



(11) **EP 4 477 776 A1**

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

(43) Date of publication:  
**18.12.2024 Bulletin 2024/51**

(21) Application number: **23752653.8**

(22) Date of filing: **23.01.2023**

(51) International Patent Classification (IPC):  
**C22C 38/00** <sup>(2006.01)</sup> **C21D 9/46** <sup>(2006.01)</sup>  
**C22C 38/58** <sup>(2006.01)</sup> **C22C 38/60** <sup>(2006.01)</sup>

(52) Cooperative Patent Classification (CPC):  
**C21D 9/46; C22C 38/00; C22C 38/58; C22C 38/60**

(86) International application number:  
**PCT/JP2023/001836**

(87) International publication number:  
**WO 2023/153185 (17.08.2023 Gazette 2023/33)**

(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 ME MK MT NL  
NO PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA**  
Designated Validation States:  
**KH MA MD TN**

(30) Priority: **10.02.2022 JP 2022019829**

(71) Applicant: **NIPPON STEEL Stainless Steel  
Corporation**  
**Tokyo 100-0005 (JP)**

(72) Inventor: **MIZOGUCHI, Taichiro**  
**Tokyo 100-0005 (JP)**

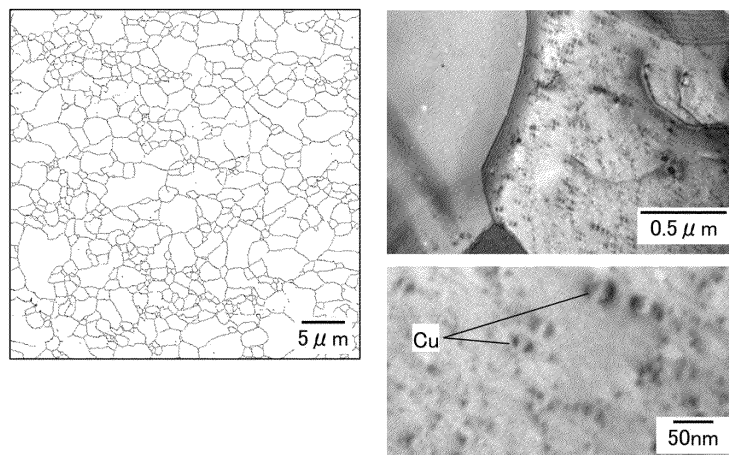
(74) Representative: **Clarke, Modet y Cía., S.L.**  
**C/ Suero de Quiñones 34-36**  
**28002 Madrid (ES)**

(54) **AUSTENITIC STAINLESS STEEL AND METHOD FOR PRODUCING AUSTENITIC STAINLESS STEEL**

(57) Provided is an austenitic stainless steel which enables both a reduction in load of working during production and an increase in strength of an end product and can be produced with high productivity. The austenitic stainless steel: contains more than 0.03% and not more than 0.15% of C, 0.1-2.0% of Si, 0.3-2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, 3.0-6.0% of Ni, 16.0-18.5% of Cr, 1.5-4.0% of Cu, and 0.005-0.25% of

N, in percent by mass, and the other part composed of Fe and an inevitable impurity; includes not less than 20% by volume of an austenite phase, a Cu-rich phase having a number density of not less than  $1.0 \times 10^3 \mu\text{m}^{-3}$  and a long diameter of not more than 30 nm, and a remaining part composed of a deformation-induced martensite phase and an inevitably formed phase; and has an  $\text{Md}_{30}$  value of 10.0-80.0.

FIG. 1



EP 4 477 776 A1

**Description**

## Technical Field

- 5 **[0001]** The present invention relates to an austenitic stainless steel and a method for producing the austenitic stainless steel.

## Background Art

- 10 **[0002]** A metastable austenitic stainless steel typified by SUS301 is known as an austenitic stainless steel which is put to uses where corrosion resistance and strength are required. Such an austenitic stainless steel is used as a material for a spring product such as a cylinder head gasket of an engine in an automobile or for a structural member such as an in-vehicle battery frame member.

- 15 **[0003]** In general, high strength is imparted to such a stainless steel by increasing a rolling reduction ratio in cold rolling or the like, and the load of working such as rolling in the production process therefore tends to be increased. In order to reduce the load, for example, Patent Literature 1 proposes, as a method for producing a spring member having a martensite phase in which a precipitate consisting of a Cu-rich phase is dispersed, a method of subjecting a steel sheet for a spring to an aging treatment which steel sheet exhibits a multiphasic system with no Cu-rich phase precipitated therein.

## 20 Citation List

[Patent Literature]

- 25 **[0004]** [Patent Literature 1]  
Japanese Patent Application Publication Tokukai No. 2008-195976

## Summary of Invention

## Technical Problem

- 30 **[0005]** Precipitation of a Cu-rich phase is effective for increasing the strength of a stainless steel. As such, according to the method disclosed in Patent Literature 1, by subjecting the steel sheet for a spring to the aging treatment to thereby cause a Cu-rich phase to be precipitated, it is possible to increase the strength of a spring member, which is an end product, while reducing the load of working in the production process of the steel sheet for a spring. However, due to the need of the aging treatment step, the method has room for improvement in productivity of the spring member.

- 35 **[0006]** An object of an aspect of the present invention is to provide an austenitic stainless steel which enables both a reduction in load of working during production and an increase in strength of an end product and which can be produced with high productivity. The inventor of the present invention paid attention to the fact that, although a lower C content is preferable for the reduction in load of working, a certain amount of C is utilized in order to obtain high strength of the end product.

## Solution to Problem

- 45 **[0007]** In order to attain the object, an austenitic stainless steel in accordance with an aspect of the present invention is an austenitic stainless steel, containing more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel including (i) not less than 20% by volume of an austenite phase, (ii) a Cu-rich phase having a number density of not less than  $1.0 \times 10^3 \mu\text{m}^{-3}$  and a long diameter of not more than 30 nm, and (iii) a remaining part composed of a deformation-induced martensite phase and an inevitably formed phase, the austenitic stainless steel having an  $Md_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) below,

- 55  $Md_{30} = 551 - 462(C+N) - 9.2Si - 8.1Mn - 29Ni - 10.6Cu - 1.37Cr - 18.5Mo$  (1):

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to

the austenitic stainless steel.

[0008] In order to attain the object, a method in accordance with an aspect of the present invention for producing an austenitic stainless steel is a method for producing an austenitic stainless steel, the austenitic stainless steel containing more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel having an  $Md_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) below, the method including a finishing annealing step of carrying out finishing annealing at a temperature of not lower than 750°C and not higher than 980°C, wherein in a case where a peak temperature in the finishing annealing step is not lower than 850°C, time during which heating is carried out at not lower than 850°C is not more than 30 seconds,

$$Md_{30} = 551-462(C+N)-9.2Si-8.1Mn-29Ni-10.6Cu-13.7Cr-18.5Mo \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

#### Advantageous Effects of Invention

[0009] According to an aspect of the present invention, it is possible to provide an austenitic stainless steel which enables both a reduction in load of working during production and an increase in strength of an end product and which can be produced with high productivity.

#### Brief Description of Drawings

#### [0010]

Fig. 1 is a diagram illustrating an EBSD grain boundary map and a TEM-captured image of an austenitic stainless steel in accordance with an embodiment.

Fig. 2 is a diagram illustrating a relationship between 0.2% proof stress (YS 18%) and reference strength (HV 60%) of austenitic stainless steels in accordance with examples and comparative examples.

#### Description of Embodiments

[0011] The following description will discuss in detail an austenitic stainless steel in accordance with an embodiment of the present invention. Note that the following description is intended to make the gist of the present invention understood better, and does not limit the present invention unless otherwise specified.

#### [Configuration of system]

[0012] The austenitic stainless steel in accordance with an embodiment of the present invention is a stainless steel including not less than 20% by volume of an austenite phase. In the present specification, "austenitic stainless steel" hereinafter means the austenitic stainless steel in accordance with an embodiment of the present invention, unless otherwise specified. The austenitic stainless steel can be, for example, a steel sheet or a steel strip.

[0013] The austenitic stainless steel includes a deformation-induced martensite phase into which a part of the austenite phase has been transformed due to a transformation induced plasticity (TRIP) phenomenon. From the viewpoint of increasing strength, a proportion of the deformation-induced martensite phase in the austenitic stainless steel is preferably not less than 5% by volume, more preferably not less than 10% by volume, even more preferably not less than 15% by volume, and most preferably not less than 20% by volume. Further, the proportion of the deformation-induced martensite phase in the austenitic stainless steel is preferably less than 80% by volume and more preferably not more than 75% by volume. A proportion of the austenite phase included in the austenitic stainless steel can be decreased in accordance with an increase in proportion of the deformation-induced martensite phase, provided that the proportion of the austenite phase is not less than 20% by volume.

[0014] The austenitic stainless steel further includes a Cu-rich phase. The "Cu-rich phase" means a phase containing not less than 60 atomic percent of Cu (copper) and is, for example, an  $\epsilon$ -Cu phase. The austenitic stainless steel includes at least a Cu-rich phase having a number density of not less than  $1.0 \times 10^3 \mu\text{m}^{-3}$  and a long diameter of not more than 30 nm. The "long diameter" means a maximum diameter among diameters of each of the particles of the Cu-rich phase which is

precipitated in particulate form. Note that the austenitic stainless steel can also include a Cu-rich phase having a long diameter of more than 30 nm. The Cu-rich phase can be dispersed in the austenite phase, can be dispersed in the deformation-induced martensite phase, or can be dispersed in an inevitably formed phase (described later).

**[0015]** The Cu-rich phase can be identified by observing a system with use of a transmission electron microscope (TEM). For example, a TEM sample including a given cross section of the austenitic stainless steel is prepared, and a predetermined portion of the cross section is observed with use of the TEM. This allows counting, in the predetermined portion, the number of Cu-rich phase particles each having a cross section of not more than 30 nm in long diameter. Further, by calculating a volume on the basis of a thickness of the TEM sample used in the number counting and an area of the portion in which the number was counted, it is possible to calculate a number density per volume. The thickness of the TEM sample, for example, can be an actually measured value of thickness of the TEM sample, or can be an estimation value of thickness estimated on the basis of the method by which the TEM sample has been prepared. Examples of the method of preparing the TEM sample include, but are not limited to, electrolytic polishing.

**[0016]** The finer the precipitated Cu-rich phase and the greater the amount of the precipitated Cu-rich phase, the higher the strength of the austenitic stainless steel. The Cu-rich phase in the above-described size and amount is effective for increasing the strength of the austenitic stainless steel. During the production of the austenitic stainless steel, such as when cold rolling is carried out prior to finishing annealing, precipitation of a Cu-rich phase is not caused. This keeps the strength low and thus reduces the load of working. Then, precipitation of a Cu-rich phase is caused in the finishing annealing step, so that the austenitic stainless steel which has been produced possesses high strength. Production steps such as the finishing annealing step will be described later.

**[0017]** The austenitic stainless steel can include an inevitably formed phase other than the austenite phase, the deformation-induced martensite phase, and the Cu-rich phase. The inevitably formed phase is not particularly limited, but examples of the inevitably formed phase include a  $\delta$  ferrite phase and a phase containing a carbide, a nitride, and/or an oxide. Examples of the phase containing a carbide, a nitride, and/or an oxide include a phase containing a carbide or nitride of Cr, Ti, and/or Nb and a phase containing an oxide of Si, Ti, Al, Mg, and/or Ca.

**[0018]** The austenitic stainless steel has an average crystal grain size of preferably not more than 10.0  $\mu\text{m}$ . The finer the crystal grains of the austenitic stainless steel, the higher the strength of the austenitic stainless steel. In general, increasing the strength of an austenitic stainless steel causes a deterioration in ductility. However, by causing the crystal grains to be finer, it is possible to achieve both an increase in strength and an improvement in ductility of the austenitic stainless steel.

**[0019]** The average crystal grain size can be measured by an electron back scattering diffraction (EBSD) method. For example, with respect to a given cross section of the austenitic stainless steel, a crystal grain size in each of a plurality of fields of view can be calculated by the EBSD method, and an average value of the crystal grain sizes thus calculated in the plurality of fields of view can be regarded as the average crystal grain size. Further, the average crystal grain size can be measured by a method other than the EBSD method. The method other than the EBSD method can be, for example, a method as indicated in JIS G0551 in which grain boundaries are caused to appear by nitric acid electrolysis and the average crystal grain size is measured using microtomy or the like.

[Composition]

**[0020]** The austenitic stainless steel contains more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and less than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 3.8% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass. The other part of the austenitic stainless steel can be composed of Fe (iron) and an inevitable impurity. The following description will discuss the significance of the amount of each element contained in the austenitic stainless steel.

(C)

**[0021]** C (carbon) is an austenite former which facilitates formation of an austenite phase, and is an element which has a high solid-solution strengthening effect and is also effective for obtaining strength. The austenitic stainless steel contains more than 0.03% by mass and not more than 0.15% by mass of C. In a case where a C content is more than 0.03% by mass, not only a sufficient solid-solution strengthening effect is exhibited but also an austenitic stainless steel having good strength can be obtained.

**[0022]** Excessively adding C causes precipitation of a Cr carbide by annealing at a relatively low temperature, and leads to deterioration in corrosion resistance of the austenitic stainless steel. For this reason, the C content is not more than 0.15% by mass. In a case where the C content is not more than 0.15% by mass, it is possible to obtain an austenitic stainless steel that has a good corrosion resistance.

(Si)

**[0023]** Si (silicon) is an element which is effective as a deoxidizer and has a solid-solution strengthening effect. The austenitic stainless steel contains not less than 0.1% by mass and not more than 2.0% by mass of Si, and preferably contains not less than 0.2% by mass and not more than 1.0% by mass of Si. In a case where a Si content is not less than 0.1% by mass, the austenitic stainless steel effectively exhibits a deoxidation effect and a solid-solution strengthening effect. It is more preferable that the Si content be not less than 0.2% by mass.

**[0024]** Further, Si is a ferrite former which facilitates formation of a ferrite phase. A  $\delta$  ferrite phase can be a cause for occurrence of edge cracking or alligating in hot rolling. From the viewpoint of reducing formation of a  $\delta$  ferrite phase, a Si content is not more than 2.0% by mass, preferably less than 1.5% by mass, and preferably not more than 1.0% by mass.

(Mn)

**[0025]** Mn (manganese) is an austenite former, and is also an element effective for maintaining an austenite phase. Further, Mn is an element having an effect of promoting precipitation of a Cu-rich phase. The austenitic stainless steel contains not less than 0.3% by mass and not more than 2.5% by mass of Mn, and preferably contains not less than 0.5% by mass and not more than 2.0% by mass of Mn. In a case where a Mn content is not less than 0.3% by mass, it is easy to ensure the amount of a Cu-rich phase precipitated. It is more preferable that the Mn content be not less than 0.5% by mass. Further, excessively adding Mn causes deterioration in hot workability of the austenitic stainless steel. As such, the Mn content is not more than 2.5% by mass, and preferably not more than 2.0% by mass.

(P)

**[0026]** P (phosphorus) is an element which is mixed in as an inevitable impurity. The lower a P content, the better. From the viewpoint of producibility, the austenitic stainless steel can contain not more than 0.04% by mass of P. In a case where the P content is not more than 0.04% by mass, it is possible to reduce an adverse effect of P on material characteristics of the austenitic stainless steel such as ductility.

(S)

**[0027]** S (sulfur) is an element which is mixed in as an inevitable impurity. The lower a S content, the better. From the viewpoint of producibility, the austenitic stainless steel can contain not more than 0.015% by mass of S. In a case where the S content is not more than 0.015% by mass, it is possible to reduce an adverse effect of S on material characteristics of the austenitic stainless steel such as ductility.

(Ni)

**[0028]** Ni (nickel) is an austenite former, and is also an element effective for maintaining an austenite phase. The austenitic stainless steel contains not less than 3.0% by mass and less than 6.0% by mass of Ni, preferably contains not less than 3.5% by mass and not more than 5.5% by mass of Ni, and more preferably contains not less than 4.0% by mass and less than 5.0% by mass of Ni. In a case where a Ni content is not less than 3.0% by mass, an austenite phase can be formed and maintained well. It is more preferable that the Ni content be not less than 4.5% by mass.

**[0029]** However, Ni is an expensive element and, when added excessively, causes a reduction in amount of a deformation-induced martensite phase formed, due to stabilization of an austenite phase. As such, the Ni content is less than 6.0% by mass, preferably not more than 5.5% by mass, and more preferably less than 5.0% by mass.

(Cr)

**[0030]** Cr (chromium) is an element effective for ensuring corrosion resistance of the austenitic stainless steel. The austenitic stainless steel contains not less than 16.0% by mass and not more than 18.5% by mass of Cr, and more preferably contains not less than 16.5% by mass and not more than 18.0% by mass of Cr. In a case where a Cr content is not less than 16.0% by mass, the corrosion resistance of the austenitic stainless steel can be ensured well. It is more preferable that the Cr content be not less than 16.5% by mass.

**[0031]** However, Cr is also a ferrite former as with Si. As such, excessively adding Cr causes excessive formation of a  $\delta$  ferrite phase. As such, the Cr content is not more than 18.5% by mass, and preferably not more than 18.0% by mass.

(Cu)

**[0032]** Cu is an austenite former, and is also an element effective for maintaining an austenite phase. Further, Cu is effective for increasing the strength of an austenitic stainless steel by precipitation of a Cu-rich phase. Cu is an element which also acts effectively for causing crystal grains to be finer. This is considered to be because a Cu-rich phase exhibits an effect of inhibiting growth of crystal grains. Further, Cu reduces work hardening of an austenite phase in a solid solution state and therefore can reduce the load of rolling in the production process of the austenitic stainless steel.

**[0033]** The austenitic stainless steel contains not less than 1.5% by mass and not more than 4.0% by mass of Cu, preferably contains not less than 2.0% by mass and not more than 3.5% by mass of Cu, and more preferably contains not less than 2.0% by mass and not more than 3.5% by mass of Cu. In a case where a Cu content is not less than 1.5% by mass, an austenite phase can be formed and maintained well and also a Cu-rich phase can be precipitated well. The Cu content is more preferably not less than 2.0% by mass, and even more preferably more than 2.0% by mass.

**[0034]** However, excessively adding Cu causes undesirable formation of a CuMn phase at the center of slab during solidification of the slab. This deteriorates hot workability of the slab. As such, the Cu content is not more than 4.0% by mass, and preferably not more than 3.5% by mass.

(N)

**[0035]** N (nitrogen) is an austenite former and is also an element which has a solid-solution strengthening effect and a corrosion resistance improving effect. In order to cause formation of an austenite phase, the austenitic stainless steel has a N content of not less than 0.005% by mass. A N content within such a range allows an austenite phase to be effectively formed.

**[0036]** In a case where N is excessively added, the load of rolling of the austenitic stainless steel is increased. As such, the N content is not more than 0.25% by mass, and is preferably not more than 0.20% by mass.

(Other elements)

**[0037]** The austenitic stainless steel can further contain, in addition to the elements described above, at least one selected from the group consisting of: not more than 1.0% of Mo; not more than 1.0% of W; not more than 0.5% of V; not less than 0.0001% and not more than 0.01% of B; not more than 0.8% of Co; not more than 0.1% of Sn; not more than 0.03% of Ca; not more than 0.03% of Mg; not more than 0.5% of Ti; not more than 0.5% of Nb; not more than 0.3% of Al; not more than 0.5% of Sb; not more than 0.5% of Zr; not more than 0.03% of Ta; not more than 0.03% of Hf; and not more than 0.2% of a rare earth metal (REM), in percent by mass.

(Mo, W, and V)

**[0038]** Mo (molybdenum), W (tungsten), and V (vanadium) are elements effective for improving corrosion resistance. However, Mo, W, and V are ferrite formers and also expensive elements. As such, it is not preferable to add Mo, W, and V excessively. As such, the austenitic stainless steel preferably contains at least one selected from the group consisting of: not more than 1.0% by mass of Mo; not more than 1.0% by mass of W; and not more than 0.5% by mass of V.

(B)

**[0039]** B (boron) is an element which improves hot workability and is effective for reducing occurrence of edge cracking and alligating in hot rolling. The austenitic stainless steel preferably contains not less than 0.0001% by mass and not more than 0.01% by mass of B. A B content of not less than 0.0001% by mass is effective for improving hot workability and reducing occurrence of edge cracking and alligating in hot rolling. However, excessively adding B to the austenitic stainless steel containing Cr causes deterioration in corrosion resistance due to precipitation of Cr<sub>2</sub>B. As such, the B content is preferably not more than 0.01% by mass.

(Co)

**[0040]** Co (cobalt) is an element effective for ensuring corrosion resistance of the austenitic stainless steel. Co also contributes to reducing coarsening of the Cu-rich phase to thereby maintain the fineness of the Cu-rich phase. In order to obtain these effects, it is preferable that Co be contained in an amount of preferably not less than 0.10% by mass. However, Co is an expensive element. From the viewpoint of reducing costs, a Co content is preferably not more than 0.8% by mass.

(Sn)

**[0041]** Sn (tin) is an element effective for ensuring corrosion resistance of the austenitic stainless steel. Further, excessively adding Sn causes deterioration in hot workability of the austenitic stainless steel. As such, a Sn content is preferably not more than 0.1% by mass.

(Al, Ca, Mg, and Ti)

**[0042]** Al (aluminum), Ca (calcium), Mg (magnesium), and Ti (titanium) are elements each having a deoxidation effect. The austenitic stainless steel preferably contains, as a deoxidizer, at least one selected from the group consisting of: not more than 0.3% by mass of Al; not more than 0.03% by mass of Ca; not more than 0.03% by mass of Mg; and not more than 0.5% by mass of Ti.

(Nb)

**[0043]** Nb (niobium) is an element effective for reducing sensitization of the austenitic stainless steel. Nb is also effective for making the system finer and more uniform. The austenitic stainless steel preferably contains not more than 0.5% by mass of Nb.

(Sb, Zr, Ta, Hf, and REM)

**[0044]** Sb (antimony), Zr (zirconium), Ta (tantalum), Hf (hafnium), and REM (rare earth metal) are each an element which improves hot workability and is also effective for oxidation resistance. The austenitic stainless steel preferably contains at least one selected from the group consisting of: not more than 0.5% by mass of Sb; not more than 0.5% by mass of Zr; not more than 0.03% by mass of Ta; not more than 0.03% by mass of Hf; and not more than 0.2% by mass of REM.

[Md<sub>30</sub> value]

**[0045]** The austenitic stainless steel has an Md<sub>30</sub> value, as represented by expression (1) below, of not less than 10.0 and not more than 80.0, and preferably not less than 20.0 and not more than 70.0.

$$\text{Md}_{30} = 551 - 462(\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 29\text{Ni} - 10.6\text{Cu} - 13.7\text{Cr} - 18.5\text{Mo} \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

**[0046]** An Md<sub>30</sub> value of an austenitic stainless steel represents a temperature (°C) at which 50% of a system of a monophasic austenitic stainless steel having only an austenite phase is transformed into a martensite phase when a 30% tensile strain is given to the austenitic stainless steel. As such, an Md<sub>30</sub> value can be used as an index of stability of an austenite phase. Further, an Md<sub>30</sub> value can be used also as an index that affects a likelihood of occurrence of a TRIP phenomenon in the austenitic stainless steel.

**[0047]** The austenitic stainless steel in accordance with an embodiment of the present invention has an Md<sub>30</sub> value of preferably not less than 10.0 and not more than 80.0. The higher the Md<sub>30</sub> value, the more likely for an austenite phase to be transformed into a deformation-induced martensite phase, so that giving a light degree of cold rolling strain enables obtaining high strength and excellent ductility is ensured. Further, also in a case where the austenitic stainless steel is subjected to molding, a portion to which processing strain is given, such as a bent part, tends to have an even higher strength due to a TRIP phenomenon.

**[0048]** Further, in a production process of the austenitic stainless steel, in order to obtain fine crystal grains by finishing annealing, the presence of a deformation-induced martensite phase in a rolled material before the finishing annealing acts effectively. Such an effect is prominently exhibited in a case where the Md<sub>30</sub> value is not less than 10.0. Further, in a case where the Md<sub>30</sub> value is more than 80.0, a TRIP phenomenon tends to occur excessively, and the characteristics of the austenitic stainless steel tends not to be stable.

**[0049]** As such, in a case where the Md<sub>30</sub> value, which serves as an index of stability of an austenite phase, is not less than 10.0 and not more than 80.0, it is possible to stably produce the austenitic stainless steel having a high strength and a good ductility.

**[0050]** Note that, in conventionally known component regression expressions of Md<sub>30</sub>, it is common that the same value is used as a coefficient of Ni and a coefficient of Cu. In contrast, in an embodiment of the present invention, a coefficient of Cu is set lower than a coefficient of Ni in a component regression expression of Md<sub>30</sub>. Many of the component regression

expressions of  $Md_{30}$  according to the conventional knowledge are based on results obtained from an austenitic stainless steel that is not an austenitic stainless steel with reduced amount of Ni. In contrast, in a component in which the amount of Ni is not reduced as in the present invention, the effect of Cu on stabilization of the austenite phase is clearly less prominent in comparison with the conventional knowledge. This is a novel finding obtained as a result of diligent study by the inventors of the present invention, and the coefficient of Cu in the component regression expression of  $Md_{30}$  has been set on the basis of the finding. This makes it easy to adjust the content of Cu and to increase a degree of freedom in production of the austenitic stainless steel.

[Production method]

**[0051]** A method for producing an austenitic stainless steel in accordance with an embodiment of the present invention is a method in which the austenitic stainless steel contains more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel having an  $Md_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) above. Further, the method for producing an austenitic stainless steel includes a finishing annealing step.

**[0052]** The method for producing an austenitic stainless steel can include processes for producing a general austenitic stainless steel, except in the finishing annealing step. The following description will discuss an example of the method for producing an austenitic stainless steel in accordance with an embodiment of the present invention, but the present invention is not limited to such an example.

**[0053]** In the method for producing an austenitic stainless steel in accordance with an embodiment of the present invention, for example, slab is produced by carrying out continuous casting of molten steel containing adjusted components. Then, the slab produced by the continuous casting is heated to a temperature of not lower than 1100°C and not higher than 1300°C, and then is subjected to hot rolling to produce a hot-rolled steel strip. The speed of precipitation of a Cu-rich phase from an austenite phase having little strain after the hot rolling is slow. As such, conditions of a finishing temperature and a winding temperature of the hot-rolled steel strip after the hot rolling can be similar to those of general methods for producing an austenitic stainless steel. From the viewpoint of minimizing precipitation of a Cu-rich phase until finishing annealing, the winding temperature at which the hot-rolled steel strip is wound up after the hot rolling is preferably not higher than 850°C, more preferably not higher than 650°C.

**[0054]** The hot-rolled steel strip which has been subjected to the hot rolling can be subjected to pickling. Note that annealing can be carried out before the pickling of the hot-rolled steel strip, or the pickling can be carried out without annealing. In a case where the hot-rolled steel strip is subjected to annealing before pickling, an annealing temperature is preferably within a range of not lower than 900°C and not higher than 1150°C. In order to bring Cu completely into a solid solution state, the annealing temperature is more preferably in a range of not lower than 980°C and not higher than 1150°C. The annealing temperature, however, is not limited to these ranges. The hot-rolled steel strip after the pickling is subjected to cold rolling until the hot-rolled steel strip has a predetermined thickness. Thus obtained is a cold-rolled steel strip.

**[0055]** In the method for producing an austenitic stainless steel, recrystallization and precipitation of a Cu-rich phase progress simultaneously in the finishing annealing step after the cold rolling step. A Cu-rich phase is precipitated particularly easily from a deformation-induced martensite phase. As such, the cold rolling step is carried out preferably at a rolling reduction ratio and a rolling temperature at which a proportion of a deformation-induced martensite phase in the cold-rolled steel strip is not less than 20% by volume of the entire volume of the cold-rolled steel strip. Carrying out the cold rolling step in this manner enables a Cu-rich phase to be effectively precipitated in the steel strip in the subsequent finishing annealing step.

**[0056]** Note that the austenitic stainless steel has an  $Md_{30}$  value adjusted to not less than 10.0 and not more than 80.0. In the austenitic stainless steel having such an  $Md_{30}$  value, a Cu-rich phase in an amount specified in an embodiment of the present invention is precipitated regardless of an amount of a deformation-induced martensite phase in the cold-rolled steel strip. However, it is even more effective for precipitation of a Cu-rich phase to, as necessary, for example, increase the rolling reduction ratio in the cold rolling step or control the temperature in the cold rolling step to be low.

**[0057]** From the viewpoint of causing the cold-rolled steel strip to include a deformation-induced martensite phase in a proportion of not less than 20% by volume, for example, the rolling reduction ratio in the cold rolling step is preferably not less than 40%, more preferably not less than 50%, and even more preferably not less than 60%. Further, the temperature in the cold rolling step is preferably not higher than 90°C and more preferably not higher than 60°C.

(Finishing annealing step)

**[0058]** The cold-rolled steel strip is subjected to finishing annealing. The finishing annealing step is carried out under



conditions that cause precipitation of a Cu-rich phase to proceed. A Cu-rich phase is effective for increasing the strength of the austenitic stainless steel. As such, the hot-rolled steel strip and the cold-rolled steel strip before precipitation of a Cu-rich phase are each relatively low in strength, and the load of rolling in the cold rolling step can therefore be reduced. Then, a Cu-rich phase is precipitated in the finishing annealing step, so that the austenitic stainless steel after the finishing annealing step is able to have high strength.

**[0059]** Further, the precipitation of a Cu-rich phase is effective for causing recrystallized grains of an austenite phase to be finer. As such, utilizing the precipitation of a Cu-rich phase makes it possible to control an average crystal grain size to be not more than 10.0  $\mu\text{m}$ .

**[0060]** Thus, according to the method in accordance with an embodiment of the present invention for producing an austenitic stainless steel, both a reduction in load of working during production and an increase in strength of an end product can be achieved to significant degrees. Further, since an additional step conventionally required, i.e., an aging treatment step, is not required in the precipitation of a Cu-rich phase, the austenitic stainless steel can be produced with good productivity.

**[0061]** The temperature of finishing annealing in the finishing annealing step is not lower than 750°C and not higher than 980°C, and preferably not lower than 800°C and not higher than 925°C, in order for a Cu-rich phase to be effectively precipitated in the austenitic stainless steel. In a case where the temperature of the finishing annealing is lower than 750°C, the system is insufficiently recrystallized. In a case where the temperature of the finishing annealing is higher than 980°C, the Cu-rich phase is dissolved, so that the amount of a Cu-rich phase remaining after the finishing annealing is insufficient.

**[0062]** Further, a Cu-rich phase precipitated from a deformation-induced martensite phase is dissolved particularly easily in an austenite phase when the Cu-rich phase is maintained at a temperature not lower than 850°C for a long time in the finishing annealing. As such, in a case where a peak temperature in the finishing annealing step is not lower than 850°C, it is preferable that time during which heating is carried out at not lower than 850°C be short. Specifically, in a case where a peak temperature in the finishing annealing step is not lower than 850°C, time during which heating is carried out at not lower than 850°C is not more than 30 seconds, and preferably not more than 15 seconds. In a case where there are a plurality of times during each of which the temperature in the finishing annealing step is not lower than 850°C, the "time during which heating is carried out at not lower than 850°C" means a total of the respective lengths of those times.

**[0063]** Since the austenitic stainless steel has a C content of not more than 0.15%, precipitation of a Cr carbide does not necessarily occur during cooling. However, since the austenitic stainless steel has a small crystal grain size and thus has many grain boundaries, a decrease in corrosion resistance due to precipitation of a Cr carbide may occur in a case where a cooling rate after the finishing annealing is low. As such, the cooling rate after the finishing annealing is preferably such that an average rate of cooling from 700°C to 500°C is preferably not less than 20°C/s, and more preferably not less than 75°C/s.

**[0064]** Note that, as necessary, process annealing and intermediate rolling can be carried out in the cold rolling step. The steel strip after the finishing annealing can be subjected to temper rolling, as necessary, in order to further increase the strength. The temperature of the process annealing is preferably not lower than 980°C and not higher than 1150°C in order to avoid precipitation of a Cu-rich phase, in a case where a reduction in load of rolling has priority. In terms of obtaining high strength by repeating a precipitation process, the conditions of the temperature of the process annealing are preferably the same as those of the finishing annealing. Note that the temperature of the process annealing is not limited to the above-described ranges.

[Evaluation of strength]

**[0065]** The austenitic stainless steel in accordance with an embodiment of the present invention is an austenitic stainless steel whose strength is kept relatively low in the production process to achieve a reduction in load of rolling and which possesses high strength after being produced. This characteristic of the austenitic stainless steel can be represented, for example, by a relationship between 0.2% proof stress (YS 18%, MPa) and reference strength (HV 60%).

**[0066]** 0.2% proof stress (YS 18%) is an index of strength of the austenitic stainless steel. 0.2% proof stress (YS 18%) indicates 0.2% proof stress exhibited by the austenitic stainless steel in a case where the austenitic stainless steel has been subjected to finishing annealing and then to temper rolling causing an elongation of 18%. 0.2% proof stress can be evaluated using a method in conformity with JIS Z2241.

**[0067]** Reference strength (HV 60%) is an index hypothetically indicating strength of the austenitic stainless steel before precipitation of a Cu-rich phase is caused in the finishing annealing step. Reference strength (HV 60%) indicates Vickers hardness exhibited by an austenitic stainless steel which has the same composition but has been produced by a method partially changed from the production method in accordance with an embodiment of the present invention such that: annealing is carried out at 1050°C after the hot rolling; and cold rolling is carried out at a rolling reduction ratio of 60%. That is, reference strength (HV 60%) does not have to indicate strength of the austenitic stainless steel in accordance with an embodiment of the present invention, but can be, for example, strength of a steel strip prepared for evaluation. Vickers hardness can be measured by a Vickers hardness test method in conformity with JIS Z2244.

**[0068]** The inventors of the present invention have found that an austenitic stainless steel which enables both a reduction in load of working during production and an increase in strength of an end product exhibits 0.2% proof stress (YS 18%) and reference strength (HV 60%) which are in a relationship satisfying expression (2) below.

$$(2): YS\ 18\% \geq 1.25\ HV\ 60\% + 525$$

**[0069]** According to the method in accordance with an embodiment of the present invention, it is possible to produce an austenitic stainless steel that satisfies expression (2) above and enables both a reduction in load of working during production and an increase in strength of an end product.

[Uses for which austenitic stainless steel is suitable]

**[0070]** The austenitic stainless steel has extremely high strength and corrosion resistance. As such, the austenitic stainless steel is suitable for use as a material for a spring product that is required to have high strength and corrosion resistance, such as a cylinder head gasket, a flat spiral spring, a spring for an electronic device component, a member for a train carriage, an in-vehicle battery frame member, a structural member, and a metal gasket.

**[0071]** Aspects of the present invention can also be expressed as follows:

An austenitic stainless steel in accordance with Aspect 1 of the present invention is an austenitic stainless steel, containing more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel including (i) not less than 20% by volume of an austenite phase, (ii) a Cu-rich phase having a number density of not less than  $1.0 \times 10^3 \mu\text{m}^{-3}$  and a long diameter of not more than 30 nm, and (iii) a remaining part composed of a deformation-induced martensite phase and an inevitably formed phase, the austenitic stainless steel having an  $Md_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) below,

$$Md_{30} = 551 - 462(C+N) - 9.2Si - 8.1Mn - 29Ni - 10.6Cu - 1.37Cr - 18.5Mo \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

**[0072]** In Aspect 2 of the present invention, the austenitic stainless steel in accordance with Aspect 1 can be configured such that the austenitic stainless steel further contains at least one selected from the group consisting of: not more than 1.0% of Mo; not more than 1.0% of W; not more than 0.5% of V; not less than 0.0001% and not more than 0.01% of B; not more than 0.8% of Co; not more than 0.1% of Sn; not more than 0.03% of Ca; not more than 0.03% of Mg; not more than 0.5% of Ti; not more than 0.5% of Nb; not more than 0.3% of Al; not more than 0.5% of Sb; not more than 0.5% of Zr; not more than 0.03% of Ta; not more than 0.03% of Hf; and not more than 0.2% of a rare earth metal, REM, in percent by mass.

**[0073]** In Aspect 3 of the present invention, the austenitic stainless steel in accordance with Aspect 1 or 2 can be configured such that the austenitic stainless steel has an average crystal grain size of not more than 10.0  $\mu\text{m}$ .

**[0074]** A method in accordance with Aspect 4 of the present invention for producing an austenitic stainless steel is a method for producing an austenitic stainless steel, the austenitic stainless steel containing more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel having an  $Md_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) below, the method including a finishing annealing step of carrying out finishing annealing at a temperature of not lower than 750°C and not higher than 980°C, wherein in a case where a peak temperature in the finishing annealing step is not lower than 850°C, time during which heating is carried out at not lower than 850°C is not more than 30 seconds,

$$Md_{30} = 551 - 462(C+N) - 9.2Si - 8.1Mn - 29Ni - 10.6Cu - 1.37Cr - 18.5Mo \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

**[0075]** The present invention is not limited to the embodiments, but can be altered by a skilled person in the art within the

scope of the claims. The present invention also encompasses, in its technical scope, any embodiment derived by combining technical means disclosed in differing embodiments.

#### Examples

**[0076]** The following description will discuss results of evaluation of austenitic stainless steels in accordance with inventive examples of the present invention and austenitic stainless steels in accordance with comparative examples.

[Evaluation conditions]

< Composition >

**[0077]** Table 1 below shows compositions (in percent by mass) and  $Md_{30}$  values of austenitic stainless steels in accordance with examples of the present invention (Inventive Steels A1 to A15) and austenitic stainless steels in accordance with comparative examples (Comparative Steels B1 to B4). The  $Md_{30}$  values were calculated by expression (1) above. Note that underlined values in Table 1 below are each a value that falls outside a range specified in the present invention. The same is true of Table 2 below.

[Table 1]

EP 4 477 776 A1

5

10

15

20

25

30

35

40

45

50

55

		C	Si	Mn	P	S	Ni	Cr	Cu	N	Mo	V	B	Co	Sn	Al	Ca	Mg	Nb	Ti	REM	Sb	Zr	W	Ta	Hf	Md30
Inventive Steel	A1	0.132	0.54	1.63	0.025	0.0012	5.35	17.13	2.67	0.015	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	46.8
Inventive Steel	A2	0.111	0.50	1.46	0.030	0.0020	4.04	17.04	3.20	0.098	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	53.5
Inventive Steel	A3	0.103	1.73	0.85	0.033	0.0022	4.68	16.57	2.53	0.102	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	43.9
Inventive Steel	A4	0.066	0.35	0.93	0.033	0.0030	4.65	18.05	2.86	0.152	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	27.1
Inventive Steel	A5	0.045	0.61	1.22	0.030	0.0015	5.46	16.84	2.03	0.125	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	46.4
Inventive Steel	A6	0.096	0.71	2.30	0.026	0.0029	3.35	16.88	3.34	0.130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	57.6
Inventive Steel	A7	0.120	0.49	1.44	0.028	0.0040	4.21	17.18	2.95	0.084	0.44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	43.7
Inventive Steel	A8	0.101	0.58	0.55	0.033	0.0021	4.63	17.63	3.24	0.093	-	0.22	-	0.34	-	-	-	-	-	-	-	-	-	-	-	-	41.4
Inventive Steel	A9	0.085	0.49	1.20	0.025	0.0033	5.08	16.77	1.74	0.112	-	-	0.0023	-	-	-	-	-	-	-	-	-	-	-	-	-	50.2
Inventive Steel	A10	0.095	0.73	1.59	0.031	0.0020	4.90	17.25	2.97	0.053	0.15	-	-	-	0.04	-	-	-	-	-	-	-	-	0.24	-	-	50.3
Inventive Steel	A11	0.106	0.68	1.75	0.028	0.0043	4.34	16.67	2.66	0.124	-	-	-	-	-	0.063	-	-	-	-	0.021	-	-	-	-	-	41.9
Inventive Steel	A12	0.089	0.54	1.50	0.031	0.0018	4.70	17.30	3.44	0.084	-	-	-	-	-	-	-	-	-	0.16	-	-	-	-	-	-	44.2
Inventive Steel	A13	0.110	0.56	1.20	0.034	0.0008	4.75	17.20	2.78	0.037	-	-	-	-	-	-	-	-	0.39	-	-	-	-	-	0.015	-	65.4
Inventive Steel	A14	0.079	1.01	1.09	0.022	0.0024	4.69	17.59	3.72	0.097	-	-	-	-	-	0.013	0.006	-	-	-	-	-	-	-	-	-	35.1
Inventive Steel	A15	0.090	0.65	1.53	0.032	0.0019	4.92	16.67	2.73	0.101	-	-	-	-	-	-	-	-	-	-	-	0.005	0.011	-	-	0.013	44.4
Comparative Steel	B1	<u>0.018</u>	0.50	1.75	0.029	0.0021	5.85	17.08	3.20	0.075	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	51.7
Comparative Steel	B2	0.085	0.47	1.53	0.033	0.0024	5.77	18.20	3.15	0.086	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u>5.2</u>
Comparative Steel	B3	0.103	0.59	0.95	0.030	0.0010	3.12	16.32	3.05	0.094	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u>100.5</u>
Comparative Steel	B4	0.092	0.59	1.80	0.025	0.0033	5.31	16.99	<u>0.61</u>	0.089	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	54.2

## &lt;Production method&gt;

**[0078]** The austenitic stainless steels in accordance with the examples of the present invention and the austenitic stainless steels in accordance with the comparative examples were produced by methods described below. Each of the austenitic stainless steels having the compositions indicated in Table 1 was dissolved and was subjected to processes from hot rolling to finishing annealing in accordance with a production method in accordance with an embodiment of the present invention (Inventive Examples C1 to C8) or a production method in accordance with a comparative example (Comparative Examples D1 and D2) to obtain a cold-rolled annealed material. Conditions of each production method are indicated in Table 2.

[Table 2]

		Thickness after hot rolling (mm)	Annealing after hot rolling	Thickness after cold rolling (mm)	Temperature of finishing annealing	Time during which temperature is not lower than 850°C
Inventive Example	C1	5	NA	1.5	890°C	5 s
Inventive Example	C2	5	1050°C	1.5	870°C	3 s
Inventive Example	C3	4	1100°C	1.2	850°C	1 s
Inventive Example	C4	3.5	NA	1	830°C	-
Inventive Example	C5	3.5	1050°C	1.5	870°C	3 s
Inventive Example	C6	3	1000°C	1	860°C	3 s
Inventive Example	C7	4	NA	1.2	910°C	10 s
Inventive Example	C8	3.5	1120°C	1	930°C	20 s
Comparative Example	D1	3	1050°C	1	<u>990°C</u>	<u>40 s</u>
Comparative Example	D2	4	1080°C	1.2	910°C	<u>65 s</u>

**[0079]** In the finishing annealing step, in a case where the finishing annealing temperature was not lower than 850°C, time during which the finishing annealing temperature was not lower than 850°C was adjusted as indicated in Table 2. Note that in Inventive Example C3, heating was adjusted such that the temperature of the finishing annealing would start to decrease at a point in time when the temperature reached 850°C, but in Table 2, time during which the temperature was not lower than 850°C is indicated as "1 s" for convenience.

## &lt;Evaluation method&gt;

**[0080]** The austenitic stainless steels in accordance with the examples of the present invention and the austenitic stainless steels in accordance with the comparative examples were evaluated as follows with respect to various indices.

(Number density of Cu-rich phase)

**[0081]** From a cold-rolled annealed material produced under each set of conditions, a TEM sample was prepared by electrolytic polishing. On a surface of the TEM sample which surface was parallel to a rolling direction of the cold-rolled annealed material, three fields of view each in a size of 400 nm×400 nm were observed. On the basis of contrasts in a TEM image, a Cu-rich phase was identified and the number of Cu-rich phase particles were counted. Assuming that the TEM sample had a thickness of 150 nm, a number density per unit volume was determined. When a Cu-rich phase was coarse, the Cu-rich phase was observed in clear shapes instead of contrasts. Cu-rich phase particles each having a long diameter of more than 30 nm were excluded from the counting.

(Number density of Cu carbide)

**[0082]** In the field of view of the sample used in the measurement of a number density of a Cu-rich phase, a precipitate with respect to which a ratio of {a Cr concentration in the precipitate as determined by TEM-EDS analysis} to {a Cr concentration in the base material} was more than 1.2 was regarded as Cr carbide. The "Cr concentration in the base material" means an average Cr concentration in the entire cold-rolled annealed material, and is a Cr content (in percent by mass) in the cold-rolled annealed material. A number density of the Cr carbide was evaluated to be "not good" in a case

where the number density was not less than  $50 \mu\text{m}^{-3}$ , and was evaluated to be a case in which the Cr carbide had a number density of not less than  $50 \mu\text{m}^{-3}$  was evaluated to be "good"

(Crystal grain size)

**[0083]** An average crystal grain size was evaluated by the EBSD method. A cross section of the cold-rolled annealed material produced under each set of conditions which cross section was parallel to the rolling direction and perpendicular to the rolled surface was subjected to mechanical polishing and then to electrolytic polishing. Then, in a field of view with a magnification of 2000 times, a  $40 \mu\text{m} \times 40 \mu\text{m}$  portion in the cross section was subjected to EBSD analysis at step intervals of 0.2  $\mu\text{m}$ . With respect to an orientation difference in a crystallographic orientation relationship that satisfies a coincidence grain boundary of  $\Sigma 3$ , an annealing twin with an orientation difference of not more than  $1^\circ$  was excluded, and a boundary with an orientation difference of not less than  $2^\circ$  was regarded as a grain boundary. A crystal grain size was calculated by expression (3) below where S ( $\mu\text{m}^2$ ) was an area of each crystal grain and D ( $\mu\text{m}$ ) was a diameter of a circle having the same area as the crystal grain. This operation was carried out with respect to five fields of view, and an average of crystal grain sizes obtained in the respective five fields of view was calculated as an average crystal grain size.

$$(3): \text{Crystal grain size} = \{\Sigma(D \times S)\} / 40 \times 40$$

(Amount of martensite phase)

**[0084]** An amount (percent by volume) of a martensite phase was measured as follows. In a case where a material which had been subjected to cold rolling or a material which had been subjected to temper rolling had a thickness of not less than 1.5 mm, the material was used as it was. In a case where a material which had been subjected to cold rolling or a material which had been subjected to temper rolling had a thickness of less than 1.5 mm, a plurality of strips of the material were laid on top of each other so that a total thickness was not less than 1.5 mm. These materials were subjected to measurement with use of a ferrite scope (FMP30, manufactured by Fischer, electromagnetic induction method), and a value thus measured was divided by 0.7475 to obtain a value which was regarded as an amount of the martensite phase. An amount (percent by volume) of an austenite phase was assumed to be a value obtained by subtracting the amount of the martensite phase from 100% by volume of the entire matrix of the austenitic stainless steel. An amount of a Cu-rich phase and an amount of an inevitably formed phase accounted for only a small part of the austenitic stainless steel and were difficult to accurately measure. As such, the amount of the Cu-rich phase and the amount of the inevitably formed phase can be calculated as extra numbers.

(Tensile characteristics)

**[0085]** As an index of tensile characteristics, evaluation was made of 0.2% proof stress (YS 18%) exhibited in a case where temper rolling causing an elongation of 18% was carried out. The 0.2% proof stress (YS 18%) was measured by preparing a JIS #13 B test piece and conducting a tensile test in conformity with JIS Z2241. The 0.2% proof stress (YS 18%) was measured at a crosshead speed of 3 mm/min.

(Strength)

**[0086]** Among the conditions of examples of the present invention and the conditions of examples, production conditions were partially changed such that annealing of a hot-rolled steel strip was carried out at  $1050^\circ\text{C}$  and cold rolling was carried out at a rolling reduction ratio of 60% to obtain a 60% rolled material. A Vickers hardness of the 60% rolled material was measured as a reference strength (HV 60%). The Vickers hardness was measured by a Vickers hardness test (JIS Z2244) with use of a Vickers hardness tester with respect to a surface of the 60% rolled material. A load at the time of measurement in the Vickers hardness test was 10 kg.

[Results]

**[0087]** With respect to Inventive Steel A2, an amount of a Cu-rich phase precipitated and a crystal grain size of the cold-rolled annealed material obtained under each set of conditions indicated in Table 2 are shown in Table 3 below. Further, 0.2% proof stress (YS 18%), an amount of a martensite phase after temper rolling causing an elongation of 18% was carried out after cold rolling (before finishing annealing), and an amount of a martensite phase after temper rolling causing an elongation of 18% was carried out after finishing annealing, under each set of conditions, are also shown in Table 3 below.

**[0088]** Note that, in Table 3 below, each underline indicates that the amount of a Cu-rich phase precipitated falls outside a range specified in the present invention.

[Table 3]

		Amount of martensite after cold rolling (vol%)	Amount of Cu precipitated ( $\mu\text{m}^{-3}$ )	Crystal grain size ( $\mu\text{m}$ )	YS 18% (MPa)	Amount of martensite after temper rolling (vol%)
Inventive Example	C1	56	$2.2 \times 10^3$	2.4	1193	18
Inventive Example	C2	61	$3.6 \times 10^3$	2.3	1206	15
Inventive Example	C3	65	$5.0 \times 10^3$	2.2	1215	11
Inventive Example	C4	60	$6.5 \times 10^3$	1.9	1190	13
Inventive Example	C5	42	$2.4 \times 10^3$	2.6	1178	20
Inventive Example	C6	54	$3.1 \times 10^3$	2.5	1220	18
Inventive Example	C7	60	$2.2 \times 10^3$	3.1	1188	19
Inventive Example	C8	60	$1.4 \times 10^3$	6.2	1165	24
Comparative Example	D1	62	<u>NA</u>	20	1087	30
Comparative Example	D2	60	<u>NA</u>	5.5	1075	27

**[0089]** With respect to Inventive Steel A2, cold-rolled annealed materials produced by the respective sets of conditions of Inventive Examples C1 to C8 each had an amount of a Cu-rich phase precipitated which fell within the range specified in the present invention and exhibited a very small average crystal grain size of not more than 10.0  $\mu\text{m}$ . In contrast, neither of the cold-rolled annealed materials produced under the respective sets of conditions of Comparative Examples D1 and D2 exhibited precipitation of a Cu-rich phase.

**[0090]** With respect to Inventive Steel A2, an EBSD grain boundary map and a TEM-captured image are shown on a left side and a right side, respectively, of Fig. 1 with respect to the cold-rolled annealed material produced under the conditions of Inventive Example C2. As indicated in the TEM-captured image on the right side of Fig. 1, precipitation of a Cu-rich phase (illustrated as "Cu" in Fig. 1) was observed in the austenitic stainless steel in accordance with an embodiment of the present invention.

**[0091]** Further, since the reference strength (HV 60%) of Inventive Steel A2 was 487, the 0.2% proof stress (YS 18%) is preferably not less than 1134 MPa according to expression (2) above. The cold-rolled annealed materials of Inventive Steel A2 produced under the respective sets of conditions of Inventive Examples C1 to C8 each exhibited a 0.2% proof stress (YS 18%) of not less than 1134 MPa. In contrast, the cold-rolled annealed materials produced under the respective sets of conditions of Comparative Examples D1 and D2 each exhibited a 0.2% proof stress (YS 18%) of less than 1134 MPa. The above indicates that under the sets of conditions of Comparative Examples D1 and D2, precipitation of a Cu-rich phase does not occur, and it is therefore difficult to obtain an austenitic stainless steel having a good balance between workability before finishing annealing and high strength after the finishing annealing.

**[0092]** Next, Table 4 below indicates (i) an amount of a Cu-rich phase precipitated in a cold-rolled annealed material produced from Inventive Steels A1 to A15 or Comparative Steels B1 to B4 under the set of production conditions indicated in Inventive Example C2 and (ii) a crystal grain size of the cold-rolled annealed material, the amount of a Cu-rich phase precipitated and the crystal grain size being exhibited by after finishing annealing. Further, Table 4 below also indicates 0.2% proof stress (YS 18%) and reference strength (HV 60%) under these conditions.

**[0093]** Note that, in Table 4 below, each underlined portion indicates that (i) the amount of a Cu-rich phase precipitated fell outside the range specified in the present invention or (ii) the value of 0.2% proof stress (YS 18%) did not satisfy expression (2) above.

[Table 4]

		Amount of Cu precipitated ( $\mu\text{m}^{-3}$ )	Crystal grain size ( $\mu\text{m}$ )	YS 18% (MPa)	HV 60%
Inventive Steel	A1	$3.0 \times 10^3$	3.0	1197	478
Inventive Steel	A2	$3.6 \times 10^3$	2.3	1206	487
Inventive Steel	A3	$2.5 \times 10^3$	3.4	1218	502

(continued)

		Amount of Cu precipitated (μm <sup>-3</sup> )	Crystal grain size (pm)	YS 18% (MPa)	HV 60%
Inventive Steel	A4	2.1×10 <sup>3</sup>	2.4	1210	485
Inventive Steel	A5	2.2×10 <sup>3</sup>	3.0	1135	463
Inventive Steel	A6	5.4×10 <sup>3</sup>	2.5	1200	493
Inventive Steel	A7	3.2×10 <sup>3</sup>	2.0	1215	499
Inventive Steel	A8	3.2×10 <sup>3</sup>	2.3	1205	485
Inventive Steel	A9	1.6×10 <sup>3</sup>	3.0	1170	507
Inventive Steel	A10	2.8×10 <sup>3</sup>	3.2	1177	472
Inventive Steel	A11	2.4×10 <sup>3</sup>	3.7	1235	504
Inventive Steel	A12	3.8×10 <sup>3</sup>	4.2	1204	476
Inventive Steel	A13	3.7×10 <sup>3</sup>	2.1	1168	485
Inventive Steel	A14	3.5×10 <sup>3</sup>	3.4	1222	493
Inventive Steel	A15	2.4×10 <sup>3</sup>	3.1	1210	480
Comparative Steel	B1	3.1×10 <sup>3</sup>	3.3	<u>1002</u>	423
Comparative Steel	B2	<u>0.4×10<sup>3</sup></u>	6.5	<u>980</u>	440
Comparative Steel	B3	6.7×10 <sup>3</sup>	3.0	<u>980</u>	572
Comparative Steel	B4	<u>Not precipitated</u>	8.2	<u>1102</u>	530

**[0094]** The cold-rolled annealed materials of Inventive Steels A1 to A15 each had an amount of a Cu-rich phase precipitated falling within the range specified in the present invention and exhibited a very small average crystal grain size of not more than 10 pm. Further, the cold-rolled annealed materials each exhibited 0.2% proof stress (YS 18%) with a good value satisfying expression (2) above.

**[0095]** The cold-rolled annealed materials of Comparative Steels B1 to B4 each exhibited a 0.2% proof stress (YS 18%) that did not satisfy expression (2) above, and it was thus not possible to obtain an austenitic stainless steel having a good balance between workability before finishing annealing and high strength after the finishing annealing.

**[0096]** Fig. 2 shows a diagram plotting a relationship between 0.2% proof stress (YS 18%) and reference strength (HV 60%) under each set of conditions in Table 4. In Fig. 2, an example of the present invention is represented by a white circle, and a comparative example is represented by a black arrowhead. In the graph shown in Fig. 2, the closer a plotted relationship is to the upper left side, the better balance between workability before finishing annealing and high strength after the finishing annealing is indicated by the plotted relationship.

**[0097]** Note that the above-described results each pertain to a cold-rolled annealed material obtained under the condition of a cooling rate after finishing annealing of 25°C/s. Now, with use of Inventive Steels A1 and A2, respective cold-rolled annealed materials were produced under the conditions of Inventive Example C2 indicated in Table 2 except that the cooling rate from 700°C to 500°C after the finishing annealing was changed within a range of 5°C/s to 100°C/s. An amount of a Cr carbonitride precipitated in each of the resultant cold-rolled annealed materials is shown in Table 5 below.

[Table 5]

	Cr carbide	
°C/s	A1	A2
5	Not good (69)	Not good (59)
10	Not good (52)	Not good (57)
20	Good (15)	Good (20)
25	Good (10)	Good (10)
60	Good (0)	Good (0)
100	Good (0)	Good (0)



[0098] At a cooling rate of not less than 20°C/s, the amount of Cr carbide precipitated in the cold-rolled annealed material was in a preferable range of less than 50  $\mu\text{m}^{-3}$ . In a case where the cooling rate was not more than 10°C/s, the amount of Cr carbide precipitated was not less than 50  $\mu\text{m}^{-3}$ . That is, precipitation of Cr carbide was observed in an amount that could slightly affect the corrosion resistance of the cold-rolled annealed material, if not to a problematic extent.

[0099] As shown in Table 4 and Fig. 2, it is indicated that a cold-rolled annealed material produced in accordance with a production method in accordance with an embodiment of the present invention with use of an austenitic stainless steel having a composition in accordance with an embodiment of the present invention enables both a reduction in load of working during production and an increase in strength of an end product.

## Claims

1. An austenitic stainless steel, comprising more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity,

the austenitic stainless steel including (i) not less than 20% by volume of an austenite phase, (ii) a Cu-rich phase having a number density of not less than  $1.0 \times 10^3 \mu\text{m}^{-3}$  and a long diameter of not more than 30 nm, and (iii) a remaining part composed of a deformation-induced martensite phase and an inevitably formed phase, the austenitic stainless steel having an  $\text{Md}_{30}$  value of not less than 10.0 and not more than 80.0 as represented by expression (1) below,

$$\text{Md}_{30} = 551 - 462(\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 29\text{Ni} - 10.6\text{Cu} - 13.7\text{Cr} - 18.5\text{Mo} \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

2. The austenitic stainless steel as set forth in claim 1, further comprising at least one selected from the group consisting of: not more than 1.0% of Mo; not more than 1.0% of W; not more than 0.5% of V; not less than 0.0001% and not more than 0.01% of B; not more than 0.8% of Co; not more than 0.1% of Sn; not more than 0.03% of Ca; not more than 0.03% of Mg; not more than 0.5% of Ti; not more than 0.5% of Nb; not more than 0.3% of Al; not more than 0.5% of Sb; not more than 0.5% of Zr; not more than 0.03% of Ta; not more than 0.03% of Hf; and not more than 0.2% of a rare earth metal, REM, in percent by mass.

3. The austenitic stainless steel as set forth in claim 1 or 2, having an average crystal grain size of not more than 10.0  $\mu\text{m}$ .

4. A method for producing an austenitic stainless steel, the austenitic stainless steel containing more than 0.03% and not more than 0.15% of C, not less than 0.1% and not more than 2.0% of Si, not less than 0.3% and not more than 2.5% of Mn, not more than 0.04% of P, not more than 0.015% of S, not less than 3.0% and less than 6.0% of Ni, not less than 16.0% and not more than 18.5% of Cr, not less than 1.5% and not more than 4.0% of Cu, and not less than 0.005% and not more than 0.25% of N, in percent by mass, and the other part composed of Fe and an inevitable impurity, the austenitic stainless steel having an  $\text{Md}_{30}$  value of not less than 10.0 and not more than 80.0 as represented by formula (1) below,

said method comprising a finishing annealing step of carrying out finishing annealing at a temperature of not lower than 750°C and not higher than 980°C,

wherein in a case where a peak temperature in the finishing annealing step is not lower than 850°C, time during which heating is carried out at not lower than 850°C is not more than 30 seconds,

$$(1): \text{Md}_{30} = 551 - 462(\text{C} + \text{N}) - 9.2\text{Si} - 8.1\text{Mn} - 29\text{Ni} - 10.6\text{Cu} - 13.7\text{Cr} - 18.5\text{Mo} \quad (1):$$

wherein in expression (1) above, a content, in percent by mass, of each element contained in the austenitic stainless steel is substituted into a corresponding element symbol, and 0 is substituted into an element symbol of an element not added to the austenitic stainless steel.

FIG. 1

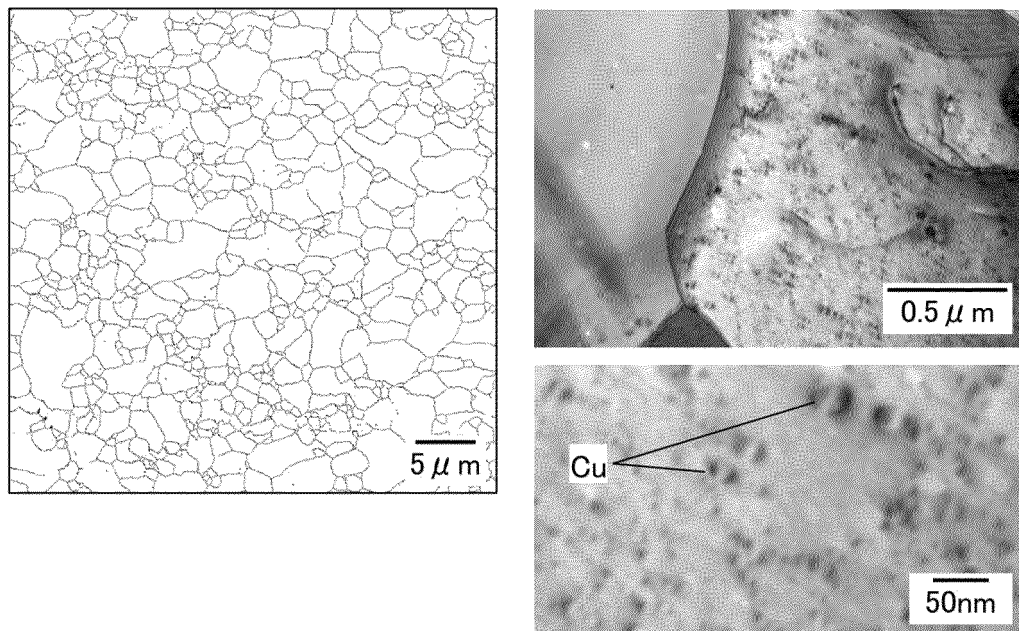
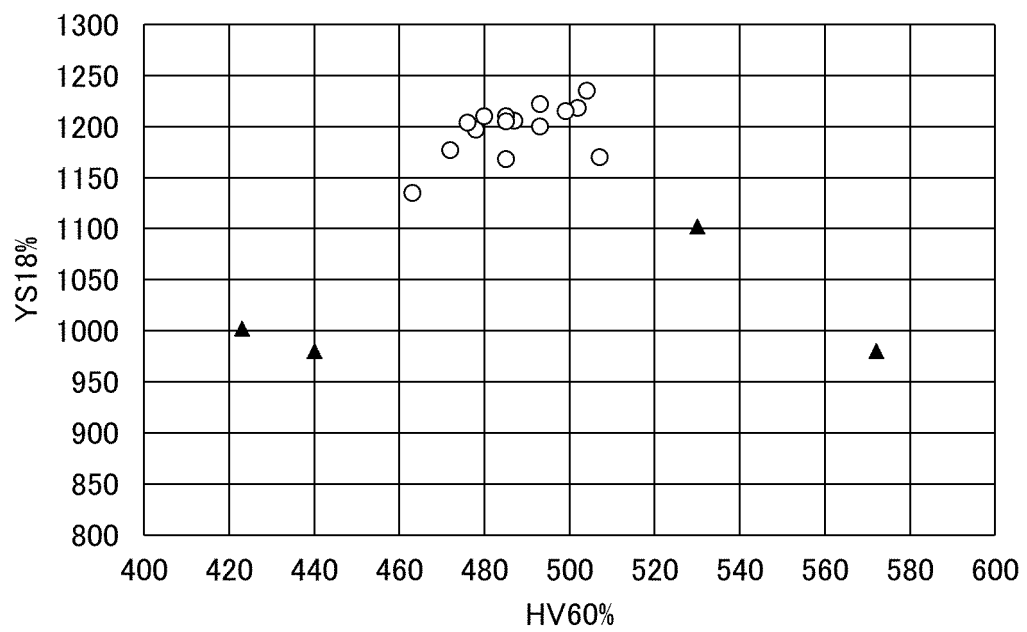


FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/001836

## A. CLASSIFICATION OF SUBJECT MATTER

**C22C 38/00**(2006.01)i; **C21D 9/46**(2006.01)i; **C22C 38/58**(2006.01)i; **C22C 38/60**(2006.01)i  
FI: C22C38/00 302Z; C21D9/46 Q; C22C38/58; C22C38/60

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)

C22C38/00-38/60; C21D9/46

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 2010-189719 A (NISSHIN STEEL CO., LTD.) 02 September 2010 (2010-09-02)	1-4
A	WO 2016/047734 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 31 March 2016 (2016-03-31)	1-4
A	JP 2009-41072 A (NISSHIN STEEL CO., LTD.) 26 February 2009 (2009-02-26)	1-4
A	JP 2017-206725 A (JFE STEEL CORP.) 24 November 2017 (2017-11-24)	1-4

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

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&amp;” document member of the same patent family

Date of the actual completion of the international search

20 March 2023

Date of mailing of the international search report

04 April 2023

Name and mailing address of the ISA/JP

Japan Patent Office (ISA/JP)  
3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915  
Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.  
**PCT/JP2023/001836**

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2010-189719 A	02 September 2010	(Family: none)	
WO 2016/047734 A1	31 March 2016	KR 10-2017-0057412 A	
		CN 107075632 A	
JP 2009-41072 A	26 February 2009	US 2009/0041613 A1	
		EP 2025770 A1	
		CN 101363103 A	
		KR 10-2009-0015817 A	
		TW 200923106 A	
JP 2017-206725 A	24 November 2017	(Family: none)	

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP 2008195976 A [0004]