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(54) **FERRITIC-AUSTENITIC DUPLEX STAINLESS STEEL MATERIAL**

(57) A ferritic-austenitic duplex stainless steel material has a composition including, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.050% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities. The ferritic-austenitic duplex stainless steel material has a metallographic structure having: an Md value as represented by the following equation (1) of 50.0 to 150.0°C; and 25 to 49% by volume of austenite phase. The value of Md of the austenite phase represented by the following equation (1) is 35.0 to 100.0°C.

$$\text{Md} = 551 - 462 (\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 29 (\text{Ni} + \text{Cu}) - 13.7\text{Cr} - 18.5\text{Mo} \quad (1)$$

in which each of the element symbols represents a content (% by mass) of each element.

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Description

[Technical Field]

[0001] The present invention relates to a ferritic-austenitic duplex stainless steel material.

[Background Art]

[0002] Ferritic-austenitic duplex stainless steel materials are used as building and structural materials because of their excellent corrosion resistance and high strength. On the other hand, the ferritic-austenitic duplex stainless steel materials have lower ductility than general-purpose austenitic stainless steel materials such as SUS 304, and have limited applications to uses that require workability. There is also a need for lean (alloy-saving) ferritic-austenitic duplex stainless steel materials that are intended to reduce alloying elements from the viewpoint of cost reduction. Therefore, the lean ferritic-austenitic duplex stainless steel materials with improved ductility are being developed.

[0003] For example, Patent Literature 1 proposes a ferritic-austenitic duplex stainless steel material, comprising, in % by mass, C: 0.05% or less, Si: 1% or less, Mn: 2 to 8%, P: 0.1% or less, S: 0.02% or less, Cr: 15 to 23%, Mo: 4% or less, Ni: 3.0% or less, Cu: 2% or less, N: 0.05 to 0.3%, the balance being Fe and unavoidable impurities, wherein a Cr equivalent and Ni equivalent satisfy the predetermined relationship. It discloses that the ductility of the duplex stainless steel material can be improved by optimizing the Cr equivalent and Ni equivalent.

[0004] Further, Patent Literature 2 describes a ferritic-austenitic stainless steel material including, in % by mass, C: 0.08% or less, Si: 0.7 to 1.1%, Mn: 2.4 to 3.5%, Cr: 17.9 to 20.7%, Ni: 0.05 to 1.15%, N: 0.18 to 0.3%, and Cu: 0.4 to 2.8%, the balance being Fe and inevitable impurities, wherein a pitting potential predicted by the predetermined formula is 360 to 440 mV. It discloses that the ductility of the duplex stainless steel material can be improved by optimizing the contents of alloying elements such as Ni, Si, Mn, and Cu.

[Citation List]

[Patent Literature]

[0005]

[PTL 1] Japanese Patent Application Publication No. 2012-126992 A

[PTL 2] Japanese Patent Application Publication No. 2019-504587 A

[Summary of Invention]

[Technical Problem]

[0006] Both of the ferritic-austenitic duplex stainless steel materials described in Patent literatures 1 and 2 have improved strength by increasing the contents of Mn and N while reducing the content of Ni. However, the increase in the content of N content may cause ferritic-austenitic duplex stainless steel materials to become excessively high-strength, resulting in reduced ductility.

[0007] Therefore, an object of the present invention is to provide a ferritic-austenitic duplex stainless steel material that is softer and more ductile than conventional ferritic-austenitic duplex stainless steel materials.

[Solution to Problem]

[0008] As a result of intensive studies for lean ferritic-austenitic duplex stainless steel materials to solve the above problems, the present inventors have obtained the following findings (1) through (3).

(1) By reducing the contents of C and N, the austenite phase can be softened while ensuring the corrosion resistance of the duplex stainless steel material.

(2) By controlling Mds of the duplex stainless steel material and austenite phase to predetermined ranges, the degree of stabilization of the austenite phase can be improved and the high ductility can be achieved by a TRIP (transformation induced plasticity) effect.

(3) By reducing the contents of austenite forming elements (C, N, Ni, etc.), excessive TRIP effect can be suppressed to achieve softening while reducing alloying.

[0009] Based on the above findings, the present inventors have found that the above problems can be solved by controlling the composition and Md of the ferritic-austenitic duplex stainless steel material and controlling a ratio and Md of the austenite phases, and have completed the present invention.

[0010] Thus, the present invention relates to a ferritic-austenitic stainless steel material having a composition comprising, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.050% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities;

wherein the ferritic-austenitic stainless steel material has a metallographic structure having: a value of Md of 50.0 to 150.0 °C, the value of Md being represented by the following equation (1):

$$Md = 551 - 462 (C + N) - 9.2Si - 8.1Mn - 29 (Ni + Cu) - 13.7Cr - 18.5Mo \dots (1)$$

in which each of the element symbols represents a content (% by mass) of each element; and 25 to 49% by volume of an austenite phase; and wherein the value of Md of the austenite phase, represented by the equation (1), is 35.0 to 100.0°C.

[Advantageous Effects of Invention]

[0011] According to the present invention, it is possible to provide a ferritic-austenitic duplex stainless steel material that is softer and more ductile than conventional ferritic-austenitic duplex stainless steel materials.

[Description of Embodiments]

[0012] Hereinafter, embodiments of the present invention will be specifically described. It is to understand that the present invention is not limited to the following embodiments, and those which have appropriately added changes, improvements and the like to the following embodiments based on knowledge of a person skilled in the art without departing from the spirit of the present invention fall within the scope of the present invention.

[0013] It should be noted that, as used herein, the expression "%" in relation to any component means "% by mass", unless otherwise specified.

[0014] The ferritic-austenitic stainless steel material according to the present invention (hereafter simply abbreviated as a "duplex stainless steel material") has a composition including, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.050% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities.

[0015] Also, the term "stainless steel material" as used herein means a material formed of stainless steel, and a shape of the material is not particularly limited. Examples of the shape of the material include a sheet shape (including a strip shape), a rod shape, and a tubular shape. Further, the material may be various shaped steels having cross-sectional shapes such as T-shape and I-shape.

[0016] The term "ferritic-austenitic" as used herein means that the metallographic structure is mainly made of two phase of a ferrite phase and an austenite phase at ordinary temperature. Therefore, the "ferritic-austenite" includes those containing minor amounts of phases other than the ferrite phase and the austenite phase (for example, martensite phases, etc.).

[0017] Further, the term "impurities" as used herein refers to components which are contaminated by raw materials such as ores and scraps, and various factors in the production steps, when the stainless steel materials are industrially produced, and which are permissible in a range that does not adversely affect the present invention. For example, the impurities include unavoidable impurities. Examples of the impurities include O. A content of O is, for example, 0.0001 to 0.0070%.

[0018] In addition, with respect to the content of each element as used herein, containing or comprising "xx % or less" means that it contains xx % or less but contains an amount more than 0% (especially, more than the impurity level).

[0019] Further, the duplex stainless steel sheet according to an embodiment of the present invention can optionally contain one or more selected from: Nb: 0.010 to 0.500%, Ti: 0.01 to 0.50%, V: 0.01 to 0.50%, W: 0.05 to 0.50%, Co: 0.01 to 0.30%, B: 0.0002 to 0.0050%, Sn: 0.010 to 0.500%, Al: 0.010 to 0.050%, Mg: 0.0002 to 0.0100%, Ca: 0.0002 to 0.0100%, Ta: 0.050% or less, Ga: 0.050% or less, Zr: 0.01 to 0.50%, and REM: 0.0002 to 0.0100%.

[0020] Each component will be described in detail below.

<C: 0.001 to 0.050%>

[0021] C is an element that has a significant effect on the degree of stability of the austenite phase. An excessively high

content of C may reduce ductility (workability) and promote deposition of Cr carbides, resulting in intergranular corrosion. Therefore, the content of C is 0.050% or less, and preferably 0.045% or less, and more preferably 0.040% or less, and still more preferably 0.35% or less, and particularly preferably 0.030% or less. In terms of corrosion resistance, a lower content of C is better, but an excessively low content of C will increase costs. Therefore, the content of C is 0.001% or more, and preferably 0.002% or more, and more preferably 0.005% or more.

<Si: 0.01 to 0.50%>

[0022] Si is added as a deoxidizing element and is also useful for improving oxidation resistance. However, an excessive high content of Si will lead to hardening and decrease ductility. Therefore, the content of Si is 0.50% or less, and preferably less than 0.50%, and more preferably 0.45% or less, and still more preferably 0.40% or less. Excessive reduction of Si also increases costs during smelting. Therefore, the content of Si is 0.01% or more, and preferably 0.02% or more, and more preferably 0.05% or more.

<Mn: 1.0 to 4.5%>

[0023] Mn is an element that is enriched in the austenite phase and plays an important role in stabilizing the austenite phase. However, an excessive high content of Mn decreases corrosion resistance and hot workability in addition to the ductility. Therefore, the content of Mn is 4.5% or less, and preferably 4.0% or less, and more preferably 3.5% or less. Excessive reduction of Mn also increases costs during smelting. Therefore, the content of Mn is 1.0% or more, and preferably 1.1% or more, and more preferably 1.2% or more.

<P: 0.050% or less>

[0024] P is an element contained in raw materials for Cr and the like. Since a higher content of P reduces formability, the content of P is 0.050% or less, and preferably 0.045% or less, and more preferably 0.040% or less. On the other hand, a lower content P is more preferred, but there is a limit to reducing the content of P. Therefore, the lower limit of the content of P is generally 0.001%, and preferably 0.002%, and more preferably 0.003%.

<S: 0.030% or less>

[0025] S is an element contained in various raw materials. Since S combines with Mn to form inclusions, which can be the starting point for rusting, a lower content of S increases the corrosion resistance. Therefore, the content of S is 0.030% or less, and preferably 0.025% or less, and more preferably 0.020% or less. On the other hand, there is a limit to reduce the content of S. Therefore, the lower limit of the content of S is generally 0.0001%, and more preferably 0.0005%.

<Ni: 1.5 to 3.5%>

[0026] Ni is an element forming an austenite phase and is an important element to adjust the degree of stability of the austenite phase. Ni also has effects of suppressing deposition of nitrides and improving corrosion resistance. Therefore, to exert these effects, the content of Ni is 1.5% or more, and preferably 1.6% or more, and more preferably 1.7% or more, and still more preferably 1.8% or more. On the other hand, an excessively high content of Ni will increase the costs of raw materials and may cause problems such as stress corrosion cracking due to the higher percentage of the austenite phases. Therefore, the content of Ni is 3.5% or less, and preferably 3.4% or less, and more preferably 3.0% or less.

<Cr: 19.6 to 24.0%>

[0027] Cr is an element required for ensuring corrosion resistance. Therefore, to exert this effect, the content of Cr is 19.6% or more, and preferably 20.0% or more, and more preferably 20.4% or more. On the other hand, an excessively high content of Cr can lead to hot work cracking and increase the costs of the refining step. Therefore, the content of Cr is 24.0% or less, and preferably 23.5% or less, and more preferably 23.0% or less.

<Mo: 0.01 to 1.00%>

[0028] Mo is an element for improving the corrosion resistance. Therefore, to exert this effect, the content of Mo is 0.01% or more, and preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, an excessively high content of Mo will lead to an increase in production cost. Therefore, the content of Mo is 1.00% or less, and preferably 0.80% or less, and more preferably 0.50% or less.

<Cu: 0.01 to 1.20%>

[0029] As with Mn and Ni, Cu is an austenite-forming element and has an effect of improving corrosion resistance by suppressing the deposition of nitrides. Therefore, to exert this effect, the content of Cu is 0.01% or more, and preferably 0.05% or more, and more preferably 0.10% or more. On the other hand, an excessively high content of Cr will lead to an increase in the cost of the raw materials and decrease the hot workability. Therefore, the content of Cu is 1.20% or less, and preferably 1.00% or less, and more preferably 0.80% or less.

<N: 0.010 to 0.090%>

[0030] As with C, N is an element that has a significant effect on the degree of stability of the austenite phase. N is also an element that leads to solid solution to improve the corrosion resistance. To exert these effects, the content of N is 0.010% or more, and preferably 0.020% or more. On the other hand, an excessively high content of N will reduce the ductility and also reduce the corrosion resistance due to the deposition of Cr nitrides. Therefore, the content of N is 0.090% or less, and preferably 0.080% or less, and more preferably 0.075% or less.

<C + N: less than 0.130%>

[0031] As the total content of C and N increases, the corrosion resistance decreases due to sensitization and the ductility decreases due to high strength. Therefore, the total content of C and N is less than 0.130%, and preferably less than 0.120%, and more preferably 0.110% or less. On the other hand, the lower limit of the total content of C and N is not particularly limited, but it may preferably be 0.010%, and more preferably 0.020%, and still more preferably 0.030%.

<Nb: 0.010 to 0.500%>

[0032] Nb has an effect of forming a nitride (NbN) and a carbide (NbC) to improve workability. To exert this effect, the content of Nb is 0.010% or more, and preferably 0.015% or more, and more preferably 0.020% or more. On the other hand, an excessively high content of Nb will deteriorate the ductility. Therefore, the content of Nb is 0.500% or less, and preferably 0.300% or less, and more preferably 0.200% or less.

<Ti: 0.01 to 0.50%>

[0033] As with Nb, Ti also has an effect of forming a nitride (TiN) and a carbide (TiC) to improve workability. To exert this effect, the content of Ti is 0.01% or more, and preferably 0.015% or more, and more preferably 0.02% or more. On the other hand, an excessively high content of Ti will deteriorate the ductility. Therefore, the content of Ti is 0.50% or less, and preferably 0.30% or less, and more preferably 0.20% or less.

<V: 0.01 to 0.50%>

[0034] V has an effect of forming nitrides to improve workability. To exert this effect, the content of V is 0.01% or more, and preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, an excessively high content of V will deteriorate the ductility and the hot workability. Therefore, the content of V is 0.50% or less, and preferably 0.45% or less, and more preferably 0.40% or less.

<W: 0.05 to 0.50%>

[0035] W is an element effective for improving the corrosion resistance. To exert this effect, the content of W is 0.05% or more, and preferably 0.08% or more, and more preferably 0.10% or more. On the other hand, an excessively high content of W will deteriorate the ductility. Therefore, the content of W is 0.50% or less, and preferably 0.45% or less, and more preferably 0.40% or less.

<Co: 0.01 to 0.30%>

[0036] Co is an element effective for increasing the high temperature strength and improving the corrosion resistance. Therefore, to exert these effects, the content of Co is 0.01% or more, and preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, an excessively high content of Co will deteriorate toughness. Therefore, the content of Co is 0.30% or less, and preferably 0.25% or less, and more preferably 0.20% or less.

<B: 0.0002 to 0.0050%>

[0037] B is an element that segregates at grain boundaries and improves the hot workability. To exert this effect, the content of B is 0.0002% or more, and preferably 0.0010% or more, and more preferably 0.0015% or more. On the other hand, an excessively high content of B will significantly deteriorate the corrosion resistance. Therefore, the content of B is 0.0050% or less, and preferably 0.0040% or less, and more preferably 0.0030% or less.

<Sn: 0.010 to 0.500%>

[0038] Sn is an element for improving the corrosion resistance. To exert this effect, the content of Sn is 0.010% or more, and preferably 0.020% or more, and more preferably 0.030% or more. On the other hand, an excessively high content of Sn will deteriorate the hot workability. Therefore, the content of Sn is 0.500% or less, and preferably 0.450% or less, and more preferably 0.400% or less.

<Al: 0.010 to 0.050%>

[0039] Al is an effective element for desulfurization and deoxidation. To exert these effects, the content of Al is 0.010% or more, and preferably 0.015% or more, and more preferably 0.020% or more. On the other hand, an excessively high content of Al will lead to an increase in manufacturing defects and an increase in production cost. Therefore, the content of Al is 0.050% or less, and preferably 0.045% or less, and more preferably 0.040% or less.

<Mg: 0.0002 to 0.0100%>

[0040] Mg is an element having effects of not only deoxidizing but also of refining the solidification structure. Therefore, to exert these effects, the content of Mg is 0.0002% or more, and preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, an excessively high content of Mg will lead to an increase in production cost. Therefore, the content of Mg is 0.0100% or less, and preferably 0.0095% or less, and more preferably 0.0090% or less.

<Ca: 0.0002 to 0.0100%>

[0041] Ca is an effective element for desulfurization and deoxidation. Therefore, to exert these effects, the content of Ca is 0.0002% or more, and preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, an excessively high content of Ca tends to generate heat work cracks and deteriorates the corrosion resistance. Therefore, the content of Ca is 0.0100% or less, and preferably 0.0080% or less, and more preferably 0.0050% or less.

<Ta: 0.050% or less>

[0042] Ta is an element that improves corrosion resistance by modifying inclusions. However, an excessively high content of Ta will lead to a decrease in the ductility at ordinary temperature and the toughness. Therefore, the content of Ta is 0.050% or less, and preferably 0.045% or less, and more preferably 0.040% or less. On the other hand, the lower limit of the content of Ta is not particularly limited, but it is preferably 0.001% and more preferably 0.003%, in order to exert the above effects of Ta.

<Ga: 0.050% or less>

[0043] Ga is an element that improves corrosion resistance and inhibits hydrogen embrittlement. However, an excessive high content of Ga will decrease the workability. Therefore, the content of Ga is 0.050% or less, and preferably 0.040% or less, and more preferably 0.030% or less. On the other hand, the lower limit of the content of Ga is not particularly limited, but it is preferably 0.001% and more preferably 0.003%, in order to exert the above effects of Ga.

<Zr: 0.01 to 0.50%>

[0044] Zr is an element that has similar effects to Nb and Ti and improves oxidation resistance. To exert these effects, the content of Zr is 0.01% or more, and preferably 0.03% or more, and more preferably 0.05% or more. On the other hand, an excessively high content of Zr will lead to increased raw material costs in addition to reduced ductility. Therefore, the content of Zr is 0.50% or less, and preferably 0.40% or less, and more preferably 0.30% or less.

<REM: 0.0002 to 0.0100%>

[0045] REM (rare earths) is at least one element effective for improving the heat workability. To exert this effect, the content of REM is 0.0002% or more, and preferably 0.0005% or more, and more preferably 0.0010% or more. On the other hand, an excessively high content of REM will impair manufacturability and increase the costs. Therefore, the content of REM is 0.0100% or less, and preferably 0.0090% or less, and more preferably 0.0080% or less.

[0046] REM is the generic name for Sc, Y, and 15 elements (lanthanoids) from La to Lu. These elements can be used alone or in combination of two or more as REM.

[0047] The duplex stainless steel according to the embodiment of the present invention has an Md value of 50.0 to 150.0°C, and preferably 55.0 to 140.0°C, and more preferably 60.0 to 130.0°C, and even more preferably 70.0 to 120.0°C, as represented by the following equation (1):

$$Md = 551 - 462(C + N) - 9.2Si - 8.1Mn - 29(Ni + Cu) - 13.7Cr - 18.5Mo \dots (1)$$

[0048] In the above equation (1), the symbol of each element represents a content (% by mass) of each element.

[0049] Here, Md is an index representing the degree of stability of the austenite phase. It means that as the Md is higher (higher temperature), the austenite phase is more unstable. If the value of Md is less than 50.0°C, the austenite phase is too stable, so that it is difficult to transform the austenite phase to a strain induced martensite phase, and the desired strength and ductility cannot be obtained. On the other hand, if the value of Md is more than 150.0°C, the amount of the strain induced martensite phase transformed from the austenite phase increases, resulting in excessively high strength so that the desired ductility cannot be obtained.

[0050] The duplex stainless steel according to the embodiment of the present invention has a metallographic structure in which the austenite phase is in the range of 25 to 49% by volume, preferably 25 to 47% by volume, more preferably 25 to 40% by volume, more preferably 26 to 38% by volume, and particularly preferably 28 to 37% by volume. If the austenite phase is less than 25% by volume, the desired ductility cannot be obtained due to the high percentage of the ferrite phase. On the other hand, if the austenite phase is more than 49% by volume, it becomes excessively high-strength and the desired ductility cannot be obtained. Also, by controlling the austenite phase to be 40% by volume or less, an average grain size of the ferrite phase is larger, resulting in easy control.

[0051] In the specification, the percentage of the austenite phase in the duplex stainless steel material can be determined using electron backscatter diffraction (EBSD). Specifically, the EBSD measurement are performed using a specimen obtained by mirror-polishing a cross section in a thickness direction parallel to a rolling direction of the duplex stainless steel material. For the data obtained from the EBSD measurement, a phase ratio map can be created using analysis software to separate the ferrite and austenite phases and determine the percentage of the austenite phase.

[0052] The austenite phase has an Md value of 35.0 to 100.0°C, preferably 40.0 to 95.0°C, more preferably 50.0 to 90.0°C, even more preferably 52.0 to 85.0°C, and particularly 53.0 to 80.0°C, as represented by the above equation (1). If the value of Md of the austenite phase is less than 35.0°C, it is difficult to transform the austenite phase to the strain induced martensite phase, and the desired strength and ductility are difficult to be obtained. On the other hand, if the value of Md of the austenite phase is more than 100.0°C, the amount of the strain induced martensite phase transformed from the austenite phase increases, resulting in excessively high strength and difficulty in achieving the desired ductility.

[0053] Here, in the specification, the content of each element in the austenite phase, which is used herein to calculate the Md of the austenite phase, can be measured by EPMA (electron probe micro-analyzer). Specifically, qualitative analysis is carried out by EPMA using a specimen obtained by mirror-polishing a cross section of the duplex stainless steel material in the thickness direction parallel to the rolling direction. Since C and N are characterized as being enriched in the austenite phase, qualitative mapping of C or N is performed on the entire cross section to identify the austenite phase. Then, C, N, Si, Mn, Cr, Ni, Cu, and Mo are quantitatively analyzed at approximately the center of the austenite phase with the electron beam not hitting the ferrite phase. The quantitative analysis is performed at three or more points, and an average value is determined to be the results of the content of each element.

[0054] The duplex stainless steel material according to an embodiment of the present invention preferably has an average grain size of the ferrite phase of 7.0 μm or more, and more preferably 7.1 μm or more, and even more preferably 7.2 μm or more. If the average grain size of the ferrite phase is less than 7.0 μm, it is difficult to obtain the desired ductility. The upper limit of the average grain size is not particularly limited, but it may be, typically, 20.0 μm, preferably 18.0 μm, and more preferably 15.0 μm.

[0055] Herein, the average grain size of the ferrite phase in the duplex stainless steel material can be determined by EBSD measurement. Specifically, the EBSD measurement are performed using a specimen obtained by mirror-polishing a cross section in a thickness direction parallel to a rolling direction of the duplex stainless steel material. The area of the grains of the ferrite phase (BCC) can be determined for the data obtained from this EBSD measurement by the area fraction method.

[0056] The duplex stainless steel according to the embodiment of the present invention has a value of DF of 50.0 to 80.0, and preferably 54.0 to 80.0, and more preferably 60.0 to 78.0, and even more preferably 65.0 to 75.0, as represented by the following equation (2):

$$DF = 7.2 (Cr + 0.88Mo + 0.78Si) - 8.9 (Ni + 0.03Mn + 0.72Cu + 22C + 21N) - 44.9 \dots (2)$$

[0057] In the above equation (2), the symbol of each element represents a content (% by mass) of each element.

[0058] Here, the DF is an index representing the amount of the ferrite phase. Therefore, 100-DF is the amount of the austenite phase. It should be noted, however, that the DF is an index determined based on the contents of the elements and does not correspond to the amount of the austenite phase actually measured. If the value of the DF is less than 50.0, it is difficult to obtain the desired ductility due to excessively high strength. On the other hand, if the value of the DF is more than 80.0, it is difficult to obtain the desired ductility due to the higher percentage of the ferrite phase.

[0059] The duplex stainless steel material according to the embodiment of the present invention preferably has a tensile strength of 800 MPa or less, and more preferably 790 MPa or less, and even more preferably 780 MPa or less. With the tensile strength in such a range, it can be said to be softer than conventional duplex stainless steel materials, thus ensuring the desired ductility. It should be noted that the lower limit of the tensile strength is not particularly limited, but it may typically be 500 MPa, and preferably 550 MPa.

[0060] Here, the tensile strength of the duplex stainless steel material can be measured in accordance with JIS Z 2241: 2011.

[0061] The duplex stainless steel material according to the embodiment of the present invention preferably has a uniform elongation of 30.0% or more, and more preferably 31.0% or more, and even more preferably 32.0% or more. With the uniform elongation in such a range, it can have better ductility than conventional duplex stainless steel materials. It should be noted that the upper limit of the uniform elongation is not particularly limited, but it may preferably be 50.0%, and more preferably 48.0%, and even more preferably 45.0%.

[0062] Here, the uniform elongation of the duplex stainless steel material can be measured in accordance with JIS Z 2241: 2011. It should be noted that the uniform elongation is determined as a permanent elongation against the maximum tensile load.

[0063] In the duplex stainless steel material according to the embodiment of the invention, when the tensile test is conducted at a strain rate of 3.3×10^{-4} to $8.3 \times 10^{-3} \text{ s}^{-1}$, an n-value ratio of an n-value in a 15 to 20% strain range to an n-value in a 20 to 25% strain range is preferably less than 0.80, and less than 0.79. The n-value ratio in this range can be considered to be improved ductility under general processing conditions. It should be noted that the lower limit of the n-value is not particularly limited, but it may typically be 0.01, and preferably 0.10. The strain rate also affects the process heat generation, and thus varies the magnitude of the TRIP effect. For example, a higher strain rate results in higher process heat generation, which will reduce the TRIP effect and decrease ductility.

[0064] Here, the n-value of the duplex stainless steel material can be measured in accordance with JIS Z 2241: 2011.

[0065] The duplex stainless steel material according to the embodiment of the present invention preferably has a 0.2% yield strength of 480 MPa or less, and more preferably 470 MPa or less. With the 0.2% yield strength in such a range, the duplex stainless steel material can be soft. It should be noted that the lower limit of the 0.2% yield strength is not particularly limited, but it may typically be 300 MPa, and preferably 350 MPa.

[0066] Here, the 0.2% yield strength of the duplex stainless steel material can be measured in accordance with JIS Z 2241: 2011.

[0067] The duplex stainless steel material according to the embodiment of the present invention may be either a hot rolled material or a cold rolled material. The hot rolled material or the cold rolled material may also be annealed or washed with an acid.

[0068] The thickness of the duplex stainless steel material according to the embodiment of the present invention may be adjusted as needed depending on applications, and is not particularly limited, but it may generally be 5.0 mm or less, preferably 4.0 mm or less, and more preferably 3.0 mm or less. If the duplex stainless steel material is in a form of a bar, the thickness means the circular equivalent diameter of the cross section. If the duplex stainless steel material is a shaped steel, the thickness means the thickness at any point in the cross section.

[0069] The duplex stainless steel material according to the embodiment of the present invention can be according to the following two aspects A and B:

<Aspect A>

[0070]

[A1] A duplex stainless steel material having a composition including, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 or

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more and less than 0.50%, Mn: 1.0 to 4.5%, P: 0.05% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities;

wherein the duplex stainless steel material has a metallographic structure having: a value of Md of 50.0 to 150.0 °C, the value of Md being represented by the following equation (1):

$$Md = 551 - 462 (C + N) - 9.2Si - 8.1Mn - 29 (Ni + Cu) - 13.7Cr - 18.5Mo \dots (1) \quad (1)$$

in which each of the element symbols represents a content (% by mass) of each element; and 25 to 49% by volume of an austenite phase; and

wherein the value of Md of the austenite phase, represented by the above equation (1), is 35.0 to 100.0°C.

[A2] The duplex stainless steel material according to [A1], further including one or more selected from the group consisting of Nb: 0.010 to 0.500%, Ti: 0.01 to 0.50%, V: 0.01 to 0.50%, W: 0.05 to 0.50%, Co: 0.01 to 0.30%, B: 0.0002 to 0.0050%, Sn: 0.010 to 0.500%, Al: 0.010 to 0.050%, Mg: 0.0002 to 0.0100%, Ca: 0.0002 to 0.0100%, Ta: 0.050% or less, Ga: 0.050% or less, Zr: 0.01 to 0.50 %, and REM: 0.0002 to 0.0100%.

[A3] The duplex stainless steel material according to [A1] or [A2], wherein a value of DF represented by the following equation (2) is 50.0 to 80.0:

$$DF = 7.2 (Cr + 0.88Mo + 0.78Si) - 8.9 (Ni + 0.03Mn + 0.72Cu + 22C + 21N) - 44.9 \dots (2) \quad (2)$$

in which each of the element symbols represents a content (% by mass) of each element.

[A4] The duplex stainless steel material according to any one of [A1] to [A3], wherein the duplex stainless steel material satisfies at least one of the following properties (a) and (b):

(a) a tensile strength of less than 800 MPa; and

(b) a uniform elongation of more than 30.0%.

<Aspect B>

[0071]

[B1] A duplex stainless steel material having a composition including, on a mass basis, C: 0.001 to 0.040%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.05% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.080%, C + N being less than 0.120%, the balance being Fe and impurities;

wherein the duplex stainless steel material has a metallographic structure having: a value of Md of 50.0 to 150.0 °C, the value of Md being represented by the following equation (1):

$$Md = 551 - 462 (C + N) - 9.2Si - 8.1Mn - 29 (Ni + Cu) - 13.7Cr - 18.5Mo \dots (1) \quad (1)$$

in which each of the element symbols represents a content (% by mass) of each element; and 25 to 40% by volume of an austenite phase; and

wherein the Md value of the austenite phase represented by the above equation (1) is 35.0 to 100.0°C, and an average grain size of the ferrite phase is 7.0 μm or more.

[B2] The duplex stainless steel material according to [B1], further including one or more selected from the group consisting of Nb: 0.010 to 0.500%, Ti: 0.01 to 0.50%, V: 0.01 to 0.50%, W: 0.05 to 0.50%, Co: 0.01 to 0.30%, B: 0.0002 to 0.0050%, Sn: 0.010 to 0.500%, Al: 0.010 to 0.050% by mass, Mg: 0.0002 to 0.0100%, Ca: 0.0002 to 0.0100%, Ta: 0.050% or less, Ga: 0.050% or less, Zr: 0.01 to 0.50 %, and REM: 0.0002 to 0.0100%.

[B3] The duplex stainless steel material according to [B1] or [B2], wherein the value of Md of the austenite phase represented by the above equation (1) is 50.0 to 90.0°C.

[B4] The duplex stainless steel material according to any one of [B1] to [B3], wherein a value of DF represented by the following equation (2) is 60.0 to 80.0:

$$DF = 7.2 (Cr + 0.88Mo + 0.78Si) - 8.9 (Ni + 0.03Mn + 0.72Cu + 22C + 21N) - 44.9 \dots (2) \quad (2)$$

in which each of the element symbols represents a content (% by mass) of each element.

[B5] The duplex stainless steel material according to any one of [B1] to [B4], wherein when the tensile test is conducted at a strain rate of 3.3×10^{-4} to $8.3 \times 10^{-3} \text{ s}^{-1}$, an n-value ratio of an n-value in a 15 to 20% strain range to an n-value in a 20 to 25% strain range is 0.80 or less.

[0072] The method for producing the duplex stainless steel material according to the embodiment of the present invention is not particularly limited as long as it is a method that can produce a duplex stainless steel sheet having the above features.

[0073] Hereinafter, an example of methods for producing duplex stainless steel materials (in particular, duplex stainless steel materials according to the aspects A and B) is described.

[0074] Each of the duplex stainless steels according to the aspects A and B can be produced by smelting stainless steel having the above composition by vacuum melting to form a steel slab, which is then hot-rolled and annealed, and then cold-rolled and finish-annealed. The key to the production method is, among others, controlling of the conditions of the heat treatment. Specific production methods for each of the aspects will be described.

<Aspect A>

[0075] In duplex stainless steel materials, the conditions of the heat treatment (annealing) (temperature increase rate, attained temperature, holding time, and cooling rate) must be controlled in order to control the percentage of the austenite phase and Md to the given ranges. All of these conditions affect the solid solution state of carbon and nitrogen. The attained temperature also affects the variation in thermodynamic austenite quantity. Further, the control of the attained temperature and holding time is also intended to ensure that the entire structure is sufficiently recrystallized.

[0076] Since the solid solution of carbon and nitrogen affects the percentage of the austenite phase (an amount produced) and Md, if they are present in large amounts as carbides or nitrides, the percentage of the austenite phase and Md cannot be controlled to the specified ranges. Therefore, in the heat treatment (annealing) step, it is necessary to suppress the deposition of carbides and nitrides during temperature increasing and cooling, while sufficiently dissolving the unconsolidated carbides and nitrides by holding them at the attained temperature. It is also necessary to control the percentage of the austenite phase by adjusting the attained temperature because the concentrations of elements (especially carbon and nitrogen) making up the austenite phase vary depending on the percentage of the austenite phase and the Md derived from it varies.

[0077] Conditions for the hot rolling are not particularly limited, and it may be carried out in accordance with an ordinary method.

[0078] The annealing after the hot rolling is carried out by increasing the temperature at a rate of $20^\circ\text{C}/\text{second}$ or more, holding it at an attained temperature of 1050 to 1150°C for 10 seconds or more, and then cooling it to 400°C or less at a cooling rate of $20^\circ\text{C}/\text{second}$ or more. The reason for annealing it under these conditions is to sufficiently dissolve carbides and nitrides deposited during cooling after the hot rolling, and to suppress the deposition of carbides and nitrides during the cooling process after annealing. In particular, if the attained temperature is lower than 1050°C , the solid solution of carbides and nitrides becomes insufficient and the percentage of the austenite phase becomes too high. If the attained temperature is higher than 1150°C , the percentage of austenite becomes too small, although the carbides and nitrides are in sufficient solid solution. Furthermore, certain amounts of carbon and nitrogen also become solid solution in the ferrite phase, and deposits may form during cooling in the ferrite phase where the solid solution limit is smaller, resulting in deterioration of corrosion resistance.

[0079] Conditions for the cold rolling are not limited, but a rolling reduction rate of 50 to 90% is preferred. The rolling reduction rate is set at 50% or more because the carbides and deposits are crushed or elongated to expand the surface area, thereby promoting solid solution in the heat treatment. The rolling reduction rate is set at 90% or less in order to suppress edge cuts due to excessive rolling. From the viewpoint of obtaining this effect stably, a rolling reduction rate of 85% or less is more preferred.

[0080] When the cold rolling is performed twice or more, intermediate annealing may be performed between the cold rolling processes. If the intermediate annealing is performed, the conditions may be in accordance with the annealing conditions after hot rolling.

[0081] The finish-annealing is carried out under conditions of a temperature increase rate of $20^\circ\text{C}/\text{second}$ or more, holding at the attained temperature of 1040 to 1120°C for 5 seconds or more, followed by cooling to 850°C or less at a cooling rate of $30^\circ\text{C}/\text{second}$ or more, followed by cooling to 400°C or less at a cooling rate of $20^\circ\text{C}/\text{second}$ or more. The finish-annealing is carried out under these conditions to suppress the deposition of carbides and nitrides during the temperature increase, to complete recrystallization, to form solid solution of carbides and nitrides, to control the percentage of the austenite phase, to suppress variations in the percentage of the austenite phase during cooling, and to suppress re-deposition of carbides and nitrides.

<Aspect B>

[0082] In the duplex stainless steel material, the conditions during the hot rolling (temperature immediately after the final pass, and the cooling rate) must be controlled in order to control the average grain size of the ferrite phase to the given range. In order to control the percentage of the austenite phase and Md to the given ranges, the conditions for the heat treatment (annealing) (temperature increase rate, attained temperature, holding time and cooling rate) must be controlled. All of these conditions affect the solid solution state of carbon and nitrogen. The attained temperature also affects the variation in thermodynamic austenite quantity. Further, the control of the attained temperature and holding time is also intended to ensure that the entire structure is sufficiently recrystallized.

[0083] Since the solid solution of carbon and nitrogen affects the percentage of the austenite phase (an amount produced) and Md, if they are present in large amounts as carbides or nitrides, the percentage of the austenite phase and Md cannot be controlled to the specified range. Therefore, in the heat treatment (annealing) step, it is necessary to suppress the deposition of carbides and nitrides during temperature increasing and cooling, while sufficiently dissolving the unconsolidated carbides and nitrides by holding them at the attained temperature. It is also necessary to control the percentage of the austenite phase by adjusting the attained temperature because the concentrations of elements (especially carbon and nitrogen) making up the austenite phase vary depending on the percentage of the austenite phase and the Md derived from it varies.

[0084] The hot rolling is performed by setting the temperature immediately after the final pass to 1030°C or more, and then cooling it to 800°C at a cooling rate of 20°C/second or more. By performing the hot rolling under these conditions, the crystal grains of the ferrite phase can be coarsened and controlled to the predetermined range.

[0085] Here, there are two main reasons for the smaller grain size of the ferrite phase. The first reason is recrystallization during hot rolling or subsequent annealing due to accumulation of hot rolling strain. As the temperature during the hot rolling is lower, the strain is more accumulated to induce recrystallization and the crystal grains of the ferrite phase are more easily refined, so that it is necessary to increase the temperature to that immediately after the final pass, which is difficult to generate it. The second reason is the suppression of grain growth of the ferrite phase due to the formation of the austenite phase. The deposition of the austenite phase in the grain boundary of the ferrite phase slows the movement of the grain boundary of the ferrite phase and suppresses grain growth. Since the austenite phase peaks around 900°C and decreases as the temperature is higher, the crystal grains of the ferrite phase tend to grow at a higher temperature. On the other hand, to maintain the high temperatures during the hot rolling, it is effective to increase the heating temperature of the slab before hot rolling or to increase the rolling rate to shorten the heat release time, but this increases fuel costs and manufacturing difficulties. Therefore, in view of these circumstances, the lower limit of the final pass temperature for the hot rolling was set to 1030°C.

[0086] The annealing after the hot rolling is carried out by increasing the temperature at a rate of 20°C/second or more, holding it at an attained temperature of 1080 to 1150°C for 10 seconds or more, and then cooling it to 400°C or less at a cooling rate of 20°C/second or more. The reason for performing the annealing under these conditions is to allow for sufficient solid solution of the carbides and nitrides deposited during cooling after hot rolling, and to suppress the deposition of the carbides and nitrides during the cooling process after annealing. The percentage of the austenite phase is relatively small, which reduces the inhibition of grain growth of the ferrite phase and facilitates coarsening of the grains of the ferrite phase. In particular, if the attained temperature is lower than 1080°C, the solid solution of carbides and nitrides becomes insufficient and the percentage of the austenite phase becomes too high. If the attained temperature is higher than 1150°C, the percentage of austenite becomes too small, although the carbides and nitrides are in sufficient solid solution. Furthermore, certain amounts of carbon and nitrogen also become solid solution in the ferrite phase, and deposits may form during cooling in the ferrite phase where the solid solution limit is smaller, resulting in deterioration of corrosion resistance.

[0087] Conditions for the cold rolling are not limited, but a rolling reduction rate of 50 to 80% is preferred. The rolling reduction rate is set to 50% or more because deposits of carbides and the like can be crushed or extended to expand the surface area, thereby promoting the solid solution in the heat treatment. On the other hand, the rolling reduction rate is set to 80% or less in order to suppress edge cuts caused by excessive rolling. This is also to prevent the structure of the finish-annealed material from becoming too fine due to the accumulation of rolling strain. As described above, many strains induce recrystallization, resulting in finer crystal grains, and this is avoided. From the viewpoint of obtaining these effects stably, the rolling reduction rate of 75% or less is more preferred.

[0088] When the cold rolling is performed twice or more, intermediate annealing may be performed between the cold rolling processes. If the intermediate annealing is performed, the conditions may be in accordance with the annealing conditions after hot rolling.

[0089] The finish-annealing is carried out under conditions of a temperature increase rate of 20°C/second or more, holding at the attained temperature of 1000 to 1150°C for 5 seconds or more, followed by cooling to 850°C or less at a cooling rate of 30°C/second or more, followed by cooling to 400°C or less at a cooling rate of 20°C/second or more. The finish-annealing is carried out under these conditions to suppress the deposition of carbides and nitrides during the

temperature increase, to complete recrystallization, to form solid solution of carbides and nitrides, to control the percentage of the austenite phase, to suppress variations in the percentage of the austenite phase during cooling, and to suppress re-deposition of carbides and nitrides. Also, the control of the structure to the cold rolling results in a structure with coarser crystal grains of the ferrite phase in the finish-annealing.

[0090] The duplex stainless steel material according to the embodiment is softer and more ductile than conventional ferritic-austenitic duplex stainless steel materials. Therefore, the duplex stainless steel material can suppress springback caused by excessive high strength during the forming process and has good shape freeze properties. The duplex stainless steel material also has higher strength and better corrosion resistance than general-purpose austenitic stainless steel materials such as SUS 304. Therefore, the duplex stainless steel material can be used for a variety of applications where these properties are required.

[Examples]

[0091] The content of the present invention will be described below in detail with reference to Examples, but the present invention is not construed as being limited thereto.

<Example of Aspect A>

[0092] Cold-rolled annealed sheets were produced as duplex stainless steel materials. Specifically, the stainless steel having each composition as shown in Table 1 (the balance being Fe and impurities) was smelted by vacuum melting to form a steel slab, and then hot-rolled and annealed in accordance with the ordinary methods. The annealing was carried out by increasing the temperature at a rate of 30°C/second, holding it at an attained temperature of 1100°C for 180 seconds, and then cooling it to 400°C or less at a cooling rate of 25°C/second. The annealed hot-rolled sheet was then cold-rolled at a rolling reduction rate of 80%, and then finish-annealed to obtain a cold-rolled annealed sheet having a thickness of 1.0 mm. The finish-annealing was carried out by increasing the temperature at a rate of 30°C/second, holding it at an attained temperature of 1080°C for 30 seconds, and then cooling it to 850°C or less at a cooling rate of 30°C/second and cooling it to 400°C or less at a cooling rate of 25°C/second. In Table 1, values of Md and DF were calculated based on the content of each element. Among the steel classes listed in Table 1, Nos. 1-M and 1-N are existing duplex stainless steel materials.

[Table 1]

Steel Class Nos.	Composition (% by mass)											Md [°C]	DF
	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Others		
1-A	0.030	0.20	2.8	0.031	0.004	2.4	21.3	0.10	0.55	0.061	--	105.2	67.3
1-B	0.021	0.30	2.9	0.033	0.002	2.6	23.0	0.20	0.45	0.073	--	74.1	79.1
1-C	0.025	0.02	2.9	0.030	0.001	2.5	21.4	0.05	0.55	0.053	--	108.7	68.3
1-D	0.040	0.21	3.8	0.019	0.001	2.2	22.1	0.10	0.71	0.055	Ti:0.11, Nb:0.022, V:0.18, Zr:0.12	85.4	72.8
1-E	0.020	0.01	2.0	0.039	0.002	2.5	21.5	0.01	0.50	0.060	Sn:0.070, Al:0.045 Co:0.18, Ta:0.011	116.0	68.9
1-F	0.020	0.01	3.0	0.035	0.001	2.3	21.4	0.01	0.20	0.075	Mg:0.0070, Ca:0.0012, REM:0.002	116.9	68.8
1-G	0.035	0.20	2.8	0.032	0.002	2.5	20.3	0.80	0.50	0.089	W:0.22, B:0.0015, Ga:0.006, REM:D.0090	89.3	57.8
1-H	0.030	0.10	3.1	0.030	0.001	1.0	21.0	0.05	0.48	0.120	--	124.1	66.1
1-I	0.024	0.20	3.2	0.038	0.001	2.4	24.1	0.06	0.55	0.040	--	76.8	92.2
1-J	0.040	0.21	2.8	0.016	0.001	5.4	18.6	0.12	0.30	0.050	B:0.0021, Ca:0.0013, Zr:0.11	62.5	23.1
1-K	0.026	0.30	1.5	0.029	0.002	1.4	19.5	0.13	0.10	0.075	Nb:0.015, Sn:0.004, Al:0.080	176.4	65.4
1-L	0.041	0.60	1.8	0.042	0.003	3.1	24.3	0.20	0.03	0.088	Ti:0.004, V:0.11, Mg:0.0050, REM:0.0080	44.1	82.0
1-M	0.014	0.54	0.8	0.033	0.001	6.8	25.2	3.04	0.21	0.144	W:0.02, Co:0.15, Sn:0.003, REM:0.0020	-138.2	67.1
1-N	0.019	0.60	5.3	0.030	0.002	1.4	21.7	0.33	0.23	0.236	V:0.17, Ta:0.012, Ga:0.004	33.2	53.4
1-O	0.023	0.30	4.2	0.030	0.002	3.4	22.1	0.32	0.23	0.056	V:0.17, Ta:0.012, Ga:0.004	63.8	70.1
The underlines indicate that they are outside the scope of the present invention.													

[0093] The following evaluations were performed on each cold-rolled annealed sheet obtained as described above.

<Percentage of Austenite phase (γ Phase) in Duplex Stainless Steel Material>

[0094] After each specimen was cut from each cold-rolled anneal sheet, the cross section in the thickness direction parallel to the rolling direction was mirror-polished and EBSD (electron backscatter diffraction) measurement was performed. The EBSD measurement was performed by measuring a 200 μm square area at the center of the specimen in the thickness direction with a step size of 0.3 μm , by means of a scanning electron microscope using measurement software TSL OIM Data Collection 7 (from TSL Solutions, Co., Ltd.). A phase ratio map was then created for the data obtained from the EBSD measurement using the analysis software TSL OIM Analysis 7 (TSL Solutions, Co., Ltd.) to separate the ferrite phase and the austenite phase. The percentage of the austenite phase in the entire observed area was then determined.

<Md of Austenite Phase (γ phase)>

[0095] After each specimen was cut from each cold-rolled annealed sheet, the cross section in the thickness direction parallel to the rolling direction was mirror-polished and subjected to component analysis by EPMA (electron probe micro-analyzer). Specifically, since C and N are characterized as being enriched in the austenite phase, qualitative mapping of C or N was performed on the entire cross section to identify the austenite phase. Subsequently, C, N, Si, Mn, Cr, Ni, Cu, and Mo were quantitatively analyzed at approximately the center of the austenite phase such that the electron beam did not hit the ferrite phase. The measurement area was an area of about 2 μm square, and at least three points were measured for each specimen, and an average value thereof was determined to be the results of the content of each element. The EPMA measurement was performed under the following conditions: an acceleration voltage of 15 kV, a current of 0.2 μA , and a step size of 0.15 μm . The Md of the austenite phase was calculated based on the content of each element thus obtained.

<Tensile Strength and Uniform Elongation>

[0096] A JIS 13 B specimen was cut out from each of the cold-rolled annealed steel sheets such that the parallel portion was in the rolling direction, and the tensile test was conducted using this specimen in accordance with JIS Z 2241: 2011. The tensile test was conducted at room temperature (25°C) in an air atmosphere at a tensile rate of 3 mm/min. In the tensile test, the highest attained strength was defined as tensile strength, and the elongation to the tensile strength was defined as uniform elongation. In the evaluation, if the tensile strength is 800 MPa or less, it can be said that the specimen is softened, and if the uniform elongation is 30.0% or more, it can be said that the specimen has improved ductility.

[0097] The results of the above evaluations are shown in Table 2.

[Table 2]

	Steel Class Nos.	γ Phase		Tensile Strength [Mpa]	Uniform Elongation [%]
		Percentage [% by volume]	Md [°C]		
Ex. 1-1	1-A	37	90.8	697	32.9
Ex. 1-2	1-B	26	64.0	551	44.5
Ex. 1-3	1-C	36	94.2	694	32.2
Ex. 1-4	1-D	29	71.5	613	40.2
Ex. 1-5	1-E	32	98.0	695	30.5
Ex. 1-6	1-F	31	99.0	694	30.1
Ex. 1-7	1-G	47	72.0	740	34.8
Comp. 1-1	<u>1-H</u>	34	<u>106.0</u>	845	26.9
Comp. 1-2	<u>1-I</u>	<u>3</u>	64.2	429	24.3
Comp. 1-3	<u>1-J</u>	<u>96</u>	47.0	923	30.9
Comp. 1-4	<u>1-K</u>	41	<u>162.6</u>	848	11.4
Comp. 1-5	<u>1-L</u>	<u>18</u>	<u>34.7</u>	477	25.6
Comp. 1-6	<u>1-M</u>	35	<u>-148.8</u>	865	16.2

(continued)

	Steel Class Nos.	γ Phase		Tensile Strength [Mpa]	Uniform Elongation [%]
		Percentage [% by volume]	Md [°C]		
Comp. 1-7	<u>1-N</u>	<u>54</u>	<u>18.5</u>	853	19.5
Comp. 1-8	1-O	29	33.0	575	29.0
The underlines indicate that they are outside the scope of the present invention.					

[0098] As shown in Table 2, Examples 1-1 through 1-7 showed good results for both tensile strength and uniform elongation because the percentage of the austenite phase and Md were controlled within the given ranges, along with the composition and Md of the cold-rolled annealed sheet (duplex stainless steel material).

[0099] In contrast, Comparative Example 1-1 had the excessive low content of Ni and the excessive high contents of N and C + N, resulting in excessively high strength and insufficient ductility.

[0100] Comparative Example 1-2 did not have sufficient ductility because the content of Cr was too high, resulting in the higher percentage of the ferrite phase.

[0101] In Comparative Example 1-3, the content of Ni was too high while the content of Cr was too low, resulting in a higher percentage of the austenite phase, which facilitated work hardening and resulted in excessively high strength.

[0102] In Comparative Example 1-4, the contents of Ni, Cr, and Sn were too low while the content of Al was too high, and the Md values of the cold-rolled annealed sheet and the austenite phase were too high, resulting in an excessively high amount of strain induced martensite phase and insufficient ductility.

[0103] Comparative Example 1-5 did not have sufficient ductility due to the excessively high contents of Si and Cr, the lower content of Ti, and the excessive low value of Md and the excessive high percentage of the ferrite phase in the cold-rolled annealed sheet.

[0104] Comparative Examples 1-6 and 1-7 are existing duplex stainless steel materials, especially with an excessively high content of N. Comparative Examples 1-6 and 1-7 had excessively high strength and insufficient ductility because the Md values of the cold-rolled and the austenite phase were too low.

[0105] Comparative Example 1-8 did not have sufficient ductility because the Md of the austenite phase was too low.

<Example of Aspect B>

[0106] Cold-rolled annealed sheets were produced as duplex stainless steel materials. The cold-rolled annealed sheets were subjected to a hot rolling step, annealing step, cold rolling step, and finish-annealing step in this order. Specifically, the stainless steel having each composition of steel classes as shown in Table 3 (the balance being Fe and impurities) was smelted by vacuum melting to form a steel slab. The steel slab was then subjected to a hot rolling step to obtain a hot-rolled sheet having a thickness of 5 mm. In the hot rolling step, the temperature immediately after the final pass was set as shown in Table 4 and cooling was carried out to 800°C by water cooling (at a cooling rate of 20°C/second or more). The annealing step after the hot rolling step was carried out by increasing the temperature at a rate of 25°C/second, holding it at the attained temperature of 1100°C (annealing temperature) for 30 seconds, and then cooling it to 400°C or less by water cooling (at a cooling rate of 20°C/second or more). The cold rolling was carried out at the rolling rate shown in Table 4 to obtain each cold-rolled sheet having the thickness shown in Table 4. The finish-annealing step was carried out by increasing the temperature at a rate of 30°C/second, holding it at the attained temperature (annealing temperature) shown in Table 4 for 30 seconds, and then cooling it to 400°C or less by water cooling (at a cooling rate of 30°C/second or more). In Table 3, values of Md and DF were calculated based on the content of each element.

[Table 3]

Steel Class Nos.	Composition (% by mass)											Md (°C)	DF	
	C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Others			C+N
2-A	0.017	0.19	2.9	0.023	0.001	2.3	21.3	0.20	0.21	0.064	--	0.081	119.6	72.7
2-B	0.030	0.21	3.8	0.019	0.001	2.2	22.1	0.10	0.71	0.055	--	0.095	85.4	72.8
2-C	0.020	0.05	2.0	0.039	0.002	2.5	21.5	0.01	0.50	0.060	Nb:0.015, V:0.10 Ta:0.003, Zr:0.01	0.080	115.6	69.1
2-D	0.020	0.08	2.0	0.039	0.002	2.5	21.5	0.01	0.50	0.060	W:0.22, Sn:0.030 Al:0.027	0.080	115.4	69.3
2-E	0.020	0.10	3.0	0.035	0.001	2.3	21.4	0.01	0.20	0.075	Ti:0.11, Co:0.12, B:0.0020 Mg:0.0020, Ca:0.0022 Ga:0.003, REM: 0.0090	0.095	116.0	69.3
2-F	0.019	0.34	3.2	0.024	0.000	2.1	21.2	0.30	0.59	<u>0.172</u>	B:0.0017, Ca:0.0024 Zr:0.01	<u>0.191</u>	58.1	52.4
2-G	0.025	0.20	3.1	0.031	0.000	3.1	23.0	0.20	0.35	<u>0.101</u>	Nb:0.017, Ti:0.02, V:0.11 Sn:0.31, Al:0.021, REM: 0.0080	0.126	<u>47.0</u>	68.7
2-H	0.024	0.20	3.2	0.038	0.001	2.4	23.9	0.06	0.55	0.040	--	0.064	79.6	90.8
2-I	0.040	0.21	2.8	0.016	0.001	<u>5.4</u>	<u>18.6</u>	0.12	0.30	0.050	W:0.13, Co:0.15, Sn:0.028 Mg:0.0050, Ta:0.005 Ga:0.002, REM:0.0020	0.090	62.5	23.1
The underlines indicate that they are outside the scope of the present invention.														

[Table 4]

	Steel Class Nos.	Hot Rolling	Cold Rolling		Finish Annealing
		Temperature immediately after Final Pass (°C)	Rolling Reduction Rate (%)	Thickness (mm)	Annealing Temperature (°C)
Ex. 2-1	2-A	1040	70	1.50	1080
Ex. 2-2	2-A	1045	70	1.50	1080
Ex. 2-3	2-A	1056	70	1.50	1080
Ex. 2-4	2-B	1032	75	1.25	1040
Ex. 2-5	2-C	1055	75	1.25	1080
Ex. 2-6	2-D	1041	75	1.25	1080
Ex. 2-7	2-E	1038	75	1.25	1080
Comp. 2-1	2-A	1033	70	1.50	1180
Comp. 2-2	2-A	1045	70	1.50	950
Comp. 2-3	<u>2-F</u>	1038	70	1.50	1080
Comp. 2-4	<u>2-G</u>	1062	75	1.25	1080
Comp. 2-5	2-H	1035	75	1.25	1080
Comp. 2-6	<u>2-I</u>	1041	75	1.25	1080
The underlines indicate that they are outside the scope of the present invention.					

[0107] The following evaluations were performed on each cold-rolled annealed sheet obtained as described above.

<Percentage of Austenite phase (γ Phase) in Duplex Stainless Steel Material>

[0108] It was determined by the same method as that of Example of the aspect A.

<Md of Austenite Phase (γ phase)>

[0109] It was determined by the same method as that of Example of the aspect A.

<Average Grain Size of Ferrite Phase (α Phase) in Duplex Stainless Steel>

[0110] After each specimen was cut from each cold-rolled anneal sheet, the cross section in the thickness direction parallel to the rolling direction was mirror-polished and EBSD (electron backscatter diffraction) measurement was performed. The EBSD measurement was performed by measuring a 200 μm square area at the center of the specimen in the thickness direction with a step size of 0.3 μm , by means of a scanning electron microscope using measurement software TSL OIM Data Collection 7 (from TSL Solutions, Co., Ltd.). The area of the grains of the ferrite phase (BCC) was determined for the data obtained from the EBSD measurement by the area fraction method.

<n-Value Ratio, 0.2% Yield Strength and Uniform Elongation>

[0111] A JIS 13 B specimen was cut out from each of the cold-rolled annealed steel sheets such that the parallel portion was in the rolling direction, and the tensile test was conducted using this specimen in accordance with JIS Z 2241: 2011. A tensile test was conducted at room temperature (25°C) in an air atmosphere at a tensile rate of 10 mm/min. In the tensile test, the elongation to the highest attained strength (tensile strength) was defined as uniform elongation.

[0112] For each n value, a relationship between stress σ and strain ε from 0.2% yield strength to the maximum load point was measured, and the true stress and strain were calculated from those measurements and plotted on a logarithmic scale with a horizontal axis as strain ($\ln \varepsilon$) and a vertical axis as stress ($\ln \sigma$). The slope of the straight line obtained by plotting was then determined to be the n value. It should be noted that the strain rate was as shown in Table 3.

[0113] In these evaluations, if the n-value ratio is 0.80 or less and the uniform elongation is 30.0% or more, the material can have improved ductility. If the 0.2% yield stress is 480 MPa or less, the material can be soft.

[0114] The results of the above evaluations are shown in Table 5.

[Table 5]

	γ Phase		α Phase	Strain Rate (S ⁻¹)	n-Value Ratio	0.2% Yield Strength (MPa)	Uniform Elongation (%)
	Percentage (% by volume)	Md (°C)	Average Grain Size (μ m)				
Ex. 2-1	30	78.1	9.1	3.3×10^{-4}	0.73	440	37.8
Ex. 2-2	30	78.1	9.1	3.3×10^{-3}	0.75	421	32.1
Ex. 2-3	30	78.1	9.1	8.3×10^{-3}	0.79	409	30.2
Ex. 2-4	37	52.9	7.2	3.3×10^{-1}	0.76	451	33.1
Ex. 2-5	34	74.6	7.4	3.3×10^{-4}	0.74	458	36.5
Ex. 2-6	34	74.6	7.4	3.3×10^{-4}	0.74	466	37.8
Ex. 2-7	34	75.4	7.4	3.3×10^{-4}	0.75	421	36.1
Comp. 2-1	<u>22</u>	58.5	12.8	3.3×10^{-4}	0.62	409	28.5
Comp. 2-2	41	<u>103.5</u>	4.3	3.3×10^{-4}	0.78	491	32.6
Comp. 2-3	<u>50</u>	<u>18.8</u>	3.9	3.3×10^{-4}	1.25	512	22.1
Comp. 2-4	34	<u>8.1</u>	7.3	3.3×10^{-4}	0.91	477	25.8
Comp. 2-5	<u>12</u>	39.5	16.9	3.3×10^{-4}	0.03	364	19.6
Comp. 2-6	<u>78</u>	<u>23.0</u>	1.9	3.3×10^{-4}	1.27	485	18.4
The underlines indicate that they are outside the scope of the present invention.							

[0115] As shown in Table 5, the results of the n-value ratio, 0.2% yield stress, and uniform elongation in Examples 2-1 to 2-7 were all good because the percentage of the austenite phase and Md were controlled to the given ranges, along with the composition and Md of the cold-rolled annealed sheet (duplex stainless steel material).

[0116] In contrast, Comparative Example 2-1 had the excessively low percentage of the austenite phase, resulting in insufficient ductility.

[0117] Comparative Example 2-2 had the excessively high Md of the austenite phase, resulting in a smaller average grain size of the ferrite phase and insufficient softening.

[0118] Comparative Example 2-3 has the higher amount of C + N due to the excessive content of N. Further, the percentage of the austenite phase was too large and the Md of the austenite phase was too low, resulting in insufficient softening and ductility.

[0119] Comparative Example 2-4 had the excessively high content of N and the excessively low value of Md of the cold-rolled annealed sheet, so that the austenite phase was highly stable and it was difficult to transform it to the strain induced martensite phase. The Md of the austenite phase was also too low, resulting in insufficient ductility.

[0120] Comparative Example 2-5 had the excessively low percentage of the austenite phase, resulting in the high percentage of the ferrite phase and insufficient ductility.

[0121] Comparative Example 2-6 has the high content of Ni and the low content of Cr. In addition, softening was insufficient due to the high percentage of the austenite phase. The Md of the austenite phase was also too low, resulting in insufficient ductility.

[0122] As can be seen from the above results, the present invention provides a ferritic-austenitic duplex stainless steel material that is softer and more ductile than conventional ferritic-austenitic duplex stainless steel materials. In other words, the present invention can provide a ferritic-austenitic duplex stainless steel material that is softer and more ductile than conventional ferritic-austenitic duplex stainless steel materials by the configurations according to the following [1] to [10]:

[1] A ferritic-austenitic duplex stainless steel material having a composition comprising, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.050% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities;

wherein the ferritic-austenitic duplex stainless steel material has a metallographic structure having: a value of Md of 50.0 to 150.0 °C, the value of Md being represented by the following equation (1):

$$Md = 551 - 462 (C + N) - 9.2Si - 8.1Mn - 29 (Ni + Cu) - 13.7Cr - 18.5Mo \dots (1) \quad (1)$$

in which each of the element symbols represents a content (% by mass) of each element; and
25 to 49% by volume of an austenite phase; and

wherein the value of Md of the austenite phase represented by the above equation (1) is 35.0 to 100.0°C.

[2] The ferritic-austenitic duplex stainless steel material according to [1], further comprising one or more selected from the group consisting of, on a mass basis, Nb: 0.010 to 0.500%, Ti: 0.01 to 0.50%, V: 0.01 to 0.50%, W: 0.05 to 0.50%, Co: 0.01 to 0.30%, B: 0.0002 to 0.0050%, Sn: 0.010 to 0.500%, Al: 0.010 to 0.050%, Mg: 0.0002 to 0.0100%, Ca: 0.0002 to 0.0100%, Ta: 0.050% or less, Ga: 0.050% or less, Zr: 0.01 to 0.50 %, and REM: 0.0002 to 0.0100%.

[3] The ferritic-austenitic duplex stainless steel material according to [1] or [2], wherein the ferritic-austenitic duplex stainless steel material comprises, on a mass basis, C: 0.001 to 0.040%, N: 0.010 to 0.080%, C + N of less than 0.120%, and 25 to 40% by volume of the austenite phase.

[4] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [3], wherein the value of Md of the austenite phase represented by the above equation (1) is 50.0 to 90.0°C.

[5] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [4], wherein an average grain size of the ferrite phase is 7.0 μm or more.

[6] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [5], wherein a value of DF is 50.0 to 80.0, the value of DF being represented by the following equation (2):

$$DF = 7.2 (Cr + 0.88Mo + 0.78Si) - 8.9 (Ni + 0.03Mn + 0.72Cu + 22C + 21N) - 44.9 \dots (2) \quad (2)$$

in which each of the element symbols represents a content (% by mass) of each element.

[7] The ferritic-austenitic duplex stainless steel material according to [6], wherein the value of DF is 60.0 to 80.0.

[8] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [7], wherein a tensile strength is 800 MPa or more.

[9] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [8], wherein a uniform elongation is 30.0% or more.

[10] The ferritic-austenitic duplex stainless steel material according to any one of [1] to [9], wherein when a tensile test is conducted at a strain rate of 3.3×10^{-4} to $8.3 \times 10^{-3} \text{ s}^{-1}$, an n-value ratio of an n-value in a 15 to 20% strain range to an n-value in a 20 to 25% strain range is 0.80 or less.

Claims

1. A ferritic-austenitic duplex stainless steel material having a composition comprising, on a mass basis, C: 0.001 to 0.050%, Si: 0.01 to 0.50%, Mn: 1.0 to 4.5%, P: 0.050% or less, S: 0.030% or less, Ni: 1.5 to 3.5%, Cr: 19.6 to 24.0 %, Mo: 0.01 to 1.00%, Cu: 0.01 to 1.20%, and N: 0.010 to 0.090%, C + N being less than 0.130%, the balance being Fe and impurities;

wherein the ferritic-austenitic duplex stainless steel material has a metallographic structure having: a value of Md of 50.0 to 150.0 °C, the value of Md being represented by the following equation (1):

$$Md = 551 - 462 (C + N) - 9.2Si - 8.1Mn - 29 (Ni + Cu) - 13.7Cr - 18.5Mo \dots (1) \quad (1)$$

in which each of the element symbols represents a content (% by mass) of each element; and
25 to 49% by volume of an austenite phase; and

wherein the value of Md of the austenite phase represented by the above equation (1) is 35.0 to 100.0°C.

2. The ferritic-austenitic duplex stainless steel material according to claim 1, further comprising one or more selected from the group consisting of, on a mass basis, Nb: 0.010 to 0.500%, Ti: 0.01 to 0.50%, V: 0.01 to 0.50%, W: 0.05 to 0.50%, Co: 0.01 to 0.30%, B: 0.0002 to 0.0050%, Sn: 0.010 to 0.500%, Al: 0.010 to 0.050%, Mg: 0.0002 to 0.0100%, Ca: 0.0002 to 0.0100%, Ta: 0.050% or less, Ga: 0.050% or less, Zr: 0.01 to 0.50 %, and REM: 0.0002 to 0.0100%.
3. The ferritic-austenitic duplex stainless steel material according to claim 1 or 2, wherein the ferritic-austenitic duplex stainless steel material comprises, on a mass basis, C: 0.001 to 0.040%, N: 0.010 to 0.080%, C + N of less than 0.120%, and 25 to 40% by volume of the austenite phase.

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4. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 3, wherein the value of Md of the austenite phase represented by the above equation (1) is 50.0 to 90.0°C.

5. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 4, wherein an average grain size of the ferrite phase is 7.0 μm or more.

6. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 5, wherein a value of DF is 50.0 to 80.0, the value of DF being represented by the following equation (2):

$$DF = 7.2 (Cr + 0.88Mo + 0.78Si) - 8.9 (Ni + 0.03Mn + 0.72Cu + 22C + 21N) - 44.9 \cdot \cdot \cdot (2)$$

in which each of the element symbols represents a content (% by mass) of each element.

7. The ferritic-austenitic duplex stainless steel material according to claim 6, wherein the value of DF is 60.0 to 80.0.

8. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 7, wherein a tensile strength is 800 MPa or more.

9. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 8, wherein a uniform elongation is 30.0% or more.

10. The ferritic-austenitic duplex stainless steel material according to any one of claims 1 to 9, wherein when a tensile test is conducted at a strain rate of 3.3×10^{-4} to $8.3 \times 10^{-3} \text{s}^{-1}$, an n-value ratio of an n-value in a 15 to 20% strain range to an n-value in a 20 to 25% strain range is 0.80 or less.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/034357

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/00(2006.01)i; **C21D 9/46**(2006.01)i; **C22C 38/58**(2006.01)i
 FI: C22C38/00 302H; C22C38/58; C21D9/46 Q

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C22C38/00; C21D9/46; C22C38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-52115 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP) 12 March 2009 (2009-03-12)	1-10
A	JP 2010-59541 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP) 18 March 2010 (2010-03-18)	1-10
A	JP 2017-88945 A (NIPPON STEEL & SUMIKIN STAINLESS STEEL CORP) 25 May 2017 (2017-05-25)	1-10
A	JP 7-41906 A (NIPPON YAKIN KOGYO CO LTD) 10 February 1995 (1995-02-10)	1-10

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

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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JP 2010-59541 A	18 March 2010	(Family: none)	
JP 2017-88945 A	25 May 2017	(Family: none)	
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REFERENCES CITED IN THE DESCRIPTION

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