaling by performing pickling in which the hot-rolled steel sheets were dipped in a 20% mass %-sulfuric acid solution having a temperature of 80° C. for 120 seconds and then dipped in a mixed acid containing 15 mass % of nitric acid and 3 mass % of fluoric acid and having a temperature of 55° C. for 60 seconds.

[0070] Further, the resultant steel sheets were cold-rolled to a thickness of 0.8 mm and subjected to recrystallization annealing in a slightly reducing atmosphere (hydrogen: 5 vol %, nitrogen: 95 vol %, and dew-point: -40° C.) at a temperature of 900° C. for one minute in order to obtain cold-rolled and annealed steel sheets. The cold-rolled and annealed steel sheets were subjected to a descaling treatment by performing electrolytic pickling in mixed acid containing 15 mass % of nitric acid and 0.5 mass % of hydrochloric acid and having a temperature of 50° C. in order to obtain cold-rolled, pickled, and annealed steel sheets.

TABLE 1-1

mass %														
Steel No.	C	Si	Mn	P	S	Cr	Ni	Al	V	Nb	Ti	N	Cu	Note
1	0.004	0.11	0.92	0.02	0.002	18.7	0.17	0.15	0.04	0.022	0.18	0.008	0.36	Example
2	0.009	0.14	0.38	0.02	0.003	16.3	0.13	0.18	0.06	0.026	0.20	0.008	0.46	Example
3	0.005	0.09	1.11	0.03	0.003	19.7	0.12	0.21	0.09	0.049	0.24	0.009	0.41	Example
4	0.013	0.13	0.83	0.03	0.003	18.9	0.08	0.16	0.05	0.034	0.25	0.014	0.46	Example
5	0.011	0.19	0.41	0.03	0.001	19.1	0.13	0.16	0.06	0.038	0.22	0.011	0.39	Example
6	0.018	0.21	1.96	0.04	0.004	19.4	0.45	0.19	0.08	0.044	0.29	0.015	0.45	Example
7	0.014	0.16	1.24	0.03	0.002	18.9	0.12	0.15	0.11	0.035	0.24	0.020	0.76	Example
8	0.016	0.10	1.25	0.02	0.004	18.8	0.14	0.22	0.13	0.043	0.28	0.018	0.59	Example
9	0.010	0.12	0.57	0.03	0.001	18.3	0.09	0.16	0.09	0.009	0.31	0.011	0.38	Example
10	0.007	0.11	0.73	0.02	0.002	17.8	0.17	0.74	0.13	0.040	0.16	0.009	0.36	Example
11	0.008	0.15	0.78	0.02	0.001	18.6	0.24	0.43	0.07	0.047	0.21	0.007	0.42	Example
12	0.010	0.07	1.02	0.03	0.004	19.2	0.16	0.19	0.14	0.036	0.25	0.012	0.31	Example
13	0.009	0.09	0.86	0.03	0.003	18.8	0.07	0.16	0.16	0.010	0.22	0.016	0.41	Example
14	0.010	0.18	0.87	0.03	0.003	19.4	0.05	0.15	0.18	0.011	0.19	0.016	0.39	Example
15	0.007	0.15	0.84	0.03	0.005	19.5	0.09	0.17	0.17	0.009	0.23	0.013	0.42	Example
16	0.010	0.13	0.91	0.02	0.001	18.9	0.10	0.19	0.17	0.005	0.21	0.014	0.44	Example
17	0.010	0.07	0.96	0.02	0.001	18.4	0.08	0.08	0.15	0.024	0.22	0.012	0.38	Example
18	0.011	0.05	0.69	0.03	0.003	18.7	0.08	0.18	0.18	0.034	0.17	0.017	0.41	Example
19	0.015	0.18	1.31	0.02	0.004	19.1	0.09	0.20	0.02	0.019	0.35	0.013	0.39	Example
20	0.014	0.22	1.02	0.03	0.004	19.2	0.07	0.18	0.19	0.036	0.26	0.011	0.42	Example
21	0.007	0.09	0.81	0.02	0.003	<u>24.1</u>	0.11	0.22	0.22	0.046	0.22	0.009	0.35	Comparative Example
22	0.009	0.13	0.78	0.03	0.002	<u>15.4</u>	0.23	0.16	0.17	0.051	0.18	0.012	0.36	Comparative Example
23	0.013	0.06	<u>0.19</u>	0.02	0.003	19.7	0.22	0.34	0.03	0.006	0.11	0.014	0.34	Comparative Example
24	0.019	0.08	<u>2.38</u>	0.02	0.005	19.4	0.10	0.27	0.08	0.041	0.18	0.018	0.42	Comparative Example
25	0.014	0.06	1.25	0.03	0.002	19.3	0.11	<u>0.93</u>	0.21	0.015	0.16	0.020	0.37	Comparative Example
26	0.014	0.10	0.82	0.02	0.002	17.6	0.15	0.23	0.16	0.016	<u>0.53</u>	0.015	0.33	Comparative Example
27	0.003	0.12	0.36	0.03	0.003	16.3	0.05	0.23	0.16	0.003	0.12	0.006	0.31	Comparative Example
28	0.004	0.14	0.50	0.02	0.004	18.5	0.06	0.17	0.08	0.035	0.18	0.007	0.34	Comparative Example
29	0.004	0.19	0.84	0.03	0.003	18.8	0.05	0.21	0.07	0.033	0.26	0.004	0.38	Comparative Example
30	0.003	0.11	0.38	0.02	0.003	18.1	0.06	0.14	0.10	0.028	0.16	0.003	0.30	Comparative Example

An underlined portion indicates a value out of the range according to the present invention.

TABLE 1-2

mass %								
Steel No.	Zr	W	REM	Co	B	Sb	Right-hand Side Value of Relational Expression (1)	Note
1	—	—	—	—	—	—	0.69	Example
2	—	—	—	—	—	—	0.74	Example
3	—	—	—	—	—	—	0.73	Example
4	—	—	—	—	—	—	0.95	Example
5	—	—	—	—	—	—	0.83	Example
6	—	—	—	—	—	—	1.59	Example
7	—	—	—	—	—	—	1.32	Example
8	—	—	—	—	—	—	1.27	Example
9	—	—	—	—	—	—	0.79	Example
10	—	—	—	—	—	—	0.74	Example
11	—	—	—	—	—	—	0.85	Example
12	—	—	—	—	—	—	0.87	Example

TABLE 1-2-continued

Steel No.	mass %						Right-hand Side Value of Relational Expression (1)	Note
	Zr	W	REM	Co	B	Sb		
13	0.07	—	—	—	—	—	0.86	Example
14	—	0.17	—	—	—	—	0.85	Example
15	—	—	0.08	—	—	—	0.79	Example
16	—	—	—	0.14	—	—	0.91	Example
17	—	—	—	—	0.0021	—	0.82	Example
18	—	—	—	—	—	0.23	0.93	Example
19	—	—	0.09	0.08	0.0016	—	1.01	Example
20	0.19	—	—	0.05	—	—	0.94	Example
21	—	—	—	—	—	—	0.70	Comparative Example
22	—	—	—	—	—	—	0.91	Comparative Example
23	—	—	—	—	—	—	0.97	Comparative Example
24	—	—	—	—	—	—	1.35	Comparative Example
25	—	—	—	—	—	—	1.12	Comparative Example
26	—	—	—	—	—	—	1.01	Comparative Example
27	—	—	—	—	—	—	<u>0.43</u>	Comparative Example
28	—	—	—	—	—	—	<u>0.48</u>	Comparative Example
29	—	—	—	—	—	—	<u>0.49</u>	Comparative Example
30	—	—	—	—	—	—	<u>0.37</u>	Comparative Example

An underlined portion indicates a value out of the range according to the present invention.

[0071] Here, Table 1-1 and Table 1-2 continued make one table as a whole.

[0072] Butt TIG welding was performed on the obtained cold-rolled steel sheet and a commercially available cold-rolled steel sheet having a thickness of 0.8 mm of austenite stainless steel, that is, SUS304 (C: 0.07 mass %, N: 0.05 mass %, Cr: 18.2 mass %, and Ni: 8.2 mass %) (cold-rolled steel sheet according to the present disclosure: base material and welding opposite material: SUS304). Welding current was 90 A, welding speed was 60 cm/min, and Ar gas containing 8 vol % of nitrogen and 2 vol % of oxygen was used as a shielding gas at a flow rate of 15 L/min. The width of the obtained weld bead at a front side was about 3 mm.

[0073] Test pieces including the obtained weld beads were taken in order to perform tests below.

[0074] 1. Pitting Potential Test on a Base Material and a Weld Zone

[0075] Test pieces of 20 mm square were taken from the cold-rolled and annealed test piece and the welded sample piece, and the sample pieces were covered with seal materials with measuring surfaces of 10 mm square being left uncovered. In the case of a welded sample piece, the test piece was taken such that the weld bead was included, and welding temper color (oxide film) was left as it was. Pitting potentials of the base material and weld zone of each of these test pieces were determined in a 3.5 mass %-NaCl solution having a temperature of 30° C. At this time, although polishing of a test piece or a passivation treatment was not performed, measuring methods other than those were in accordance with JIS G 0577 (2005).

[0076] A case where the pitting potential of a base material was 150 mV or more and the pitting potential of a weld zone was 0 mV or more was judged as satisfactory.

[0077] 2. Cyclic Neutral Salt Spray Test

[0078] A test piece of 100 mm square was taken from the welded sample piece such that the weld bead was included in the test piece, the surface of the test piece was subjected to polish finishing with a #600 emery paper, the end faces of the

test piece were sealed, and then the test piece was subjected to a cyclic neutral salt spray test in accordance with JIS H 8502. One cycle of a cyclic neutral salt spray test includes spraying 5 mass %-NaCl solution (35° C., 2 hours)->drying (60° C., 4 hours, relative humidity: 20% to 30%)->moistness (40° C., 2 hours, relative humidity: 95% or more). After performing this cycle 15 times, a case where corrosion did not occur in a base material and a weld zone was judged as satisfactory.

[0079] 3. Determination of the Grain Boundary Coverage Factor of a Ferrite Phase by Cr Carbonitrides

[0080] A test piece for the observation of metallographic microstructure was taken in a direction at a right angle to the weld bead direction of the welded sample piece, the test piece was subjected to mirror polishing and etching using picric acid-hydrochloric acid solution in order to expose metallographic structure and precipitations, and the observation of microstructure and the phase identification of precipitations were performed by using a scanning electron microscope and energy dispersive X-ray spectrometry in order to determine the grain boundary coverage factor of a ferrite phase by Cr carbonitrides in a weld bead.

[0081] Grain boundary length of crystal grains in the obtained microstructure photograph was determined by using an image analyzer, the diameter in a direction parallel to the grain boundary of a Cr carbonitride, which was precipitated at the grain boundary, was determined by using the image analyzer in the same way as the case with grain boundary length was determined, and then the grain boundary coverage factor was calculated by the equation: grain boundary coverage factor (%)=(the sum of the diameter in the direction parallel to the grain boundary of Cr carbides at the grain boundaries)/(the sum of the grain boundary lengths of crystal grains)×100.

[0082] A case where the grain boundary coverage factor of a ferrite phase by Cr carbonitrides was 40% or less was judged as satisfactory.

[0083] 4. Evaluation of Mechanical Properties

[0084] A JIS 13B tensile test piece was taken from the obtained cold-rolled and annealed steel sheet in the direction

parallel to the rolling direction, and a tensile test was performed in accordance with JIS Z 2241 in order to determine breaking elongation.

[0085] A case where breaking elongation was 25% or more was judged as satisfactory.

[0086] 5. Evaluation of Surface Quality

[0087] By performing a visual test on the surface of the descaled steel sheet after cold rolling and annealing had been performed, it was checked whether or not unsatisfactory descaling or surface defect such as streaky defects are observed.

[0088] A case where satisfactory aesthetic surface appearance was obtained without residual scale or surface defects was judged as satisfactory.

[0089] The test results are given in Table 2.

[0091] On the other hand, in the case of steel No. 21, whose Cr content was over the range according to the present disclosure, there was a significant deterioration in the toughness of a steel sheet after hot rolling has been performed, and it was not possible to perform the manufacturing processes following the hot rolling. Hence, it was not possible to evaluate the properties of the steel.

[0092] In the case of steel No. 22, whose Cr content was below the range according to the present disclosure, sufficient pitting potentials were not achieved, and corrosion occurred in a base material and a weld zone under the cyclic neutral salt spray test. Hence, it was not possible to achieve the specified corrosion resistance.

TABLE 2

Steel No.	Pitting Potential of Base Material V/c100 [mV vs SCE]	Pitting Potential of Weld Bead V/c100 [mV vs SCE]	Existence of Corrosion in Neutral Salt Spray Cyclic Corrosion Test	Grain Boundary Coverage Factor of Ferrite Phase by Cr Carbonitride [%]	Breaking Elongation [%]	Surface Quality	Note
1	182	42	No	8	36	Satisfactory	Example
2	152	18	No	24	35	Satisfactory	Example
3	203	38	No	6	31	Satisfactory	Example
4	187	39	No	13	30	Satisfactory	Example
5	205	24	No	22	33	Satisfactory	Example
6	165	39	No	6	29	Satisfactory	Example
7	174	41	No	6	34	Satisfactory	Example
8	172	34	No	12	33	Satisfactory	Example
9	179	31	No	10	30	Satisfactory	Example
10	163	26	No	12	31	Satisfactory	Example
11	183	32	No	18	33	Satisfactory	Example
12	191	17	No	16	32	Satisfactory	Example
13	183	27	No	11	33	Satisfactory	Example
14	206	25	No	14	30	Satisfactory	Example
15	204	27	No	11	31	Satisfactory	Example
16	185	29	No	9	31	Satisfactory	Example
17	171	26	No	13	30	Satisfactory	Example
18	185	29	No	13	32	Satisfactory	Example
19	180	39	No	6	29	Satisfactory	Example
20	192	41	No	6	30	Satisfactory	Example
21	—	—	—	—	—	—	Comparative Example
22	<u>97</u>	<u>-27</u>	<u>Yes</u>	21	35	Satisfactory	Comparative Example
23	<u>226</u>	<u>-21</u>	<u>Yes</u>	33	27	Satisfactory	Comparative Example
24	155	42	No	1	<u>19</u>	Satisfactory	Comparative Example
25	184	34	No	4	<u>22</u>	Satisfactory	Comparative Example
26	150	39	No	3	27	<u>Surface Defect</u>	Comparative Example
27	151	<u>-24</u>	<u>Yes</u>	<u>61</u>	32	Satisfactory	Comparative Example
28	188	<u>-34</u>	<u>Yes</u>	<u>59</u>	33	Satisfactory	Comparative Example
29	189	<u>-29</u>	<u>Yes</u>	<u>58</u>	32	Satisfactory	Comparative Example
30	183	<u>-31</u>	<u>Yes</u>	<u>67</u>	35	Satisfactory	Comparative Example

An underlined portion indicates a value out of the range according to the present invention.

[0090] In the case of all of steel Nos. 1 through 20, which satisfied the requirements according to the present disclosure, the pitting potential of a base material was 150 mV or more, the pitting potential of a weld bead was 0 mV or more, corrosion did not occur in a cyclic neutral salt spray test, and hence sufficient corrosion resistance was achieved even when welding with austenite stainless steel was performed. In addition, in the case of all of steel Nos. 1 through 20, the grain boundary coverage factor of a ferrite phase by Cr carbonitrides after welding was 40% or less, and the specified effect of preventing sensitization was realized. Moreover, in all these cases, breaking elongation in a tensile test was 25% or more, which means satisfactory workability was achieved, and further surface defects were not observed.

[0093] In the case of steel No. 23, whose Mn content was below the range according to the present disclosure, although sufficient corrosion resistance for a base material was achieved, sufficient corrosion resistance for a weld zone was not achieved.

[0094] On the other hand, in the case of steel Nos. 24 and 25, whose Mn content or Al content was over the range according to the present disclosure, although the specified corrosion resistance for a base material and a weld zone was achieved, since there was a deterioration in ductility due to an increase in the hardness of the steel sheet, it was not possible to achieve the specified mechanical properties.

[0095] In the case of steel No. 26, whose Ti content was over the range according to the present disclosure, although

the specified corrosion resistance and mechanical properties were achieved, since surface defects occurred due to Ti-based coarse inclusions being formed in a large amount, it was not possible to achieve the specified surface quality.

[0096] In the case of steel Nos. 27 through 30 where the contents of the constituent elements were within the ranges according to the present disclosure and where the contents of austenite-stabilizing elements were below the ranges according to relational expression (1), the specified corrosion resistance and mechanical properties for a base material were achieved. However, the specified pitting potential for a weld bead or the specified corrosion resistance for a weld zone was not achieved. From the results of the investigation of microstructure in the cross section of a weld zone of Nos. 27 to 30, it was clarified that Cr carbonitrides were precipitated at ferrite phase grain boundaries in a very large amount of 50% or more in terms of grain boundary coverage factor. It is considered that, in the case of steel Nos. 27 through 30, since the contents of austenite-stabilizing elements were insufficient, it was not possible to inhibit the formation of Cr carbonitrides at the grain boundaries due to the formation of a ferrite phase during cooling after welding had been performed, which caused the occurrence of marked sensitization and results in the specified corrosion resistance for a weld zone not being achieved.

[0097] From the results described above, it is clarified that, according to the present disclosure, it is possible to obtain ferritic stainless steel excellent in terms of corrosion resistance, mechanical properties, and surface quality without needing to add excessive amounts of Ti and Nb.

INDUSTRIAL APPLICABILITY

[0098] Ferritic stainless steel according to the present disclosure can suitably be used in applications, in which structures are manufactured by performing welding, for example, materials for automobile exhaust system such as mufflers and architectural materials such as fittings, air vents, and ducts.

1. Ferritic stainless steel having a chemical composition comprising:

C: 0.001% or more and 0.025% or less, by mass %;
 Si: 0.05% or more and 0.30% or less, by mass %;
 Mn: 0.35% or more and 2.0% or less, by mass %;
 P: 0.05% or less, S: 0.01% or less, by mass %;
 Al: 0.05% or more and 0.80% or less, by mass %;
 N: 0.001% or more and 0.025% or less, by mass %;
 Cr: 16.0% or more and 20.0% or less, by mass %;

Ti: 0.12% or more and 0.50% or less, by mass %;
 Nb: 0.002% or more and 0.050% or less, by mass %;
 Cu: 0.30% or more and 0.80% or less, by mass %;
 Ni: 0.05% or more and less than 0.50%, by mass %;
 V: 0.01% or more and 0.50% or less, by mass; and
 Fe and inevitable impurities
 wherein Expression (1) >0.50 ,

$$25 \times C + 18 \times N + Ni + 0.11 \times Mn + 0.46 \times Cu \quad (1),$$

where, atomic symbols in Expression (1) respectively represent the contents (mass %) of the corresponding elements.

2. The ferritic stainless steel according to claim 1, wherein the steel further includes one or more selected from the group consisting of:

Zr: 0.01% or more and 0.50% or less, by mass %;
 W: 0.01% or more and 0.20% or less, by mass %;
 REM: 0.001% or more and 0.10% or less, by mass %;
 Co: 0.01% or more and 0.20% or less, by mass %;
 B: 0.0002% or more and 0.010% or less, by mass %; and
 Sb: 0.05% or more and 0.30% or less by mass %.

3. The ferritic stainless steel according to claim 1, wherein the steel includes Mn in the range from 0.50% to 1.5%, by mass %.

4. The ferritic stainless steel according to claim 1, wherein the steel includes Mn in the range from 0.75% to 1.25%, by mass %.

5. The ferritic stainless steel according to claim 1, wherein the steel includes N in the range from 0.003% to 0.015%, by mass %.

6. The ferritic stainless steel according to claim 1, wherein the steel includes Cr in the range from 16.5% to 19.0%, by mass %.

7. The ferritic stainless steel according to claim 1, wherein the steel includes Cu in the range from 0.35% to 0.50%, by mass %.

8. The ferritic stainless steel according to claim 1, wherein the steel includes C in the range from 0.003% to 0.018%, by mass %.

9. The ferritic stainless steel according to claim 1, wherein Expression (1) ≥ 0.60 .

10. The ferritic stainless steel according to claim 1, wherein Expression (1) ≥ 0.70 .

11. The ferritic stainless steel according to claim 1, wherein:

$$0.50 < \text{Expression (1)} \leq 1.59.$$

* * * * *