(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 831 978 A1

(12) EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
09.06.2021 Bulletin 2021/23

(21) Application number: 18928736.0

(22) Date of filing: 02.11.2018

(51) Int Cl.:
C22C 38/26 (2006.01) *C22C 38/28* (2006.01)
C22C 38/00 (2006.01) *C22C 38/02* (2006.01)
C22C 38/04 (2006.01) *C22C 38/06* (2006.01)

(86) International application number:
PCT/KR2018/013229

(87) International publication number:
WO 2020/027380 (06.02.2020 Gazette 2020/06)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
KH MA MD TN

(30) Priority: 03.08.2018 KR 20180090874

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(54) TI- AND NB-ADDED FERRITIC STAINLESS STEEL EXCELLENT IN LOW-TEMPERATURE TOUGHNESS OF WELDS

(57) A Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of present disclosure includes, in percent (%) by weight of the entire composition, C: 0.004 to 0.015%, N: 0.004 to 0.015%, Si: 0.01 to 0.7%, Mn: 0.01 to 0.7%, P: 0.0001 to 0.04%, S: 0.0001 to 0.005%, Cr: 10 to 30%, Al: 0.005 to 0.04%, Ti: 0.1 to 0.5%, Nb: 0.1 to 0.6%, Ca: 0.0001 to 0.003%, the remainder of iron (Fe) and other inevitable impurities, satisfies the following equation (1), and Al-Ca-Ti-Mg-O-based oxide and Ti-Nb-C-N carbonitride containing the oxide have an average diameter of 3 to 10 μm and a distribution density of 4 /mm^2 or more.

$$\{(Ti + 0.5*Nb)*(C + N)\}/Al > 0.25 \quad (1)$$

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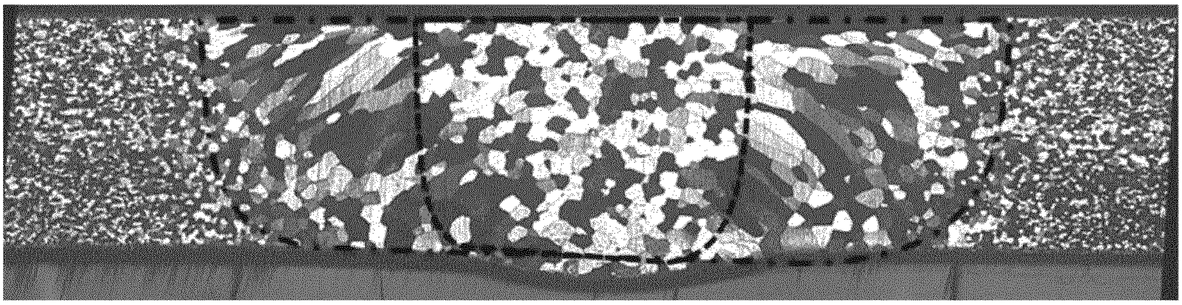


FIG. 1

Description

[Technical Field]

[0001] The present disclosure relates to a ferritic stainless steel, and more specifically, Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone.

[Background Art]

[0002] The main use of ferritic stainless steel is parts for automobile exhaust system. Mainly, the final product is made by forming through press processing and welding these processed products, or by expanding and forming the welded pipe. Therefore, as an important requirement of ferritic stainless steel for automobile exhaust system, the processing characteristics of the weld zone are mentioned.

[0003] The welding process of ferritic stainless steel generally melts the base metal using arc heat, and the molten metal is rapidly cooled to form a solidified structure, and the grain size and shape of the solidified structure have a great influence on the workability of the weld zone.

[0004] In particular, the welding method for automobile exhaust system has a large heat input and a wide range, which increases the probability of cracking during subsequent processing due to coarsening of the grains in the weld zone. In addition, coarsening of weld zone grains has a characteristic of impairing low-temperature toughness characteristics, and particularly, there is a problem in that the rate of occurrence of weld zone cracks increases rapidly during product processing in winter.

[0005] Therefore, it was found that it was necessary to refine the solidified structure of the molten part to satisfy the weld zone characteristics of automobile exhaust system parts.

[0006] As a solidified structure refinement technique, a low-temperature casting method and an electromagnetic stirring are used, but these techniques can refine the solidified structure of the base material, but have no effect on the refinement of the solidified structure of the molten part during welding.

[0007] In particular, the solidification condition of the weld zone has a characteristic that the solidified structure becomes coarse because the cooling rate is faster than that of the normal solidification condition, so it is advantageous to grow into a columnar crystal. Therefore, in order to refine the solidified structure of the weld zone, it is possible by promoting non-uniform nucleation. When the re-dissolved molten part re-solidifies during welding, non-uniform nucleation occurs due to the remaining oxide, which promotes nucleation and growth of the equiaxed crystal, and the solidified structure is expected to be refined.

[0008] As an example of non-uniform using oxides of ferritic stainless steel, Prior Document 1 discloses a technology for refining the base material structure using Al-Mg-based inclusions. The Prior Document 2 discloses a technique of manufacturing stainless steel mainly using a composite oxide containing Ti and Ca. In addition, Prior Document 3 discloses that MgO and MgO-Al_2O_3 can be produced to secure a base material structure.

[0009] However, Prior Documents 1 to 3 above focus on refinement of the solidified structure of the base material, and do not consider the composition of oxides or the number of sizes of oxides for the solidified structure of the weld zone. In particular, in the case of the weld zone, unlike the usual casting structure, the melting temperature is high, so that the effect may be lost due to re-dissolution of the oxide, and the cooling rate is fast, so that the size control of the oxide for refinement is required. Therefore, in the case of the prior documents, it cannot be said to be a preferred method for refinement the solidified structure of the weld zone.

(Prior Document 1) Korean Patent Application Publication No. 10-2011-0074217 (published on June 30, 2011)

(Prior Document 2) Japanese Patent Application Publication No. 2000-001715 (published on Jan. 7, 2000)

(Prior Document 3) Japanese Patent Application Publication No. 2001-254153 (published on September 18, 2001)

[Disclosure]

[Technical Problem]

[0010] Embodiments of the present disclosure are intended to provide ferritic stainless steel capable of improving low-temperature toughness of weld zone through refinement of the base material structure of stainless steel and the solidified structure of the weld zone.

[Technical Solution]

[0011] In accordance with an aspect of the present disclosure, a Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone includes, in percent (%) by weight of the entire composition, C: 0.004 to 0.015%, N: 0.004 to 0.015%, Si: 0.01 to 0.7%, Mn: 0.01 to 0.7%, P: 0.0001 to 0.04%, S: 0.0001 to 0.005%, Cr: 10 to 30%, Al: 0.005 to 0.04%, Ti: 0.1 to 0.5%, Nb: 0.1 to 0.6%, Ca: 0.0001 to 0.003%, the remainder of iron (Fe) and other inevitable impurities, satisfies the following equation (1), and Al-Ca-Ti-Mg-O-based oxide and Ti-Nb-C-N carbonitride containing the oxide have an average diameter of 3 to 10 μm and a distribution density of 4 /mm^2 or more.

$$\{(Ti + 0.5*Nb)*(C + N)\}/Al > 0.25 \qquad (1)$$

[0012] Here, Ti, Nb, C, N, and Al mean the content (% by weight) of each element.
[0013] The distribution density may be 4/mm^2 or more and 15/ mm^2 or less.
[0014] The ferritic stainless steel may further include: any one or more selected from the group consisting of Mo: 0.1 to 2.0%, Ni: 0.1 to 2.0% and Cu: 0.1 to 2.0%.
[0015] The Al-Ca-Ti-Mg-O-based oxide may satisfy the following equations (2) to (4).

$$\%(TiO_2) + \%(CaO) + \%(Al_2O_3) \geq 80 \qquad (2)$$

$$\{\%(TiO_2) + \%(CaO)\}/\{\%(TiO_2) + \%(CaO) + \%(Al_2O_3)\} \geq 0.3 \qquad (3)$$

$$0.3 \leq \%(CaO)/\%(TiO_2) \leq 0.8 \qquad (4)$$

[0016] The Ti-Nb-C-N carbonitride may have the Al-Ca-Ti-Mg-O-based oxide as a nucleus and may be formed to surround the Al-Ca-Ti-Mg-O-based oxide.
[0017] The average grain size of the solidified structure of the weld zone may be less than 150 μm.
[0018] The impact energy of the weld zone may be 90J/cm^2 or more at -30°C.
[0019] The DBTT of the weld zone may be -25°C or less.

[Advantageous Effects]

[0020] Examples of the present disclosure can control the size and distribution density of effective nucleation products in the base metal of stainless steel by controlling the composition of Ti, Nb-added ferritic stainless steel, and accordingly, the solidified structure of the weld zone can be refined, and the low-temperature toughness of weld zone can be improved.

[Description of Drawings]

[0021]

FIG. 1 is a photograph showing a solidified structure of a Ti, Nb-added ferritic stainless steel weld zone according to an embodiment of the present disclosure.

FIG. 2 is a photograph showing the solidified structure of a Ti, Nb-added ferritic stainless steel weld zone according to a comparative example.

FIG. 3 is a graph showing a result of analysis of nucleation inclusions in the center of a grain of a weld zone solidified structure of Ti, Nb-added ferritic stainless steel according to an embodiment of the present disclosure.

FIG. 4 is a graph showing the distribution of the number of effective nucleation products by size of the inventive example and comparative example according to the present disclosure.

FIG. 5 is a graph showing the number of effective nucleation products having a size of 3 to 10 μm per unit area in an inventive example and a comparative example according to the present disclosure.

FIG. 6 is a graph showing the results of measuring the average grain size of the weld zone solidified structure of the inventive example and comparative example according to the present disclosure.

FIG. 7 is a graph showing the result of measuring the impact energy of the weld zone of the inventive example and comparative example according to the present disclosure.

FIG. 8 is a graph showing a result of measuring a weld zone DBTT of an inventive example and a comparative example according to the present disclosure.

FIG. 9 is a graph showing the correlation between the value of Equation (1) and the average grain size of the weld zone of the inventive example and comparative example according to the present disclosure.

[Best Mode]

[0022] A Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of present disclosure includes, in percent (%) by weight of the entire composition, C: 0.004 to 0.015%, N: 0.004 to 0.015%, Si: 0.01 to 0.7%, Mn: 0.01 to 0.7%, P: 0.0001 to 0.04%, S: 0.0001 to 0.005%, Cr: 10 to 30%, Al: 0.005 to 0.04%, Ti: 0.1 to 0.5%, Nb: 0.1 to 0.6%, Ca: 0.0001 to 0.003%, the remainder of iron (Fe) and other inevitable impurities, satisfies the following equation (1), and Al-Ca-Ti-Mg-O-based oxide and Ti-Nb-C-N carbonitride containing the oxide have an average diameter of 3 to 10 μm and a distribution density of 4 /mm^2 or more.

$$(1) \qquad \{(Ti + 0.5*Nb)*(C + N)\}/Al > 0.25$$

[0023] Here, Ti, Nb, C, N, and Al mean the content (% by weight) of each element.

[Modes of the Invention]

[0024] Hereinafter, the embodiments of the present disclosure will be described in detail with reference to the accompanying drawings. The following embodiments are provided to transfer the technical concepts of the present disclosure to one of ordinary skill in the art. However, the present disclosure is not limited to these embodiments, and may be embodied in another form. In the drawings, parts that are irrelevant to the descriptions may be not shown in order to clarify the present disclosure, and also, for easy understanding, the sizes of components are more or less exaggeratedly shown.

[0025] The inventers of present disclosure have to control the size and number of Ti-Nb-CN carbonitride including oxides that promote nucleation of delta ferrite to act as an effective nucleation product. As a result, the effective nucleation product formation conditions could be derived.

[0026] The inventors of the present disclosure understand that the size and number of Ti-Nb-CN carbonitride including oxides that promote nucleation of delta ferrite must be controlled in order to act as an effective nucleation product, and for this purpose, control of components in molten steel is the key. As a result of the experiment, the conditions for forming an effective nucleation product could be derived.

[0027] In the present disclosure, an effective nucleation product means an Al-Ca-Ti-Mg-O-based oxide and Ti-Nb-C-N carbonitride including the same.

[0028] A Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of present disclosure includes, in percent (%) by weight of the entire composition, C: 0.004 to 0.015%, N: 0.004 to 0.015%, Si: 0.01 to 0.7%, Mn: 0.01 to 0.7%, P: 0.0001 to 0.04%, S: 0.0001 to 0.005%, Cr: 10 to 30%, Al: 0.005 to 0.04%, Ti: 0.1 to 0.5%, Nb: 0.1 to 0.6%, Ca: 0.0001 to 0.003%, the remainder of iron (Fe) and other inevitable impurities.

[0029] Hereinafter, the reason for the numerical limitation of the content of the alloy component element in the embodiment of the present disclosure will be described. Hereinafter, unless otherwise specified, the unit is% by weight.

[0030] The content of C and N is 0.004 to 0.015%, respectively.

[0031] It was confirmed that the roles of C and N in Ti-Nb composite added steel have a great influence on the refinement of the weld zone structure. That is, after the oxide is formed, a Ti-Nb composite carbonitride is formed, and delta ferrite nucleation are generated based on the carbonitride. Here, the content of C and N is related to the crystallization temperature of Ti-Nb-C-N carbonitride, and must have a minimum value in order to have an effective effect on the nucleation of delta ferrite. Therefore, each content is limited to at least 0.004% or more, and the influence of the content value will be described in detail later in setting the Ti and Nb content. Also, in the case of C and N, both elements are interstitial elements and when the amount of addition increases, workability decreases during molding due to lower elongation, and each maximum value is limited to 0.015% due to lower corrosion resistance due to the formation of grain boundary Cr carbonitride.

[0032] The content of Si and Mn is 0.01 to 0.7%, respectively.

[0033] For Si and Mn, corrosion resistance and formability must be considered at the same time, and it is limited to 0.01% or more in terms of corrosion resistance and 0.7% or less in terms of workability.

[0034] Si is an element added in terms of corrosion resistance, and if it is less than 0.01%, it is difficult to obtain sufficient corrosion resistance. When Si exceeds 0.7%, the impurities of the material increase, the elongation and work hardening index (n value) decrease, and the Si-based inclusions increase, resulting in poor workability. Therefore, the content range thereof is preferably 0.01 to 0.7%.

[0035] Mn is an element added in terms of corrosion resistance, and if it is less than 0.01%, it is difficult to obtain sufficient corrosion resistance, but if it exceeds 0.7%, there is a problem that elongation and corrosion resistance decrease due to increased impurities in the material. Therefore, the content range thereof is preferably 0.01 to 0.7%.

[0036] It is preferable that both P and S are low, but in consideration of manufacturing cost, P is limited to 0.0001 to 0.04% and S is limited to 0.0001 to 0.005%.

[0037] The content of P is preferably low in terms of corrosion resistance. Preferably, the lower limit of the content is 0.0001% in consideration of the cost in the steelmaking process. Therefore, it is preferable that its content range is 0.0001 to 0.04%.

[0038] The content of S is preferably low in terms of corrosion resistance. Preferably, the lower limit of the content is 0.0001% in consideration of the cost in the steelmaking process. Therefore, it is preferable that the content range is 0.0001 to 0.005%.

[0039] The content of Cr is 10 to 30%.

[0040] When the content of Cr is less than 10%, corrosion resistance as stainless steel is insufficient, and when the content of Cr is more than 30%, formability decreases, and the content range thereof is preferably 10 to 30%.

[0041] The content of Al is 0.005 to 0.04%.

[0042] In the case of Al, it is absolutely necessary as a deoxidation element, but when a large amount is added, it is difficult to improve the low-temperature toughness because it cannot suppress the coarsening of the weld zone grains due to the formation of an invalid oxide. Therefore, the maximum value is limited to 0.04% for grain refinement of the weld zone while including at least 0.005% in consideration of the deoxidization effect.

[0043] The content of Ti is 0.1 to 0.5%.

[0044] Ti is the most important element that determines the effective nucleation product of the present disclosure, and the lower limit of Ti is limited to 0.1% to satisfy the composition, size, and distribution of the effective nucleation product suggested in the present disclosure through a series of experiments. In addition, when a large amount is added in excess of 0.5%, linear defects due to inclusions in the final product occur frequently due to a high melting point nitride such as TiN, so the upper limit is limited to 0.5%.

[0045] The content of Nb is 0.1 to 0.6%.

[0046] Nb is an essential element for securing high temperature strength of high-temperature exhaust system components, and at the same time has an influence on the formation of effective nucleation products. In particular, in order to secure the characteristics as a high-temperature exhaust system component of 660°C or higher, it must contain at least 0.1%, and if excessively added exceeding 0.6%, the cost of raw materials is higher than the increase in high-temperature strength, so the upper limit is limited to 0.6%.

[0047] The content of Ca is 0.0001 to 0.003%.

[0048] In the case of Ca, as a deoxidation element, it is an important element in the formation of effective oxides in the present disclosure. However, when a large amount is contained, the formation of effective oxides is suppressed and the corrosion resistance is also adversely affected, so the maximum value is limited to 0.003%, and the minimum value is 0.0001 %, which is the minimum value for effective oxide formation.

[0049] In addition, Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of the present disclosure may further include, in percent (%) by weight, any one or more selected from the group consisting of Mo: 0.1 to 2.0%, Ni: 0.1 to 2.0%, and Cu: 0.1 to 2.0%.

[0050] The amount of Mo is 0.1 to 2.0%.

[0051] Mo may be additionally added as a composition to increase the corrosion resistance of stainless steel, and if it is added in an excessive amount, the impact characteristics are deteriorated, thereby increasing the risk of breakage during processing and increasing the cost of the material. Therefore, it is preferable to limit the content of Mo to 0.1 to 2.0% in consideration of this in the present disclosure.

[0052] The amount of Ni is 0.1 to 2.0%. Ni is an element that improves corrosion resistance, and if it is added in a large amount, it is not only hardened, but also stress corrosion cracking may occur, so it is preferable to be 2.0% or less.

[0053] The amount of Cu is 0.1 to 2.0%. It is preferable that Cu contains 0.1 to 1.0% to improve corrosion resistance. However, when it exceeds 1.0%, there is a problem that workability is deteriorated.

[0054] The remainder of the ferritic stainless steel except for the aforementioned alloying elements is made of Fe and other inevitable impurities.

[0055] In the case of high Cr ferritic stainless steel with Ti-Nb composite addition, the impact energy change according to temperature does not change rapidly. Therefore, a temperature having an impact energy value (90J/cm^2) that decreases by 50% compared to the impact energy at room temperature was defined as the ductile brittle transition temperature (DBTT), and is shown in FIG. 8. Based on the DBTT temperature, the fracture behavior changes from ductile fracture to brittle fracture, which is the main cause of cracking during welding zone processing under low temperature conditions. Therefore, it is desirable that the DBTT is low.

[0056] Based on the apparent difference in the weld zone solidified structure even under the same steel grade and similar component conditions and the DBTT value also changing, the solidified structure refinement mechanism was identified, and based on this, a present disclosure that could improve the low-temperature toughness of weld zone was proposed.

[0057] As a result of investigating the interaction of the molten steel composition with the refinement of the weld zone solidified structure in addition to limiting the range of the above-described molten steel components, the following equation (1) could be derived.

$$(1) \qquad \{(Ti + 0.5*Nb)*(C + N)\}/Al > 0.25$$

[0058] When the calculated value of {(Ti+0.5*Nb)*(C+N)}/Al exceeds 0.25 with the content range of Ti, Nb, C, N, and Al of the above composition, Al-Ca-Ti -Mg-O-based oxide and Ti-Nb-CN carbonitride including the same are easily formed. By forming such an effective nucleation product, the weld zone solidified structure is refined and excellent DBTT characteristics can be obtained. On the other hand, if Equation (1) is not satisfied, the composition of the Al-Ca-Ti-Mg-O-based oxide does not satisfy Equations (2) to (4) to be described later, and as a result, the number of Ti-Nb-CN carbonitrides based on the oxide is extremely low. Accordingly, the grains of the weld zone solidified structure are coarse with an average of 150 μm or more, and the DBTT value is also increased to -20°C or more, which lowers the low-temperature processing characteristics.

[0059] FIG. 1 is a photograph showing a solidified structure of a Ti, Nb-added ferritic stainless steel weld zone according to an embodiment of the present disclosure. FIG. 2 is a photograph showing the solidified structure of a Ti, Nb-added ferritic stainless steel weld zone according to a comparative example.

[0060] When comparing the weld zone solidified structure of the inventive example of FIG. 1 and the comparative example of Figure 2, in the case of a comparative example, it can be seen that most are columnar crystals, and equiaxed crystals are formed in some centers. However, in the case of the inventive example, columnar crystals exist, but it can be seen that a fraction of fine equiaxed crystals is widely formed.

[0061] FIG. 3 is a graph showing a result of analysis of nucleation inclusions in the center of a grain of a weld zone solidified structure of Ti, Nb-added ferritic stainless steel according to an embodiment of the present disclosure.

[0062] In order to confirm the cause of the difference in the solidified structure in the weld zone region of the inventive examples and comparative examples of FIGS. 1 and 2, Fig. 3 shows the results of closely observing nucleation inclusions in the center of the equiaxed crystal with an electron microscope. In the case of inventive example, a spherical oxide and carbonitride of Ti-Nb-C-N surrounding it were observed, and most of the Ti-Nb-C-N carbonitride of 3 μm or more contained a spherical oxide therein. When the spherical oxide is closely observed through an electron transmission microscope, it can be seen that a crystalline CaO-TiO_2 phase and an Al_2O_3-MgO phase exist together. On the other hand, in the case of a comparative example, the size of Ti-Nb-C-N carbonitride was small and the number was small, it was confirmed that the oxide composition in Ti-Nb-C-N carbonitride was a single Al_2O_3-MgO phase, an Al_2O_3-MgO and MgO composite phase, or an Al_2O_3-MgO and Al_2O_3 composite phase. Therefore, from the above results, the refinement of the weld zone solidified structure could be confirmed by the oxide composed of multiple oxide crystal phases including CaO-TiO_2 phase, and the Ti-Nb-C-N carbonitride formed by using these oxides as nuclei.

[0063] In particular, it was confirmed that Ti-Nb-C-N carbonitride has a high crystallization temperature compared to TiN nitride found in a conventional Ti alone-added steel. That is, in the case of Ti-Nb composite steel, it was found through experiments and thermodynamic analysis that Ti-Nb-C-N carbonitride was crystallized at a higher temperature under the same Ti component condition than that of the Ti alone-added steel. Therefore, Ti-Nb-C-N carbonitride is easily formed around the effective oxide formed in the present disclosure, and as a result, delta-ferrite nucleation easily occurs below the liquidus temperature, thereby improving the equiaxed crystal rate of the weld zone.

[0064] As described above, in order to confirm that Ti-Nb-CN carbonitride causes a difference in the solidified structure of the weld zone region, the size and number distributions of Ti-Nb-C-N carbonitrides present in the base material of the inventive example and the comparative example were compared and analyzed and shown in FIG. 4.

[0065] FIG. 4 is a graph showing the distribution of the number of effective nucleation products by size of the inventive example and comparative example according to the present disclosure. FIG. 5 is a graph showing the number of effective nucleation products having a size of 3 to 10 μm per unit area in an inventive example and a comparative example according to the present disclosure.

[0066] Referring to FIG. 4, in the case of a comparative example, a large amount of Ti-Nb-C-N carbonitride of less than 3 μm is distributed, while the number of Ti-Nb-C-N carbonitrides of 3 μm or more is rapidly decreased. In the case of the inventive example, it can be seen that a number of Ti-Nb-C-N carbonitrides having a size of 3 μm or more are distributed. Based on these results, it can be confirmed that the refinement of the solidified structure of the weld zone is a Ti-Nb-C-N carbonitride of 3 μm or more. On the other hand, when the size of Ti-Nb-C-N carbonitride exceeds 10 μm, float separation is easily performed on the surface of the molten part, so it cannot play the role of delta-ferrite nucleation.

[0067] In addition, as shown in FIG. 5, as a result of comparing the number per unit area, it was confirmed that the distribution density should be 4 /mm^2 or more. However, when the number of Ti-Nb-C-N carbonitrides exceeds 15/ mm^2, they form an aggregate and this becomes a major factor of surface defects, so it is desirable to have a distribution density of 15/ mm^2 or less.

[0068] According to the embodiment of the present disclosure, as a method for refinement of the weld zone solidified structure, it should contain Al-Ca-Ti-Mg-O-based oxide that does not re-dissolve in molten steel even at high welding heat and remains in a solid state. This provides a nucleation site of Ti-Nb-C-N carbonitride when the molten metal in the weld zone is solidified, and as a result, the amount of equiaxed crystal formation increases.

[0069] Usually, the oxide observed under Al deoxidation conditions is Al-Ca-Ti-Mg-O. Al-Ca-Ti-Mg-O-based oxides include TiO_2, CaO, Al_2O_3, MgO, etc., and the conditions for simultaneously forming the CaO- TiO_2 phase and the Al_2O_3-MgO phase, which are advantageous oxides for nucleation of ferrite, can be predicted from the Al_2O_3-TiO_2-CaO ternary phase diagram. As a result of precise analysis and statistics of oxides present in the base material of the inventive examples and comparative examples, the average oxide composition of the base metal with improved low-temperature toughness of weld zone should satisfy the following equations (2) to (4).

[0070] According to an embodiment of the present disclosure, the Al-Ca-Ti-Mg-O-based oxide may satisfy the equations (2) to (4) below.

$$(2) \qquad \%(TiO_2) + \%(CaO) + \%(Al_2O_3) \geq 80$$

$$(3) \qquad \{\%(TiO_2) + \%(CaO)\}/\{\%(TiO_2) + \%(CaO) + \%(Al_2O_3)\} \geq 0.3$$

$$(4) \qquad 0.3 \leq \%(CaO)/\%(TiO_2) \leq 0.8$$

[0071] According to the equation (2), the inclusions during Al deoxidation are Al-Ca-Ti-Mg-O, and the total ratio of %(TiO_2), %(CaO) and %(Al_2O_3) should be 80% or more. When the total ratio of %(TiO_2), %(CaO) and %(Al_2O_3) is less than 80%, it is difficult to form a CaO-TiO_2 phase effective for nucleation as it is stabilized with MgO rich oxide or Al_2O_3-MgO oxide. Due to the high crystallization temperature, it is difficult to remain in the liquid phase because they are easily coarsened during the cooling process.

[0072] According to the equation (3), the total ratio of %(TiO_2), %(CaO) and %(Al_2O_3) to the total ratio of %(CaO) and %(TiO_2) which is the source of CaO- TiO_2 is set, and this is to secure a large amount of CaO- TiO_2 phase, which is advantageous as an equiaxed crystal nucleation site of the solidified structure of the weld zone. If the ratio is less than 0.3, sufficient refinement of the average grain diameter of the weld zone solidified structure becomes difficult.

[0073] According to the equation (4), even if the equations (2) and (3) are satisfied, when the %(CaO)/%(TiO_2) ratio is less than 0.3, the oxide composition cannot sufficiently secure a CaO-TiO_2 phase which is advantageous for nucleation. When the ratio of %(CaO)/%(TiO_2) exceeds 0.8, the oxide composition transitions to a coarse low melting point oxide of CaO- Al_2O_3 and transitions an oxide ineffective for nucleation.

[0074] FIG. 6 is a graph showing the results of measuring the average grain size of the weld zone solidified structure of the inventive example and comparative example according to the present disclosure. As a result of comparing the size of the equiaxed crystal of the weld zone of the inventive examples and comparative examples, in the case of the inventive example, it can be seen that the size of the equiaxed crystal is finer by about 40% compared to the comparative example. Specifically, the average grain diameter of the weld zone solidified structure of ferritic stainless steel according to the inventive examples is 97.5 μm, which is 110 μm or less, but the average grain diameter of the weld zone solidified structure of ferritic stainless steel according to comparative examples is 167.1 μm, which is 150 μm or more.

[0075] That is, the average grain size of the weld zone solidified structure of Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of the present disclosure may be less than 150 μm.

[0076] FIG. 7 is a graph showing the result of measuring the impact energy of the weld zone of the inventive example and comparative example according to the present disclosure. FIG. 8 is a graph showing a result of measuring a weld zone DBTT of an inventive example and a comparative example according to the present disclosure.

[0077] Referring to FIGS. 7 and 8, the ductile brittle transition temperature (DBTT) can be obtained from the weld zone impact energy graph of FIG. 6, and it was evaluated as - 35.8°C in the inventive example and -17.8°C in the comparative example. It can be seen that the inventive example has a DBTT of about 20°C lower than that of the comparative example.

[0078] That is, the weld zone impact energy at -30°C of Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone according to an embodiment of the present disclosure may be 90J/cm^2 or more, and the weld zone DBTT may be -25°C or less.

[0079] The evaluation results of the above-described low-temperature toughness of weld zone and weld zone microstructure results are summarized as follows. When the weld zone has a fine solidified structure, it has low DBTT characteristics. The refinement of the weld zone solidified structure for this was confirmed that Al-Ca-Ti-Mg-O-based oxides that satisfies all equations (2) to (4) along with the satisfaction of equation (1) and Ti-Nb-CN carbonitrides with an average diameter of 3 to 10 μm including the same should have a distribution density of 4/mm^2 or more.

[0080] On the other hand, the oxides present in the test specimens may appear mixed with various types, among these, in the case of a specimen whose distribution of Ti-Nb-C-N carbonitride containing oxides satisfying equations (2) to (4) does not satisfy the above conditions, the weld zone solidified structure was also coarse and the DBTT value was also high.

[0081] Therefore, in the case of Ti, Nb-added ferritic stainless steel according to the present disclosure, the oxide whose composition satisfies equation (1) and satisfies all equations (2) to (4), and Ti-Nb-CN carbonitride having an average diameter of 3 to 10 μm including the same, should have a distribution density of 4/mm^2 or more.

[0082] Hereinafter, the present disclosure will be described in more detail through inventive examples.

Inventive example 1 to 8

[0083] After manufacturing a cast steel through the process of electric furnace (EAF)-refining furnace (AOD)-component adjustment (LT)-tundish-continuous casting process for stainless steel containing the composition of the base material according to inventive examples 1 to 8 of Table 1 below, cold-rolled coils with a final thickness of 2.0 mm were manufactured through hot rolling and annealing, and cold rolling and annealing.

Comparative example 1 to 7

[0084] After manufacturing a cast steel through the process of electric furnace (EAF)-refining furnace (AOD)-component adjustment (LT)-tundish-continuous casting process for stainless steel containing the composition of the base material according to comparative examples 1 to 7 of Table 1 below, cold-rolled coils with a final thickness of 2.0 mm were manufactured through hot rolling and annealing, and cold rolling and annealing.

<Table 1 >

	Cr	C	Mn	Si	P	S	Al	Ti	Nb	N	Mo	equation (1)
comparative example 1	17.7	0.0068	0.219	0.362	0.0206	0.0009	0.030	0.189	0.373	0.0076	0.002	0.180
comparative example 2	17.8	0.0062	0.244	0.405	0.0289	0.0007	0.026	0.173	0.362	0.0084	0.001	0.199
comparative example 3	18.0	0.0063	0.266	0.376	0.0246	0.0006	0.054	0.241	0.491	0.0074	0.004	0.123
comparative example 4	17.7	0.0091	0.223	0.436	0.0246	0.0005	0.046	0.224	0.505	0.0086	0.001	0.183
comparative example 5	17.9	0.0070	0.236	0.358	0.0232	0.0004	0.024	0.148	0.361	0.0074	0.003	0.197
comparative example 6	18.4	0.0065	0.237	0.201	0.0218	0.0008	0.027	0.232	0.381	0.0062	0.127	0.199
comparative example 7	18.6	0.0070	0.225	0.184	0.0234	0.0005	0.026	0.195	0.442	0.0066	0.135	0.218
inventive example 1	17.8	0.0103	0.216	0.395	0.0226	0.0005	0.028	0.219	0.501	0.0075	0.001	0.298
inventive example 2	17.8	0.01 20	0.237	0.357	0.0271	0.0007	0.022	0.219	0.331	0.0089	0.003	0.365
inventive example 3	18.0	0.00 93	0.208	0.384	0.0235	0.0004	0.027	0.258	0.444	0.0067	0.002	0.284
inventive example 4	18.0	0.00 93	0.208	0.384	0.0235	0.0004	0.027	0.258	0.337	0.0067	0.001	0.253
inventive example 5	17.8	0.00 97	0.233	0.405	0.0273	0.0006	0.019	0.194	0.354	0.0093	0.004	0.371
inventive example 6	17.8	0.0075	0.222	0.382	0.0220	0.0003	0.023	0.191	0.492	0.0098	0.003	0.329
inventive example 7	18.5	0.0059	0.228	0.204	0.0259	0.0005	0.018	0.180	0.466	0.0108	0.133	0.383
inventive example 8	18.4	0.0060	0.219	0.173	0.0229	0.0007	0.015	0.201	0.462	0.0077	0.129	0.395

[0085] Thereafter, after welding by the GTA process in order to evaluate the welding characteristics of the steel sheet manufactured according to the inventive examples and comparative examples, the grain size of the weld zone, weld zone cross-section and surface analysis, hardness analysis, Ericsson test, and weld zone impact energy were investigated. The molten steel components as the main influencing factors and the types and size distributions of internal oxides according thereto were investigated and shown in Table 2 below.

<Table 2>

	equation (2)	equation (3)	equation (4)	*effective nucleation product distribution density (pieces/mm^2)	weld zone solidified structure average grain size (μm)	DBTT (°C)
comparative example 1	52	0.25	0.25	2.7	190	-14
comparative example 2	54	0.27	0.41	3.2	170	-18
comparative example 3	58	0.18	0.33	3.7	169	-15
comparative example 4	55	0.19	0.31	3.5	160	-18
comparative example 5	75	0.25	0.25	3.4	169	-19
comparative example 6	81	0.30	0.23	3.8	150	-21
comparative example 7	83	0.28	0.27	4.0	162	-20
inventive example 1	85	0.33	0.37	5.0	109	-31
inventive example 2	88	0.40	0.41	5.1	110	-37
inventive example 3	82	0.38	0.37	5.2	107	-35
inventive example 4	84	0.38	0.42	5.5	102	-37
inventive example 5	86	0.41	0.36	6.1	88	-40
inventive example 6	88	0.39	0.45	6.7	102	-38
inventive example 7	86	0.40	0.41	6.7	80	-33
inventive example 8	87	0.54	0.44	6.7	80	-35

[0086] The *effective nucleation product means an Al-Ca-Ti-Mg-O-based oxide having an average diameter of 3 to 10 μm and Ti-Nb-C-N carbonitride containing the oxide.

[0087] Referring to Tables 1 and 2, inventive examples 1 to 6 satisfy the Al-Ca-Ti-Mg-O oxide composition of equations (2) to (4) by satisfying the conditions of the equation (1). At the same time, the distribution density of Ti-Nb-C-N carbonitride (effective nucleation product) including this was also 4/mm^2 or more. Specifically, the average grain size of the weld zone solidified structure was smaller as 30 ~ 60 μm than the comparative examples 1 to 5, and the DBTT temperature was also reduced by about 15°C compared to the comparative example.

[0088] In addition, in the case of inventive examples 7 and 8, if the condition of the equation (1) is satisfied in the same way for high Cr ferritic stainless steel with Mo added, it was confirmed that the average grain size was small and the

DBTT temperature was also low compared to comparative examples 6 and 7 of the same steel type.

[0089] FIG. 9 is a graph showing the correlation between the value of Equation (1) and the average grain size of the weld zone of the inventive example and comparative example according to the present disclosure.

[0090] In conclusion, as can be seen from the inventive examples of Table 2 and FIG. 9, in order to secure a low-temperature toughness of weld zone, even if the composition is included in the scope of the present disclosure, if the equation (1) is not satisfied, it can be seen that the average grain size of the weld zone solidified structure is coarse because the distribution density of effective nucleation product of 3 to 10 μm cannot be secured.

[0091] In the foregoing, exemplary inventive examples of the present disclosure have been described, but the present disclosure is not limited thereto, and a person with ordinary knowledge in the relevant technical field does not depart from the concept and scope of the following claims. It will be appreciated that various changes and modifications are possible in.

[Industrial Applicability]

[0092] The ferritic stainless steel according to the present disclosure can refine the grain size of the weld zone solidified structure, thereby securing excellent low-temperature toughness of weld zone.

Claims

1. A Ti, Nb-added ferritic stainless steel with excellent low-temperature toughness of weld zone comprising, in percent (%) by weight of the entire composition, C: 0.004 to 0.015%, N: 0.004 to 0.015%, Si: 0.01 to 0.7%, Mn: 0.01 to 0.7%, P: 0.0001 to 0.04%, S: 0.0001 to 0.005%, Cr: 10 to 30%, Al: 0.005 to 0.04%, Ti: 0.1 to 0.5%, Nb: 0.1 to 0.6%, Ca: 0.0001 to 0.003%, the remainder of iron (Fe) and other inevitable impurities, and
satisfying the following equation (1),
Al-Ca-Ti-Mg-O-based oxide and Ti-Nb-C-N carbonitride containing the oxide have an average diameter of 3 to 10 μm and a distribution density of 4 /mm^2 or more.

$$(1) \qquad \{(Ti + 0.5^*Nb)^*(C + N)\}/Al > 0.25$$

(Here, Ti, Nb, C, N, and Al mean the content (% by weight) of each element)

2. The ferritic stainless steel of claim 1, wherein the distribution density is 4/mm^2 or more and 15/ mm^2 or less.

3. The ferritic stainless steel of claim 1, further comprising: any one or more selected from the group consisting of Mo: 0.1 to 2.0%, Ni: 0.1 to 2.0% and Cu: 0.1 to 2.0%.

4. The ferritic stainless steel of claim 1, wherein the Al-Ca-Ti-Mg-O-based oxide satisfies the following equations (2) to (4).

$$(2) \qquad \%(TiO_2) + \%(CaO) + \%(Al_2O_3) \geq 80$$

$$(3) \qquad \{\%(TiO_2) + \%(CaO)\}/\{\%(TiO_2) + \%(CaO) + \%(Al_2O_3)\} \geq 0.3$$

$$(4) \qquad 0.3 \leq \%(CaO)/\%(TiO_2) \leq 0.8$$

5. The ferritic stainless steel of claim 1 or claim 4, wherein the Ti-Nb-C-N carbonitride has the Al-Ca-Ti-Mg-O-based oxide as a nucleus and is formed to surround the Al-Ca-Ti-Mg-O-based oxide.

6. The ferritic stainless steel of claim 1, wherein the average grain size of the solidified structure of the weld zone is less than 150 μm.

7. The ferritic stainless steel of claim 1, wherein an impact energy of the weld zone is 90J/cm^2 or more at -30°C.

8. The ferritic stainless steel of claim 1, wherein a DBTT of the weld zone is -25°C or less.

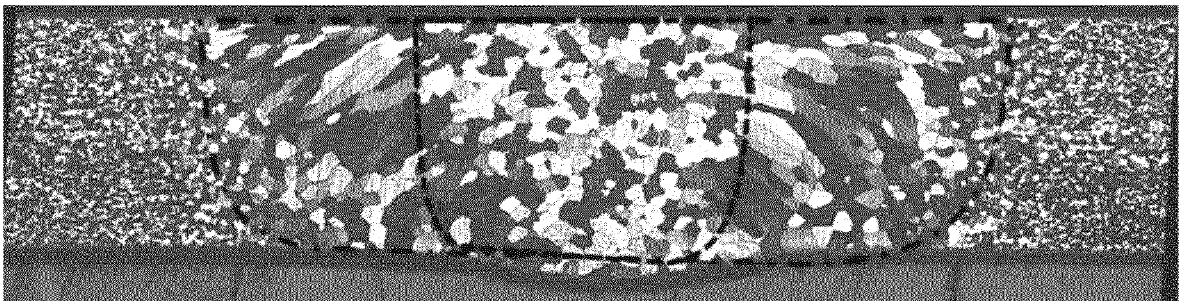


FIG. 1

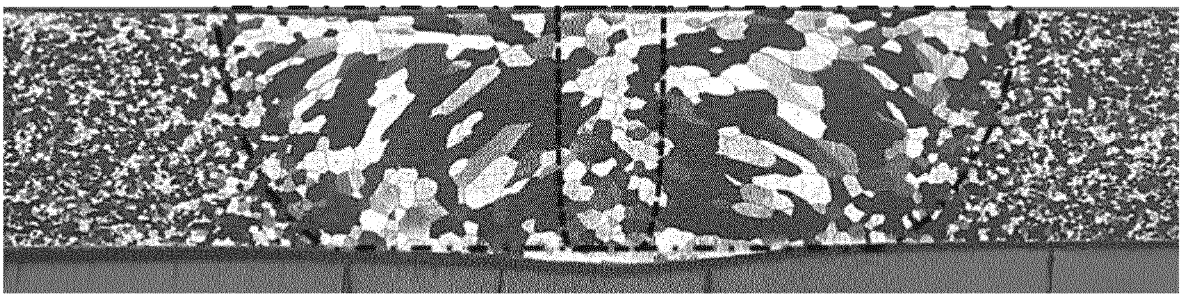


FIG. 2

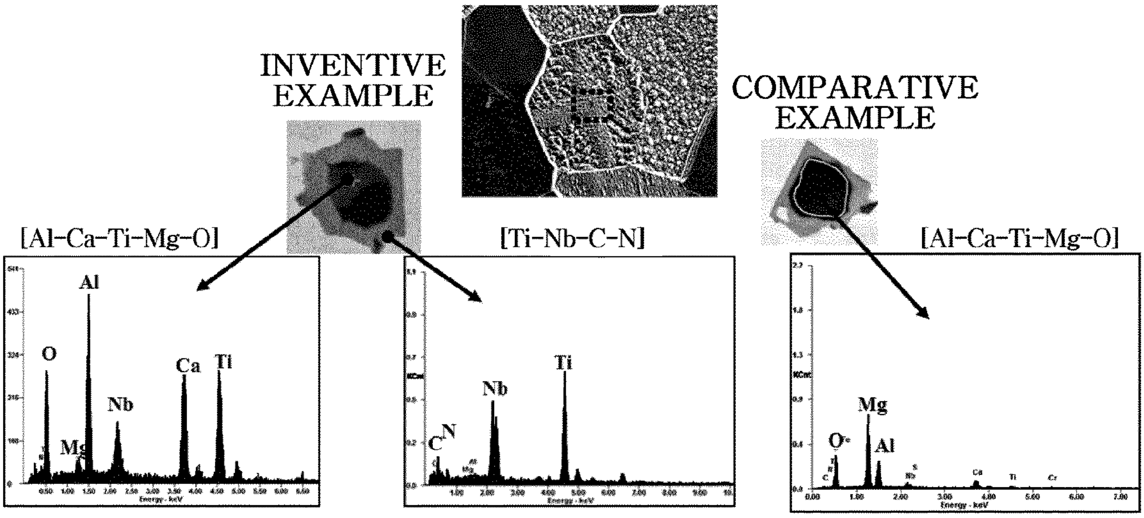
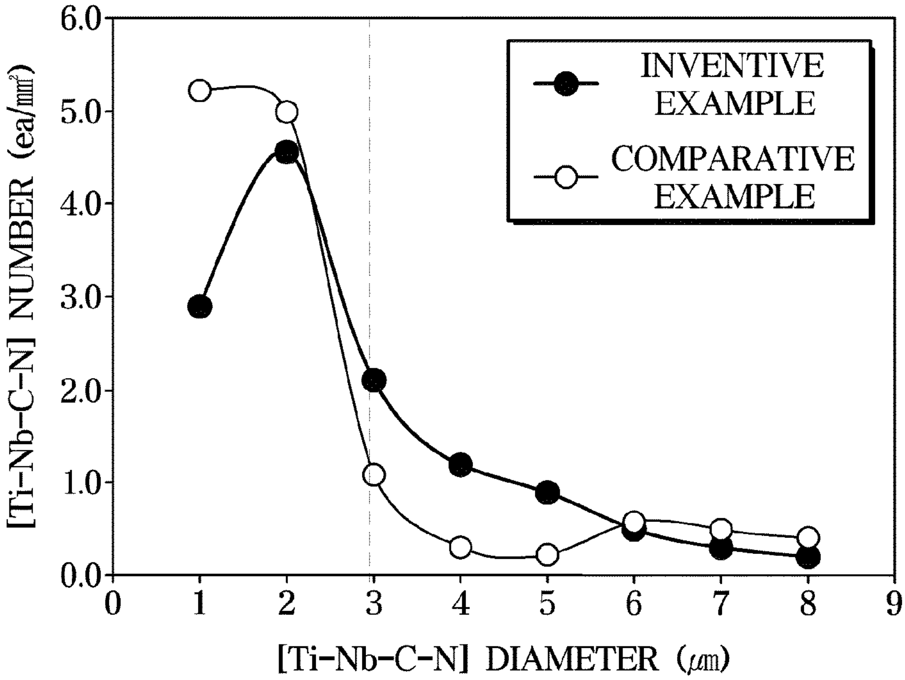

INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE
[Al-Ca-Ti-Mg-O]
[Ti-Nb-C-N]
[Al-Ca-Ti-Mg-O]
Al
O
Ca
Ti
Nb
Mg
C
N
Nb
Ti
Mg
O
Al
Energy - keV

FIG. 3



6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
1
2
3
4
5
6
7
8
9
[Ti-Nb-C-N] NUMBER (ea/㎟)
[Ti-Nb-C-N] DIAMETER (㎛)
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE

FIG. 4

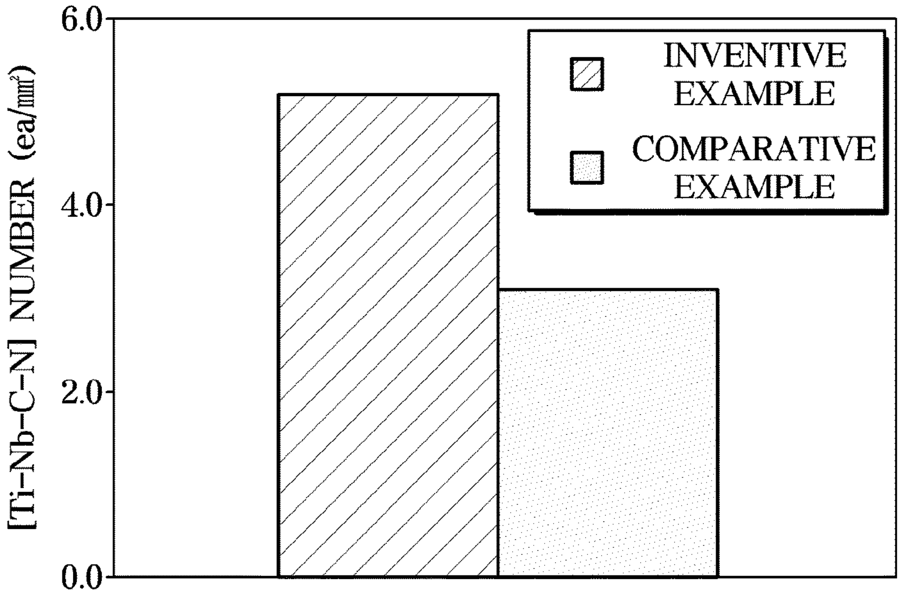

6.0
4.0
2.0
0.0
[Ti-Nb-C-N] NUMBER (ea/㎟)
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE

FIG. 5

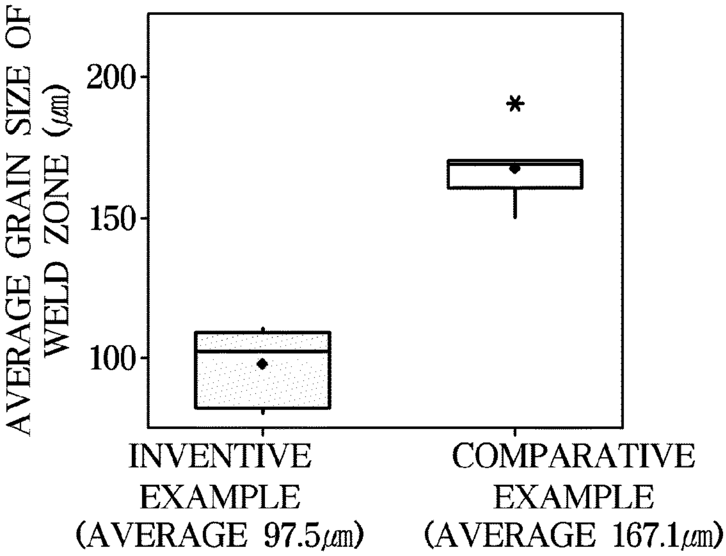
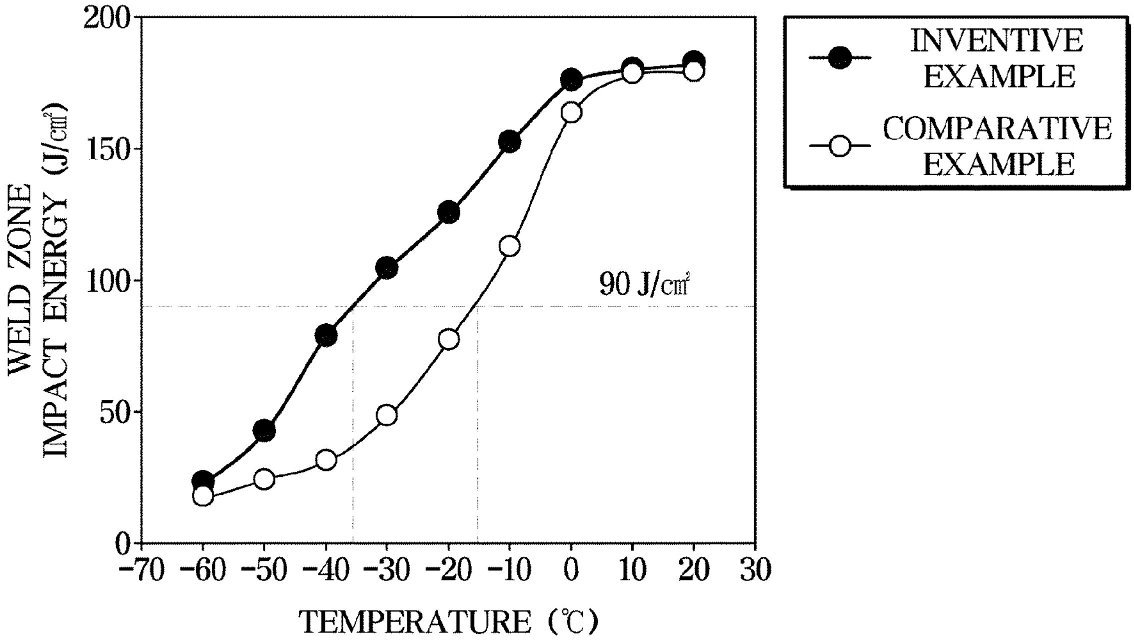

AVERAGE GRAIN SIZE OF WELD ZONE (㎛)
200
150
100
INVENTIVE EXAMPLE (AVERAGE 97.5㎛)
COMPARATIVE EXAMPLE (AVERAGE 167.1㎛)

FIG. 6



WELD ZONE IMPACT ENERGY (J/㎠)
200
150
100
50
0
-70 -60 -50 -40 -30 -20 -10 0 10 20 30
TEMPERATURE (℃)
90 J/㎠
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE

FIG. 7

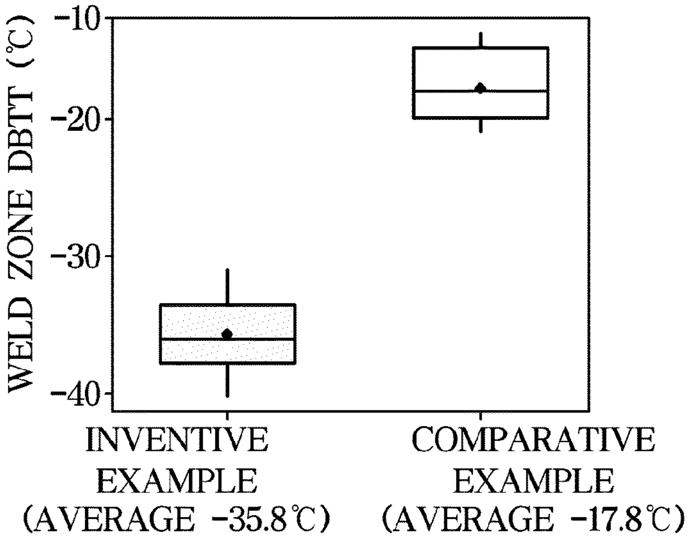

WELD ZONE DBTT (℃)
-10
-20
-30
-40
INVENTIVE EXAMPLE (AVERAGE -35.8℃)
COMPARATIVE EXAMPLE (AVERAGE -17.8℃)

FIG. 8

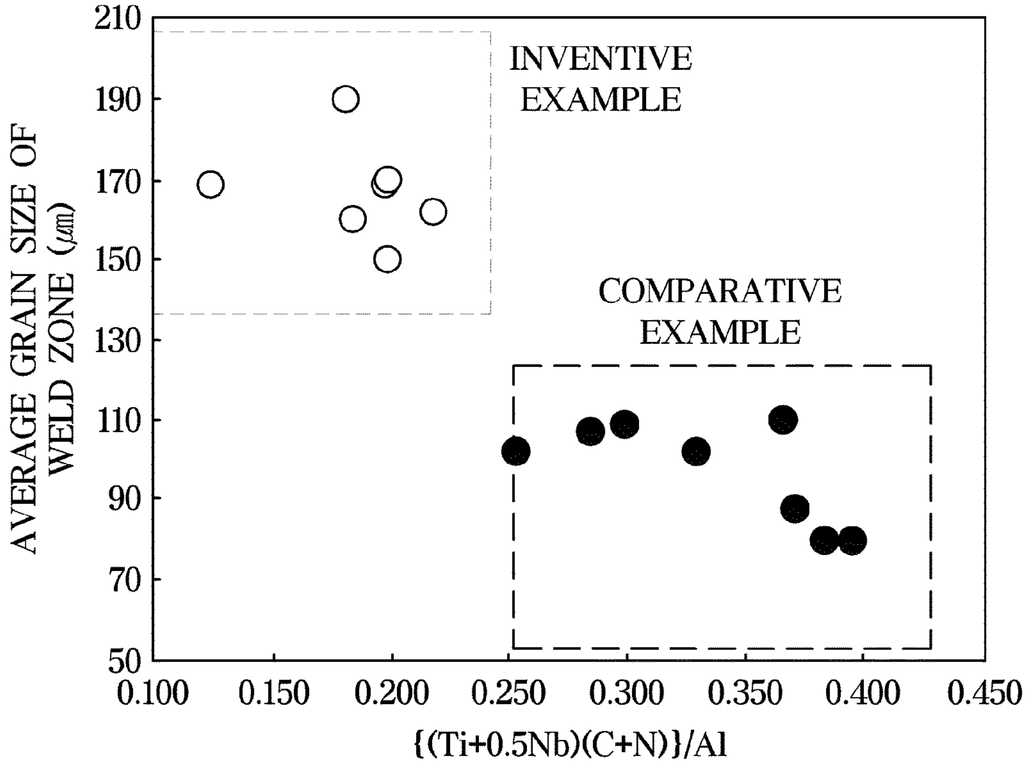

AVERAGE GRAIN SIZE OF WELD ZONE (㎛)
210
190
170
150
130
110
90
70
50
0.100
0.150
0.200
0.250
0.300
0.350
0.400
0.450
{(Ti+0.5Nb)(C+N)}/Al
INVENTIVE EXAMPLE
COMPARATIVE EXAMPLE

FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2018/013229

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/26(2006.01)i, C22C 38/28(2006.01)i, C22C 38/00(2006.01)i, C22C 38/02(2006.01)i, C22C 38/04(2006.01)i, C22C 38/06(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)

C22C 38/26; B23K 9/23; C22C 38/00; C22C 38/04; C22C 38/20; C22C 38/22; C22C 38/28; C22C 38/02; C22C 38/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: stainless steel, welding part, low temperature toughness, ferrite, solidified structure miniaturization, Al-Ca-Ti-Mg-O based oxide, Ti-Nb-C-N carbon nitride

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2015-0000893 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORPORATION) 05 January 2015 See paragraphs [0012], [0071]-[0081] and claims 1, 4.	1-8
A	JP 2010-261074 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP.) 18 November 2010 See paragraphs [0032]-[0036] and claims 1-3.	1-8
A	KR 10-0718410 B1 (KABUSHIKI KAISHA KOBE SEIKO SHO (KOBE STEEL, LTD.)) 14 May 2007 See paragraphs [0015]-[0016] and claims 1-4.	1-8
A	KR 10-2007-0068211 A (POSCO) 29 June 2007 See paragraphs [0104]-[0120] and claims 1-4.	1-8
A	JP 2003-311418 A (NIPPON STEEL CORP.) 05 November 2003 See paragraph [0019] and claims 4-8.	1-8

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

* Special categories of cited documents:
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- "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
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- "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	Date of mailing of the international search report
26 APRIL 2019 (26.04.2019)	**29 APRIL 2019 (29.04.2019)**

Name and mailing address of the ISA/KR	Authorized officer
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Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2018/013229

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KR 10-2007-0068211 A	29/06/2007	None	
JP 2003-311418 A	05/11/2003	JP 3837083 B2	25/10/2006

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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- JP 2000001715 A **[0009]**
- JP 2001254153 A **[0009]**