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#### (54) HOT STAMPED COMPACT

(57) Provided is a hot stamped body having a predetermined chemical composition and a metallographic structure comprising, by volume ratio, martensite in 90% or more, wherein an average grain size of former austenite grains is  $3.0~\mu m$  or less, a standard deviation in grain

size distribution of former austenite grains is 1.5  $\mu m$  or less, and a difference of a maximum value and a minimum value in a Vickers hardness distribution in a sheet thickness direction is 35% or less of an average value of the Vickers hardness distribution.

#### Description

**FIELD** 

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5 [0001] The present invention relates to a hot stamped body.

**BACKGROUND** 

**[0002]** In recent years, in the automobile industry, lighter weight of car bodies has been sought from the viewpoint of improvement of fuel economy. To achieve both lighter weight of car bodies and collision safety, one effective method is to increase the strength of the steel sheet used. A high strength steel sheet is being developed due to such a background. On the other hand, if making a steel sheet higher in strength, the formability falls, and therefore achieving both strength and formability in the steel sheet is generally difficult.

[0003] In relation to this, PTL 1 describes a steel material having a predetermined chemical composition, wherein a Ceq defined by C+1/24Si+1/6Mn+1/40Ni+1/SCr+1/4Mo+1/14V is 0.10 to 1.00, and a metallographic structure comprising, by vol%, 95.0% or more of martensite, wherein a former austenite grain size is 5.0  $\mu$ m or less, and a number of packets in the former austenite grain is 3.0 or less. Further, PTL 1 teaches that it is possible to obtain a steel material having an ultrafine structure with an average grain size of 5.0  $\mu$ m or less and excellent in strength, ductility, and toughness.

**[0004]** Hot stamping (hot pressing) is known as a technique for press-forming a steel material such as described in PTL 1 which is high in strength and therefore difficult to form. Hot stamping is a technique of hot forming which heats then forms a material to be formed. This technique heats then forms the material, and therefore at the time of forming, the steel material is soft and has good formability. Therefore, even a high strength steel material can be formed into a complex shape with a good precision. Further, it is hardened at the same time as being formed by the press dies, and therefore the formed steel material is known to have sufficient strength.

[0005] In relation to this, PTL 2 describes a hot stamped body having a predetermined chemical composition and a microstructure comprising former austenite with an average grain size of 3  $\mu$ m or less and, further, containing at least one of lower bainite, martensite, and tempered martensite in an area ratio of 90% or more, wherein a grain boundary solid solution ratio Z, defined by Z=(mass% of one or both of Nb and Mo at the grain boundaries)/(mass% of one or both of Nb and Mo at time of melting), is 0.3 or more. Further, PTL 2 teaches that by making the grain size of the former austenite 3  $\mu$ m or less and, further, making one or both of Nb and Mo dissolve at the former austenite grain boundaries to raise the brittle strength of the grain boundaries, a shock absorption ability better than the past is obtained, more specifically, discloses that a hot stamped body having the above constitution has a tensile strength of 2000 MPa or more and is suppressed in early fracture.

[0006] PTL 3 describes a steel sheet for hot stamping having a predetermined chemical composition and a microstructure comprising at least one of lower bainite, martensite, and tempered martensite in an area ratio of 90% or more, wherein a grain boundary solid solution ratio Z, defined by Z=(mass% of one or both of Nb and Mo at the grain boundaries)/(mass% of one or both of Nb and Mo at time of melting), is 0.4 or more, an X-ray random intensity ratio of  $\{112\}$ <111> of the crystal grains forming the lower bainite, martensite, or tempered martensite is 2.8 or more, and a number density of cementite and epsilon carbide with a grain size of 50 nm or less is a total of  $1\times10^{16}$ /cm³ or more. Further, PTL 3 teaches that by controlling the X-ray random intensity ratio of  $\{1\ 12\}$ <1 1 1> of the crystal grain orientation of the crystal grains of the lower bainite, martensite, or tempered martensite in a steel sheet for hot stamping, due to the texture memory effect of austenite and martensite, crystal orientations with high crack propagation inhibiting effect in the hot stamped body are formed and excellent bending deformation ability is obtained in the hot stamped body, more specifically discloses that a hot stamped body having the above constitution has a tensile strength of 2000 MPa or more and has a maximum bending angle of 50° or more.

[CITATIONS LIST]

[PATENT LITERATURE]

[0007]

[PTL 1] Japanese Unexamined Patent Publication No. 2020-012173

[PTL 2] WO 2019/186928

[PTL 3] WO 2019/186927

#### SUMMARY

#### [TECHNICAL PROBLEM]

- [0008] If receiving an impact exceeding the yield strength, plastic deformation occurs, and therefore from the viewpoint of securing the collision safety of automobiles, improvement of not only the tensile strength, but also the yield strength is sought in a hot stamped body. However, in a hot stamped body having such a high strength, sometimes hydrogen embrittlement cracking (also referred to as "delayed fracture", etc.) becomes a problem. "Hydrogen embrittlement cracking" is the phenomenon where a steel member which is acted on by a high stress under conditions of use suddenly fractures due to hydrogen penetrating the steel from the environment. In general, it is known that hydrogen embrittlement cracking occurs more easily the higher the strength of the steel material. On the other hand, in the automobile industry, etc., further reduction of weight of the steel material is sought. To achieve such lighter weight, a need arises to raise the strength more than the past. Therefore, there is a great need for a steel material, more specifically a hot stamped body, able to solve the problem of hydrogen embrittlement even if raising the strength equal to the past or more than the same.
- [0009] Therefore, the present invention has as its object to provide a hot stamped body which is high in strength and able to suppress hydrogen embrittlement by a novel constitution.

#### [SOLUTION TO PROBLEM]

- [0010] The inventors conducted studies so as to achieve the above object, in particular focusing on the metallographic structure of the hot stamped body. As a result, the inventors discovered that by increasing the fineness and the uniformity of the former austenite grains in a hot stamped body and in relation to this reducing the variation in hardness in the metallographic structure of the hot stamped body, it is possible to suppress or reduce microstress concentration and that, further, it is possible to reduce the amount of hydrogen trapped per unit grain boundary area by the increase in grain boundary area accompanying increasing the fineness and the uniformity of the former austenite grains, discovered that, due to the combination of suppression or reduction of such microstress concentration and reduction of the amount of hydrogen trapped per unit grain boundary area, it is possible to remarkably improve the hydrogen embrittlement resistance despite the hot stamped body having a high tensile strength and yield strength, and thereby completed the present invention
- 30 **[0011]** The present invention able to achieve this object is as follows:
  - (1) A hot stamped body having a chemical composition comprising, by mass%,

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C: 0.40 to 0.70%,
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              Si: 0.01 to 1.30%,
              Mn: 0.05 to 3.00%,
              P: 0.100% or less,
              S: 0.0100% or less.
              N: 0.0200% or less,
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              O: 0.0200% or less.
             Al: 0.001 to 1.000%.
              Cr: 0.01 to 1.00%,
             Nb: 0 to 0.200%,
              Ti: 0 to 0.200%,
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             Mo: 0 to 1.00%,
             B: 0 to 0.1000%,
              Co: 0 to 4.00%,
              Ni: 0 to 3.00%,
              Cu: 0 to 3.00%,
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              V: 0 to 3.00%,
              W: 0 to 1.00%,
              Ca: 0 to 1.000%,
              Mg: 0 to 1.000%,
              REM: 0 to 1.000%,
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              Sb: 0 to 1.000%,
             Zr: 0 to 1.000%,
              Sn: 0 to 1.000%,
              As: 0 to 0.100%, and
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balance: Fe and impurities, and

a metallographic structure comprising, by volume ratio, martensite in 90% or more, wherein an average grain size of former austenite grains is 3.0  $\mu$ m or less,

- a standard deviation in grain size distribution of former austenite grains is 1.5  $\mu$ m or less, and
- a difference of a maximum value and a minimum value in a Vickers hardness distribution in a sheet thickness direction is 35% or less of an average value of I Vickers hardness distribution.
- (2) The hot stamped body according to (1), wherein the chemical composition contains, by mass%, one or more selected from the group consisting of,

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Nb: 0.001 to 0.200%, Ti: 0.001 to 0.200%, Mo: 0.001 to 1.00%, B: 0.0001 to 0.1000%, Co: 0.001 to 4.00%,

15 Co: 0.001 to 4.00%, Ni: 0.001 to 3.00%, Cu: 0.001 to 3.00%, V: 0.001 to 3.00%,

V: 0.001 to 3.00%, W: 0.001 to 1.00%, Ca: 0.0001 to 1.000%,

Mg: 0.0001 to 1.000%, REM: 0.0001 to 1.000%,

Sb: 0.001 to 1.000%, Zr: 0.001 to 1.000%, Sp: 0.001 to 1.000% an

25 Sn: 0.001 to 1.000%, and As: 0.001 to 0.100%.

#### [ADVANTAGEOUS EFFECTS OF INVENTION]

<sup>30</sup> **[0012]** According to the present invention, it is possible to provide a hot stamped body which is high in strength and able to suppress hydrogen embrittlement.

#### **DESCRIPTION OF EMBODIMENTS**

35 <Hot Stamped Body>

**[0013]** The hot stamped body according to an embodiment of the present invention has a chemical composition comprising, by mass%,

40 C: 0.40 to 0.70%,

Si: 0.01 to 1.30%,

Mn: 0.05 to 3.00%,

P: 0.100% or less,

S: 0.0100% or less,

N: 0.0200% or less,

O: 0.0200% or less,

AI: 0.001 to 1.000%,

Cr: 0.01 to 1.00%,

Nb: 0 to 0.200%,

Ti: 0 to 0.200%,

Mo: 0 to 1.00%,

B: 0 to 0.1000%,

Co: 0 to 4.00%,

Ni: 0 to 3.00%,

Cu: 0 to 3.00%,

V: 0 to 3.00%,

W: 0 to 1.00%,

Ca: 0 to 1.000%,

Mg: 0 to 1.000%, REM: 0 to 1.000%, Sb: 0 to 1.000%, Zr: 0 to 1.000%, Sn: 0 to 1.000%, As: 0 to 0.100%, and

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balance: Fe and impurities, and

a metallographic structure comprising, by volume ratio, martensite in 90% or more, wherein an average grain size of former austenite grains is 3.0 µm or less,

a standard deviation in grain size distribution of former austenite grains is 1.5  $\mu$ m or less, and a difference of a maximum value and a minimum value in a Vickers hardness distribution in a sheet thickness direction is 35% or less of an average value the Vickers hardness distribution.

[0014] As explained above, it is known that hydrogen embrittlement cracking becomes easier to occur the higher the strength of the steel material. For example, in a high strength steel material, to secure high strength, the metallographic structure generally contains martensite. In particular, in a hot stamped body having a tensile strength of 2000 MPa or more, the body is often controlled to a metallographic structure mainly comprised of martensite. Such a mainly martensite structure is high in dislocation density. On the other hand, dislocations can become trap sites for hydrogen. Therefore, in a high strength hot stamped body mainly comprised of martensite, there is an ongoing need for solving the problem of hydrogen embrittlement. Therefore, the inventors conducted studies from the viewpoint of reducing or suppressing regions able to become starting points for hydrogen embrittlement cracking in such a high strength hot stamped body mainly comprised of martensite, in particular focusing on the metallographic structure of the hot stamped body. More specifically, the inventors first discovered that if there is a large variation in former austenite grain size in the metallographic structure of a hot stamped body, the hardness becomes higher in a region with a smaller former austenite grain size and that such a local high hardness region can become a starting point of hydrogen embrittlement cracking. As opposed to this, the inventors discovered that by increasing the fineness of the former austenite grains and reducing the average grain size to 3.0  $\mu$ m or less and by controlling the standard deviation in the grain size distribution to 1.5  $\mu$ m or less to increase the uniformity and in relation to this controlling the difference of a maximum value and minimum value in a Vickers hardness distribution in a sheet thickness direction to 35% or less of the average value of the Vickers hardness distribution, it is possible to suppress a rise in such a local hardness to reliably suppress or reduce microstress concentration.

[0015] While not intending to be bound to any specific theory, it is believed that at the time of hot stamping, the starting temperature of martensite transformation changes in accordance with the size of the austenite grains. If explained in more detail, it is believed that austenite grains having larger size are higher in starting temperature of martensite transformation compared with austenite grains having smaller size and austempering proceeds in the period from the completion of transformation to cooling to room temperature, and therefore the hardness becomes lower. Austenite grains having smaller size rise in hardness since martensite transformation occurs at a lower temperature than large grains. Therefore, to suppress or reduce the rise in such local hardness, it is important to reduce the variation in the austenite grain size before martensite transformation. In other words, it is believed that by reducing the variation in the austenite grain size before martensite transformation, it is possible to reduce the variation in the former austenite grain size after martensite transformation and as a result it is possible to reduce the variation in hardness in the metallographic structure of the hot stamped body. Due to such a reason, it is believed that by controlling the difference between the maximum value and minimum value of the Vickers hardness distribution in the metallographic structure of the hot stamped body to 35% or less of the average value of the Vickers hardness distribution to reduce the variation in hardness, it would be possible to remarkably suppress the rise in local hardness due to differences in timing of martensite transformation. If there is locally a region of a high hardness, it is believed that there will be a high possibility of stress concentrating in particular at the interfaces of former austenite grains with differences in hardness and causing hydrogen embrittlement cracking, and therefore reducing the variation in hardness in the metallographic structure of a hot stamped body would be extremely effective in suppressing or reducing microstress concentration and improving the hydrogen embrittlement resistance.

**[0016]** Furthermore, in the hot stamped body according to an embodiment of the present invention, the former austenite grains have an average grain size of  $3.0~\mu m$  or less, and therefore are extremely fine. Further, the standard deviation in the grain size distribution of former austenite grains is controlled to  $1.5~\mu m$  or less, i.e., the former austenite grains are increased in uniformity to a high degree. The fine former austenite grains are believed to transform to martensite at a lower temperature as described above. Further, these are increased in uniformity to a high degree, and therefore it is believed that a metallographic structure including former austenite grains increased in fineness and uniformity in this way transforms to martensite at a lower temperature in the metallographic structure as a whole. For this reason, a hot stamped body including such a metallographic structure can enable overall hardness to be remarkably improved, and therefore an extremely high strength, specifically an extremely high tensile strength and yield strength, can be achieved. In addition, in a metallographic structure including such former austenite grains increased in fineness and uniformity, the

grain boundary area greatly increases, and therefore it is possible to remarkably reduce the amount of hydrogen trapped per unit grain boundary area. Hydrogen embrittlement cracking, for example, is caused by hydrogen penetrating the steel from the environment being trapped at the grain boundaries in the state where a high stress is acting. For this reason, by reducing the amount of hydrogen trapped per unit grain boundary area, it is possible to greatly reduce the risk of hydrogen embrittlement cracking. Therefore, according to the hot stamped body according to an embodiment of the present invention, in addition to the effect of improvement of the hydrogen embrittlement resistance due to the reduction in variation in hardness explained previously, it is also possible to improve the hydrogen embrittlement resistance of a hot stamped body from the viewpoint of increase of the grain boundary area due to increased fineness and increased uniformity of the former austenite grains.

**[0017]** Below, the hot stamped body according to the embodiment of the present invention will be explained in more detail. In the following explanation, the "%" of the units of content of the elements, unless otherwise indicated, means "mass%". Further, in this Description, "to" showing a numerical range, unless otherwise indicated, is used in the sense including the numerical values described before and after it as the upper limit value and lower limit value.

[C: 0.40 to 0.70%]

**[0018]** C is an element improving the strength of a hot stamped body. If the C content is less than 0.40%, it is not possible to obtain the desired strength at the hot stamped body. For this reason, the C content is 0.40% or more. The C content is preferably more than 0.40%, 0.42% or more, 0.44% or more, or 0.45% or more.

**[0019]** On the other hand, if the C content is more than 0.70%, the strength becomes too high and sometimes excellent hydrogen embrittlement resistance cannot be obtained. For this reason, the C content is 0.70% or less. Preferably, the C content is 0.68% or less, 0.67% or less, 0.65% or less, or 0.60% or less.

[Si: 0.01 to 1.30%]

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**[0020]** Si is an element improving the strength of a hot stamped body by solution strengthening. If the Si content is less than 0.01%, the desired strength cannot be obtained. For this reason, the Si content is 0.01% or more. The Si content is preferably 0.05% or more, 0.10% or more, 0.20% or more, more than 0.25%, 0.26% or more, 0.27% or more, 0.30% or more, or 0.40% or more.

[0021] On the other hand, if the Si content is more than 1.30%, the amount of ferrite increases and sometimes the desired metallographic structure cannot be obtained. For this reason, the Si content is 1.30% or less. The Si content is preferably 1.20% or less, 1.00% or less, 0.80% or less, 0.60% or less, or 0.50% or less.

[Mn: 0.05 to 3.00%]

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**[0022]** Mn is an element raising the hardenability of steel and contributing to improvement of the strength. If the Mn content is less than 0.05%, such an effect cannot be sufficiently obtained. For this reason, the Mn content is 0.05% or more. The Mn content is preferably 0.10% or more, 0.50% or more, 1.00% or more, 1.30% or more, or 1.50% or more.

**[0023]** On the other hand, if the Mn content is more than 3.00%, Mn segregation becomes remarkable. Due to this, sometimes variation in grain size of former austenite grains cannot be sufficiently suppressed. For this reason, the Mn content is 3.00% or less. The Mn content is preferably 2.80% or less, 2.50% or less, 2.30% or less, or 2.00% or less.

[P: 0.100% or Less]

[0024] P is an impurity element and segregates at the grain boundaries to cause the hydrogen embrittlement resistance to deteriorate. For this reason, the P content is 0.100% or less. The P content is preferably 0.070% or less, 0.050% or less, or 0.010% or less.

**[0025]** The lower limit of the P content is not particularly prescribed, but if less than 0.0001%, the dephosphorization cost greatly rises making this not preferable economically. For this reason, the P content may also be 0.0001% or more.

[S: 0.0100% or Less]

**[0026]** S is an impurity element and forms inclusions in the steel. The inclusions cause the hydrogen embrittlement resistance to deteriorate, and therefore the S content is 0.0100% or less. The S content is preferably 0.0080% or less, 0.0050% or less, 0.0030% or less, or 0.0020% or less.

**[0027]** The lower limit of the S content is not particularly prescribed, but if less than 0.0001%, the desulfurization cost greatly rises making this not preferable economically. For this reason, the S content may also be 0.0001% or more.

[N: 0.0200% or Less]

**[0028]** N is an impurity element and forms nitrides in the steel. The nitrides cause the hydrogen embrittlement resistance to deteriorate, and therefore the N content is 0.0200% or less. The N content is preferably 0.0180% or less, 0.0150% or less, 0.0100% or less, 0.0060% or less, or 0.0040% or less.

**[0029]** The lower limit of the N content is not particularly prescribed, but if reducing this to less than 0.0001%, the denitridation cost greatly rises making this not preferable economically. For this reason, the N content may also be 0.0001% or more.

10 [O: 0.0200% or Less]

**[0030]** O, if contained in a large amount in the steel, forms coarse oxides and causes the hydrogen embrittlement resistance to deteriorate. For this reason, the O content is 0.0200% or less. The O content is preferably 0.0150% or less, 0.0100% or less, 0.0070% or less, or 0.0040% or less.

**[0031]** From the viewpoint of reducing the refining costs, the O content may also be 0.0001% or more. To make a large number of fine oxides disperse at the time of deoxidation of the molten steel, the O content may be 0.0005% or more.

[AI: 0.001 to 1.000%]

[0032] Al is an element having the action of deoxidizing the molten steel and making the steel sounder. If the Al content is less than 0.001%, the deoxidation will not sufficiently proceed and coarse oxides will be formed causing the hydrogen embrittlement resistance to deteriorate. For this reason, the Al content is 0.001% or more. The Al content is preferably 0.003% or more, 0.005% or more, 0.010% or more, or 0.030% or more.

**[0033]** On the other hand, if the Al content is more than 1.000%, coarse oxides will form in the steel causing the hydrogen embrittlement resistance of the hot stamped body to fall. For this reason, the Al content is 1.000% or less. The Al content is preferably 0.800% or less, 0.600% or less, 0.400% or less, 0.200% or less, or 0.100% or less.

[Cr: 0.01 to 1.00%]

[0034] Cr is an element dissolving in the former austenite grains before hot stamping and thereby raising the strength of the hot stamped body. If the Cr content is less than 0.01%, the desired strength cannot be obtained. For this reason, the Cr content is 0.01% or more. The Cr content is preferably 0.05% or more, 0.10% or more, 0.15% or more, or 0.20% or more.
 [0035] On the other hand, if the Cr content is more than 1.00%, coarse intermetallic compounds are formed at the hot stamped body and the hydrogen embrittlement resistance of the hot stamped body deteriorates. For this reason, the Cr content is 1.00% or less. The Cr content is preferably 0.80% or less, 0.60% or less, 0.50% or less, or 0.40% or less.

[0036] The basic chemical composition of the hot stamped body according to an embodiment of the present invention is as explained above. Furthermore, the hot stamped body may, if necessary, contain at least one of the following optional elements in place of part of the balance of Fe. For example, the hot stamped body may contain at least one element selected from the group comprising Nb: 0 to 0.200%, Ti: 0 to 0.200%, Mo: 0 to 1.00%, B: 0 to 0.1000%, Co: 0 to 4.00%, Ni: 0 to 3.00%, Cu: 0 to 3.00%, V: 0 to 3.00%, and W: 0 to 1.000%. Further, the hot stamped body may contain at least one element selected from the group comprising Ca: 0 to 1.000%, Mg: 0 to 1.000%, and REM: 0 to 1.000%. Further, the hot stamped body may contain at least one element selected from the group comprising Sb: 0 to 1.000%, Zr: 0 to 1.000%, and Sn: 0 to 1.000%. Further, the hot stamped body may contain As: 0 to 0.100%. Below, these optional elements will be explained in detail.

[Nb: 0 to 0.200%]

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**[0037]** Nb is an element forming carbonitrides in steel and and improving the strength of the hot stamped body by precipitation strengthening. The Nb content may be 0.001% or more, but to reliably obtain this effect, the Nb content is preferably 0.010% or more or 0.020% or more.

**[0038]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Nb content is preferably 0.200% or less. The Nb content may also be 0.180% or less, 0.150% or less, 0.100% or less, 0.080% or less, or 0.060% or less.

<sup>55</sup> [Ti: 0 to 0.200%]

**[0039]** Ti is an element forming carbonitrides in steel and and improving the strength of the hot stamped body by precipitation strengthening. The Ti content may be 0.001% or more, but to reliably obtain this effect, the Ti content is

preferably 0.010% or more or 0.020% or more.

**[0040]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Ti content is preferably 0.200% or less. The Ti content may also be 0.180% or less, 0.150% or less, 0.100% or less, 0.080% or less, or 0.060% or less.

[Mo: 0 to 1.00%]

**[0041]** Mo is an element improving the hardenability of steel. The Mo content may be 0.001% or more, but to reliably obtain this effect, the Mo content is preferably 0.005% or more or 0.01% or more.

**[0042]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Mo content is preferably 1.00% or less. The Mo content may also be 0.80% or less, 0.60% or less, 0.50% or less, 0.30% or less, or 0.10% or less.

[B: 0 to 0.1000%]

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**[0043]** B is an element improving the hardenability of steel. The B content may be 0.0001% or more, but to reliably obtain this effect, the B content is preferably 0.0005% or more or 0.0010% or more.

**[0044]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the B content is preferably 0.1000% or less. The B content may also be 0.0500% or less, 0.0100% or less, 0.0050% or less, 0.0030% or less, or 0.0015% or less.

[Co: 0 to 4.00%]

[0045] Co is an element improving the strength of the hot stamped body by solution strengthening. The Co content may be 0.001% or more, but to reliably obtain this effect, the Co content is preferably 0.01% or more or 0.05% or more.

**[0046]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Co content is preferably 4.00% or less. The Co content may also be 3.00% or less, 2.00% or less, 1.00% or less, 0.80% or less, or 0.60% or less.

30 [Ni: 0 to 3.00%]

**[0047]** Ni has the action of dissolving in the austenite grains at the time of heating in the hot stamping step and thereby raising the strength of the hot stamped body. The Ni content may be 0.001% or more, but to reliably obtain this effect, the Ni content is preferably 0.01% or more.

**[0048]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Ni content is preferably 3.00% or less. The Ni content may also be 2.80% or less, 2.50% or less, 2.00% or less, 1.50% or less, 1.00% or less, or 0.80% or less.

[Cu: 0 to 3.00%]

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**[0049]** Cu has the action of dissolving in the austenite grains at the time of heating in the hot stamping step and thereby raising the strength of the hot stamped body. The Cu content may be 0.001% or more, but to reliably obtain this effect, the Cu content is preferably 0.01% or more or 0.05% or more.

[0050] On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Cu content is preferably 3.00% or less. The Cu content may also be 2.00% or less, 1.00% or less, 0.50% or less, 0.30% or less, or 0.10% or less.

[V: 0 to 3.00%]

[0051] V has the effect of forming carbonitrides in the steel to thereby improve the strength of the hot stamped body by precipitation strengthening. The V content may be 0.001% or more, but to reliably obtain this effect, the V content is preferably 0.01% or more or 0.05% or more.

**[0052]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the V content is preferably 3.00% or less. The V content may also be 2.00% or less, 1.00% or less, 0.50% or less, 0.30% or less, or 0.10% or less.

[W: 0 to 1.00%]

**[0053]** Wis an element improving the hardenability of steel. The W content may be 0.001% or more, but to reliably obtain this effect, the W content is preferably 0.005% or more or 0.01% or more.

**[0054]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the W content is preferably 1.00% or less. The W content may also be 0.80% or less, 0.60% or less, 0.50% or less, 0.30% or less, or 0.10% or less.

[Ca: 0 to 1.000%]

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**[0055]** Ca is an element able to control the form of sulfides. The Ca content may be 0.0001% or more, but to reliably obtain this effect, the Ca content is preferably 0.0005% or more or 0.001% or more.

**[0056]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Ca content is preferably 1.000% or less. The Ca content may also be 0.500% or less, 0.100% or less, 0.050% or less, 0.010% or less, 0.005% or less, or 0.002% or less.

[Mg: 0 to 1.000%]

**[0057]** Mg is an element able to control the form of sulfides. The Mg content may be 0.0001% or more, but to reliably obtain this effect, the Mg content is preferably 0.0005% or more or 0.001% or more.

**[0058]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Mg content is preferably 1.000% or less. The Mg content may also be 0.500% or less, 0.100% or less, 0.050% or less, 0.005% or less, 0.005% or less.

<sup>25</sup> [REM: 0 to 1.000%]

**[0059]** REM is an element able to control the form of sulfides. The REM content may be 0.0001% or more, but to reliably obtain this effect, the REM content is preferably 0.0005% or more or 0.001% or more.

**[0060]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the REM content is preferably 1.000% or less. The REM content may be 0.500% or less, 0.100% or less, 0.050% or less, 0.010% or less, 0.005% or less, or 0.002% or less.

[0061] In the present embodiment, "REM" is the general term for the 17 elements of atomic number 21 scandium (Sc), atomic number 39 yttrium (Y), and the lanthanoids of atomic number 57 lanthanum (La) to atomic number 71 lutetium (Lu). The REM content is the total content of these elements.

[Sb: 0 to 1.000%]

**[0062]** Sb is an element inhibiting the formation of oxides. To reliably obtain this effect, the Sb content is preferably 0.001% or more.

[0063] On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Sb content is preferably 1.000% or less. The Sb content may also be 0.800% or less, 0.500% or less, 0.200% or less, 0.100% or less, or 0.050% or less.

[Zr: 0 to 1.000%]

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**[0064]** Zr is an element inhibiting the formation of oxides. To reliably obtain this effect, the Zn content is preferably 0.001% or more.

**[0065]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Zr content is preferably 1.000% or less. The Zr content may also be 0.800% or less, 0.500% or less, 0.200% or less, 0.100% or less, or 0.050% or less.

[Sn: 0 to 1.000%]

**[0066]** Sn is an element inhibiting the formation of oxides. To reliably obtain this effect, the Sn content is preferably 0.001% or more.

**[0067]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the Sn content is preferably 1.000% or less. The Sn content may also be 0.800% or less, 0.500% or less, 0.200% or less, 0.100% or less, or 0.050% or less.

[As: 0 to 0.100%]

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**[0068]** As makes the single austenite phase forming temperature fall, and therefore contributes to increased fineness of the former austenite grains. To reliably obtain this effect, the As content is preferably 0.001% or more.

**[0069]** On the other hand, even if made to be contained in a large amount, the effect becomes saturated, and therefore the As content is preferably 0.100% or less. The As content may also be 0.080% or less, 0.050% or less, 0.020% or less, 0.010% or less, or 0.005% or less.

[0070] In the hot stamped body according to an embodiment of the present invention, the balance besides the above elements is comprised of Fe and impurities. The "impurities" are constituents, etc., entering due to various factors in the production process starting from materials such as ore and scrap, etc., when industrially producing hot stamped bodies. [0071] The chemical composition of the above hot stamped body may be measured by a general analysis method. For example, it may be measured using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry). C and S may be measured using the combustioninfrared absorption method, N may be measured using the inert gas melting-thermal conductivity method, and O may be measured by the inert gas melting-nondispersion type infrared absorption method. [0072] If the surface of the hot stamped body is provided with a plating layer, mechanical polishing may be used to remove the plating layer, then the chemical composition analyzed.

[Martensite: 90% or More]

20 [0073] The metallographic structure of the hot stamped body according to an embodiment of the present invention contains, by volume ratio, martensite in 90% or more. The balance of the structure is not particularly limited, but may be comprised of 10% or less of at least one of bainite, ferrite, retained austenite, and pearlite. Martensite is an extremely hard structure. Therefore, by including martensite in the hot stamped body in a volume ratio of 90% or more, a high tensile strength and yield strength, specifically a tensile strength of 2200 MPa or more and a yield strength of 1800 MPa or more, become able to be achieved. On the other hand, if the volume ratio of the martensite is low and the ratio of ferrite or other soft structures becomes high, the variation in hardness in the sheet thickness direction will become remarkable and the ratio of the difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction with respect to the average value will become larger. Therefore, the larger the volume ratio of the martensite the more preferable. For example, it may be 92% or more, 94% or more, 96% or more, or 98% or more. The upper limit of the volume ratio of martensite is not particularly prescribed, but may be 100%.

[Identification of Metallographic Structure and Calculation of Volume Ratio]

[0074] The metallographic structure of the hot stamped body is identified and the volume ratio is calculated as follows: First, a sample is taken so that a cross-section parallel to the sheet thickness direction of the hot stamped body becomes the examined surface. Next, the examined surface is polished to a mirror finish and corroded by a Nital corrosion solution, then the structure is examined using a scan type electron microscope (SEM). A 300 μm×300 μm range is captured at 1000X centered about the sheet thickness 1/4 depth position of the examined surface. The obtained microstructure photo is digitalized to white and black, then is analyzed to identify the pearlite, bainite, and ferrite. The total of the area ratios of these is found using a method based on "Steels-micrographic determination of the apparent grain size" prescribed in JIS G 0551: 2020. Furthermore, the area ratio of the above structures is converted to volume ratio by the line segment method. The line segment method is based on the technique described in, for example, Robert T. DeHoff, Frederik N. Rhines coedit (Quantitative Microscopy, 1968). Retained austenite is difficult to differentiate from martensite by an SEM, and therefore X-ray diffraction is used to measure the volume ratio of the retained austenite. Finally, the total volume ratio of the pearlite, bainite, ferrite, and retained austenite obtained by the above method is subtracted from 100% to determine the volume ratio of martensite.

[Average Grain Size of Former Austenite Grains: 3.0 µm or Less]

[0075] In an embodiment of the present invention, the average grain size of the former austenite grains is 3.0 μm or less. Such an increased fineness of the former austenite grains contributes to making the hot stamped body higher in strength by combination with the increase uniformity of the former austenite grains explained later. By making the grain boundary area increase to reduce the amount of hydrogen trapped per unit grain boundary area, it is possible to improve the hydrogen embrittlement resistance of the hot stamped body. From the viewpoint of increasing the strength of the hot stamped body and improving the hydrogen embrittlement resistance, the smaller the average grain size of the former austenite grains, the better. For example, it may be 2.8 μm or less, 2.5 μm or less, 2.3 μm or less, or 2.0 μm or less. The lower limit is not particularly prescribed, but the average grain size of the former austenite grains may also be, for example, 1.0 μm or more, 1.2 μm or more, or 1.5 μm or more.

[Standard Deviation in Grain Size Distribution of Former Austenite Grains: 1.5 µm or Less]

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[0076] In an embodiment of the present invention, the standard deviation in the grain size distribution of the former austenite grains is  $1.5~\mu m$  or less. Increasing the uniformity of the former austenite grain in this way to keep down variation in the former austenite grain size, as already explained in relation to the average grain size of the former austenite grains, can make the hot stamped body higher in strength and further improve the hydrogen embrittlement resistance by increasing the grain boundary area. In addition, according to an embodiment of the present invention, by controlling the standard deviation in the grain size distribution of former austenite grains to  $1.5~\mu m$  or less to reduce the variation in former austenite grain size, it is possible to reduce the variation in hardness and in turn remarkably suppress a rise in local hardness in the hot stamped body. By suppressing a rise in local hardness at the hot stamped body, it is possible to reliably suppress or reduce the microstress concentration, and therefore it is possible to further improve the hydrogen embrit-tlement resistance of the hot stamped body. From the viewpoint of improving these effects, the smaller the standard deviation in the grain size distribution of former austenite grains, the better. For example, it may be  $1.4~\mu m$  or less,  $1.2~\mu m$  or less,  $1.0~\mu m$  or less, or  $0.8~\mu m$  or less. The lower limit is not particularly prescribed, but the standard deviation, for example, may be  $0.1~\mu m$  or more,  $0.2~\mu m$  or more, or  $0.4~\mu m$  or more.

[Method of Determination of Average Grain Size and Standard Deviation in Grain Size Distribution of Former Austenite Grains]

[0077] The average grain size and the standard deviation in the grain size distribution of former austenite grains are determined in the following way. First, a sample is cut out from any position 50 mm or more from an end face of the hot stamped body (if a sample cannot be taken from this position, a position away from the end parts) so as to enable a sheet thickness cross-section vertical to the surface to be examined. The size of the sample, while depending also on the measuring device, is made a size enabling 10 mm or so to be examined in a direction vertical to the sheet thickness direction. The cross-section of the sample is polished using #600 to #1500 silicon carbide paper, then a liquid comprised of particle size 1 to 6 µm diamond powder dispersed in alcohol or other diluent or pure water is used to polish the surface to a mirror finish. Next, the examined surface is finished by electrolytic polishing. An area of a length 50 μm and 50 μm in the sheet thickness direction centered at a 1/4 depth position of the sheet thickness at any position in the long direction of the sample cross-section is measured at 0.1 µm measurement intervals by electron backscatter diffraction to obtain crystal orientation information. For the measurement, an EBSD analysis apparatus comprised of a thermal field emission type scan electron microscope and EBSD detector may be used. For example, an EBSD analysis apparatus comprised of a JSM-7001F made by JEOL and a DVC5 model detector made by TSL may be used. At that time, the vacuum degree inside the EBSD analysis apparatus may be  $9.6 \times 10^{-5}$  Pa or less, the acceleration voltage may be 15 kV, and the beam current level may be made 13. The obtained crystal orientation information is used to calculate the crystal orientation of the former austenite grains from the crystallographic orientation relationship of general former austenite grains and crystal grains having body-centered cubic structures after transformation. For the method of calculating the crystal orientations of the former austenite grains, the following method is used. First, a crystal orientation map of the former austenite grains is prepared by the method described in Acta Materialia, 58(2010), 6393-6403. The average value between the shortest diameter and the longest diameter of one former austenite grain included in the examined field is calculated. That average value is made the size of the former austenite grain. The above operation is performed for all of the former austenite grains except for the former austenite grains where the crystal grains as a whole are not included in the captured field, such as at the end parts of the captured field, to find the sizes of all of the former austenite grains in the captured field. From the obtained sizes of all former austenite grains, the average grain size and standard deviation are calculated whereupon the average grain size and the standard deviation in the grain size distribution of former austenite grains are determined.

[Difference of Maximum Value and Minimum Value in Vickers Hardness Distribution in Sheet Thickness Direction: 35% or Less of Average Value of Vickers Hardness Distribution]

[0078] In an embodiment of the present invention, the difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction is 35% or less of the average value of the Vickers hardness distribution. By keeping the variation in Vickers hardness distribution within such a range, it is possible to remarkably suppress in rise of local hardness at the hot stamped body. As a result, it is possible to reliably suppress or reduce microstress concentration, and therefore it is possible to improve the hydrogen embrittlement resistance of the hot stamped body. From the viewpoint of improving the hydrogen embrittlement resistance of the hot stamped body, the smaller the difference of the maximum value and minimum value of the Vickers hardness distribution, the better. For example, it may be 30% or less, 25% or less, 20% or less, or 15% or less of the average value of the Vickers hardness distribution. The lower limit is not particularly prescribed, but the difference of the maximum value and minimum value of the Vickers hardness distribution may, for example, be 1% or more, 3% or more, or 5% or more of the average value of the

Vickers hardness distribution.

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[0079] As explained above, by reducing the variation in austenite grain size, it is possible to reduce the variation in hardness. However, in an embodiment of the present invention, the standard deviation in the grain size distribution of former austenite grains is measured and determined at a region centered about the same sheet thickness 1/4 depth position, while the difference of the maximum value and minimum value of the Vickers hardness distribution is determined based on the values of Vickers hardness measured at various depth positions in the sheet thickness direction. Therefore, it is not possible to say that by the standard deviation in the grain size distribution of former austenite grains being 3.0  $\mu$ m or less, naturally the difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction would become 35% or less of the average value of the Vickers hardness distribution. In addition, the effect obtained by reducing the variation in former austenite grain size and the effect obtained by reducing the variation in hardness also do not completely match. For example, as explained above, reduction of variation in former austenite grain size (increased uniformity), by combination with the former austenite grain size, contributes to increasingly higher strength of the hot stamped body and improvement of the hydrogen embrittlement resistance by increase of the grain boundary area, while reduction of variation of hardness suppresses the rise of local hardness in the hot stamped body to suppress or reduce microstress concentration and thereby improve the hydrogen embrittlement resistance of the hot stamped body. The object of "provision of a hot stamped body which is high in strength and able to inhibit hydrogen embrittlement" according to the present invention is achieved by satisfaction of all requirements of the chemical composition of the hot stamped body plus the average grain size and standard deviation in the grain size distribution of the former austenite grains and the difference of the maximum value and minimum value of the Vickers hardness distribution. It is not, for example, achieved by only the provisions of the chemical composition of the hot stamped body and the average grain size and standard deviation in the grain size distribution of the former austenite grains.

[Method of Determination of Difference of Maximum Value and Minimum Value in Vickers Hardness Distribution in Sheet Thickness Direction]

[0080] The difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction is determined in the following way: First, a sample is cut out from any position of the hot stamped body 50 mm or more separated from an end face so that a cross-section vertical to the surface (sheet thickness cross-section) can be examined. The sample, while depending also on the measuring device, is made a size enabling 10 mm to be examined in a direction vertical to the sheet thickness direction. The cross-section of the sample is polished using #600 to  $\#1500 \ silicon\ carbide\ paper, then\ a\ liquid\ comprised\ of\ particle\ size\ 1\ to\ 6\ \mu m\ diamond\ powder\ dispersed\ in\ alcohol\ or\ other$ diluent or pure water is used to polish the surface to a mirror finish. The cross-section polished to a mirror finish is measured for Vickers hardness using a micro Vickers hardness tester by a load of 25 gf at 25 to 30 µm intervals in the sheet thickness direction from a position of 100 µm depth from the surface of the hot stamped body (if there is a plating layer present at the surface, the surface of the hot stamped body after removing the plating layer) to obtain the measured values of Vickers hardness for a distance of half or more of the sheet thickness minus 100 µm from the front and back surfaces of the hot stamped body. The intervals between measurement points in the sheet thickness direction (intervals between centers of indentations) have to be 3 times or more the distance of an indentation. "3 times or more the distance of an indentation" means a distance of 3 times or more of the length of the diagonal at the rectangular shaped opening of an indentation formed by the diamond indenter at the time of measurement of the Vickers hardness. If the hot stamped body to be measured is thin and it is difficult to make the intervals between measurement points 3 times or more the distance of an indentation and strike the sheet linearly in the sheet thickness direction, the intervals between measurement points can be made 3 times or more the distance of an indentation while striking the sheet zigzag in the sheet thickness direction. Finally, the maximum value and minimum value are selected from all of the measured values of the Vickers hardness and the difference of the same is calculated. Using the calculated difference of the maximum value and minimum value and the average value obtained by arithmetically averaging all of the measured values of the Vickers hardness, the ratio of the difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction with respect to the average value is determined.

<sup>50</sup> [Plating]

**[0081]** The hot stamped body according to the present embodiment may having a plating layer at its surface. By having a plating layer at the surface, the corrosion resistance can be improved. As the plating layer, an aluminum plating layer, aluminum-zinc plating layer, aluminum-silicon plating layer, hot dip galvanized layer, electrogalvanized layer, hot dip galvannealed layer, zinc-nickel plating layer, aluminum-magnesium-zinc based plating layer, etc., may be illustrated.

#### [Mechanical Properties]

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[0082] According to the hot stamped body of an embodiment of the present invention, excellent mechanical properties, for example, a tensile strength of 2000 MPa or more, can be achieved. The tensile strength is preferably 2300 MPa or more, more preferably 2400 MPa or more, most preferably2500 MPa or more. The upper limit is not particularly prescribed, but, for example, the tensile strength may be 3500 MPa or less, 3300 MPa or less, or 3000 MPa or less. Similarly, according to the hot stamped body of an embodiment of the present invention, a 1800 MPa or more yield strength can be achieved. The yield strength is preferably 1900 MPa or more, more preferably 2000 MPa or more, most preferably 2100 MPa or more. The upper limit is not particularly prescribed, but, for example, the yield strength may also be 3000 MPa or less, 2800 MPa or less, or 2500 MPa or less. The tensile strength and the yield strength of the hot stamped body are measured by preparing a No. 5 test piece and conducting a tensile test based on JIS Z 2241: 2011.

**[0083]** The hot stamped body according to an embodiment of the present invention, despite as explained above having a for example 2200 MPa or more high tensile strength and 1800 MPa or more high yield strength, is excellent in hydrogen embrittlement resistance, and therefore is extremely useful for use as, for example, a frame member or bumper of an automobile or other structural member and reinforcing member where strength is required.

<Method of Production of Hot Stamped Body>

**[0084]** Next, a preferable method of production of the hot stamped body according to an embodiment of the present invention will be explained. The following explanation is intended to illustrate the characteristic method for producing the hot stamped body according to the embodiment of the present invention and is not intended to limit the hot stamped body to one produced by the method of production such as explained below.

**[0085]** In order to increase the fineness and the uniformity of the former austenite grains to reduce the variation in hardness in relation to the same, in particular, the method of production of the hot stamped body according to an embodiment of the present invention is characterized by cold working hot rolled steel sheet having a metallographic structure mainly comprised of tempered martensite and, further, rapidly heating the same at the time of hot stamping. More specifically, the method of production of the hot stamped body according to the embodiment of the present invention comprises:

hot rolling a slab having a chemical composition explained above in relation to the hot stamped body, then cooling it by an average cooling speed of 50°C/s or more and coiling it at a temperature of Ms point or lower (hot rolling step), tempering the obtained hot rolled steel sheet in a temperature region of 400 to 600°C (tempering step), cold rolling the tempered hot rolled steel sheet by a rolling reduction of 30% or more (cold rolling step), and heating the obtained cold rolled steel sheet by an average heating speed of more than 100°C/s from 600°C to the heat treatment temperature: A3+50 to A3+150°C and holding it there for 30 seconds or less, then starting hot stamping in the period up to when the temperature becomes 550°C and cooling it by an average cooling speed of 10°C/s or more (hot stamping step).

[0086] To obtain fine former austenite grains in the metallographic structure of the finally obtained hot stamped body, it is important to form a large number of austenite nucleation sites at the time of heating in the hot stamping step. In relation to this, in martensite structures, the former austenite grain boundaries can become austenite nucleation sites, but it is known that martensite structures further have packets, blocks, laths, and other substructures in the former austenite grains and that the boundaries (interfaces) of these, etc., also can become austenite nucleation sites. For this reason, martensite structures have very many more austenite nucleation sites compared with for example ferrite, pearlite, and other structures. Therefore, in the present method of production, first, in the hot rolling step, the hot rolled slab is cooled by a cooling speed of the critical cooling speed or more, more specifically by an average cooling speed of 50°C/s or more, and coiled at a temperature of Ms point or lower to thereby form a hot rolled steel sheet having a structure mainly comprised of martensite. Next, the obtained hot rolled steel sheet is heat treated at a suitable temperature region in the tempering step to thereby form (precipitate) a large number of carbides at the former austenite grain boundaries, packet-block interfaces, and between laths, etc., in the martensite structure. The interfaces of the precipitated large number of carbides and their substructures also become major austenite nucleation sites at the time of heating in the hot stamping step. For this reason, by performing the hot stamping step after going through the tempering step, compared with when performing the hot stamping step without going through the tempering step, it is possible to form austenite from a greater number of austenite nucleation sites.

**[0087]** Next, by cold working (cold rolling) the tempered hot rolled steel sheet by a predetermined rolling reduction, it is possible to increase the fineness of the metallographic structure to increase the interfaces of the substructures and as a result possible to further increase the austenite nucleation sites. For example, in the tempering step, carbides precipitating at the interfaces of the packets, blocks, laths, and other substructures in the same grains are close in relative orientations,

and therefore if heating at the hot stamping step as is, the relative orientations of the austenite formed using the interfaces of these carbides and the substructures as nucleation sites can also become close. In such a case, the austenite grains formed easily become connected and it is difficult to maintain the final metallographic structure fine. As opposed to this, by cold rolling in a predetermined rolling reduction, it is possible to change the relative orientations among such carbides to make the relative orientations of the austenite formed using the interfaces of these carbides and the substructures as nucleation sites random. For this reason, the austenite formed is harder to be connected and therefore the finally obtained metallographic structure in the subsequent hot stamping step can be not only kept fine, but also kept in a uniform state. Finally, the cold rolled steel sheet having the cold worked metallographic structure mainly comprised of tempered martensite is rapidly heated at the time of heating for hot stamping through the temperature range, in which recrystallization occurs, by a predetermined average heating speed. If recrystallization proceeds at the time of heating in hot stamping, the austenite nucleation sites formed in the steps up to then are reduced or eliminated, and therefore it is impossible to achieve the desired increased fineness and uniformity in the final metallographic structure. Therefore, in the present method of production, such a recrystallization promoting temperature range is passed by predetermined rapid heating in a short time to thereby suppress recrystallization and in turn suppress the reduction or elimination of the austenite nucleation sites due to the progression of this recrystallization to enable increased fineness and uniformity in the finally obtained metallographic structure. According to the present method of production, the austenite grains made finer in the process of production will not be connected or will be difficult to be connected, and therefore not only it is possible to make the former austenite grains obtained after the heating and cooling in the hot stamping step finer, but also it is possible to increase the uniformity. As a result, it is possible to reduce the variation in size of former austenite grains and reliably reduce the variation in hardness. Below, the steps will be explained in more detail.

#### [Hot Rolling Step]

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[0088] In the hot rolling step, first, a slab having the chemical composition explained above in relation to the hot stamped body is heated. The method of casting the molten steel is not particularly limited. The slab may be produced by continuous casting, ingot forming, or thin slab casting. The heating before the hot rolling is not particularly limited, but the slab used contains a relatively large amount of alloying elements for obtaining a high strength steel sheet. For this reason, the slab may also be heated before being sent on for hot rolling. For the purpose of making the alloying elements dissolve in the slab, the heating temperature may be 1100°C or more. Further, the heated slab may optionally be rough rolled before the finish rolling so as to adjust the sheet thickness, etc. The rough rolling need only be able to secure the desired sheet bar dimensions. The conditions are not particularly limited. The heated slab or the slab additionally rough rolled as needed is next finish rolled. The finish rolling is not particularly limited, but in general is performed under conditions giving an end temperature of the finish rolling of 650°C or more. If the end temperature of the finish rolling is too low, the rolling reaction force becomes higher and the desired sheet thickness becomes difficult to stably obtain. The upper limit is not particularly prescribed, but in general the end temperature of finish rolling is 950°C or less.

### [Coiling]

[0089] Next, the finish rolled hot rolled steel sheet is cooled by an average cooling speed of 50°C/s or more and coiled at a temperature of Ms point or lower. By making the average cooling speed 50°C/s or more, preferably 100°C/s or more, and making the coiling temperature the Ms point or lower, it is possible to form a metallographic structure mainly comprised of martensite at the coiled hot rolled steel sheet and becomes possible to reliably form cold rolled steel sheet having a metallographic structure mainly comprised of tempered martensite at the subsequent tempering step. If the average cooling speed is less than 50°C/s and/or the coiling temperature is higher than the Ms point, it is not possible to form a metallographic structure mainly comprised of martensite at the coiled hot rolled steel sheet and even if suitably performing the subsequent steps, in the finally obtained hot stamped body, the desired hard structures cannot be obtained and/or increased fineness and increased uniformity of the former austenite grains can no longer be realized and reduction of the variation of hardness can no longer be achieved. From the viewpoint of increasing the fineness of the metallographic structure, preferably the average cooling speed is 100°C/s or more and the coiling temperature is the Mf point or less. By making the average cooling speed 100°C/s or more and making the coiling temperature the Mf point or less, the percentage of the martensite structures obtained can be made higher. Martensite structures, as explained above, have pluralities of substructures. Using these substructures and the carbides, etc., precipitating at the tempering step, a large number of austenite nucleation sites can be created. For this reason, martensite structures can be said to be extremely effective structures in promoting the increased fineness of the metallographic structure. However, on the other hand, if raising the percentage of martensite structures as hard structures in the hot rolled steel sheet, the rolling load of the rolling mill becomes remarkably higher in the subsequent cold rolling step. Therefore, the technical idea of trying to realize both increased fineness and increased uniformity by the combination of coiling at a low temperature of Ms point or lower, the subsequent tempering and cold rolling, and further the rapid heating at the hot stamping step had not existed up to now. It

was first devised by the present inventors. Here, the Ms point (°C) and Mf point (°C) can be calculated by approximation based on the following formulas 1 and 2:

Ms=550-361x[C]-39x[Mn]-35x[V]-20x[Cr]-17x[Ni]-10x[Cu]-5x([Mo]+[W])+15x[Co]+ formula 1

formula 1

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 $Mf=410.5-407.3\times[C]-7.3\times[Si]-37.8\times[Mn]-20.5\times[Cu]-19.5\times[Ni]-19.8\times[Cr]-4.5\times[Mo]$  ...

formula 2

where, [C], [Mn], [V], [Cr], [Ni], [Cu], [Mo], [W], [Co], [Al], and [Si] are the contents (mass%) of the elements in the hot stamped body.

[Tempering Step]

[0090] Next, the obtained hot rolled steel sheet is tempered at the tempering step in a temperature region of 400 to 600°C. By tempering the hot rolled steel sheet in the temperature region, it is possible to make a large number of carbides precipitate at the former austenite grain boundaries, packet and block boundaries, between the laths, etc., in the martensite structures and as a result becomes possible to form many austenite nucleation sites at the interfaces of the resultant precipitated large number of carbides and the substructures of the same. If not performing the tempering step or the tempering temperature is lower than 400°C, it is not possible to make sufficient carbides precipitate. Therefore, even if suitably performing the subsequent steps, it becomes impossible to achieve the desired increased fineness and/or increased uniformity in the metallographic structure. Preferably, the tempering temperature is 450°C or more. On the other hand, if the tempering temperature is higher than 600°C, the precipitated carbides become coarser and similarly it becomes impossible to achieve the desired increased fineness and/or increased uniformity in the metallographic structure. Preferably, the tempering temperature is 550°C or less. From the viewpoint of making carbides sufficiently precipitate, the tempering time is preferably 1200 seconds or more. The upper limit is not particularly prescribed, but, for example, the tempering time may be 7200 seconds or less.

<sup>30</sup> [Pickling Step]

**[0091]** Before the cold rolling step, optionally, pickling may be performed for removing the oxide scale formed on the surface of the hot rolled steel sheet. The pickling may be formed under conditions suitable for removing oxide scale. It may be performed at one time or may be performed divided into several times so as to reliably remove the oxide scale. Such a pickling step is not necessarily limited to being performed before the cold rolling step. For example, it may also be performed after the cold rolling step.

[Cold Rolling Step]

**[0092]** The tempered hot rolled steel sheet is cold rolled by a rolling reduction of 30% or more. By cold rolling by a rolling reduction of 30% or more, as explained above, it is possible to increase the fineness of the metallographic structure to increase the interfaces with the substructures of martensite and change the relative orientations of the carbides precipitated at the tempering step so as to reliably randomize the relative orientations of the austenite formed using the interfaces of these carbides and the substructures as nucleation sites. If the rolling reduction of the cold rolling is low, such an effect cannot be sufficiently obtained. Preferably, the rolling reduction of the cold rolling is 40% or more. The upper limit is not particularly prescribed, but from the viewpoint of reducing the rolling load of the rolling mills, the rolling reduction of the cold rolling may be, for example, 80% or less or 70% or less.

[Annealing Step]

**[0093]** For example, after the cold rolling step, annealing may optionally be performed so as to adjust the metallographic structure and/or properties. While not particularly limited, from the viewpoint of avoiding the elimination of the metallographic structures built in at the steps up to there, for example, the elimination of austenite nucleation sites due to progression of recrystallization, etc., the heating temperature of the annealing step is preferably, for example, 600°C or less.

[Plating Step]

[0094] For the purpose of improving the corrosion resistance, etc., the surface of the cold rolled steel sheet may also be plated. The plating may be hot dip coating, alloyed hot dip coating, electroplating, or other treatment. For example, as the plating, the steel sheet may be hot dip galvanized. After hot dip galvanization, alloying treatment may be performed. As the plating layer, an aluminum plating layer, aluminum-zinc plating layer, aluminum-silicon plating layer, hot dip galvanized layer, electrogalvanized layer, hot dip galvannealed layer, zinc-nickel plating layer, aluminum-magnesium-zinc based plating layer, etc., may be illustrated. The specific conditions of the plating and alloying treatment are not particularly limited and may be any suitable conditions known to persons skilled in the art. However, in the same way as the case of the annealing step, from the viewpoint of avoiding the elimination of austenite nucleation sites due to the progression of recrystallization, etc., the plating treatment and alloying treatment are preferably performed at as low a temperature and as short a time as possible.

[Temper Rolling Step]

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**[0095]** To correct the shape of the steel sheet or adjust the surface roughness, etc., it is possible, for example, to temper roll the steel sheet after the cold rolling step, after the annealing step, or after the plating step. The rolling reduction of the temper rolling is preferably, for example, 1.0% or less.

20 [Hot Stamping Step]

[0096] Finally, the obtained cold rolled steel sheet is, at the hot stamping step, heated by an average heating speed of more than 100°C/s from 600°C to the heat treatment temperature: A3+50 to A3+150°C and held at the heat treatment temperature for 30 seconds or less, then started to be hot stamped in the period until the temperature became 550°C and is cooled by an average cooling speed of 10°C/s or more. By rapidly heating by an average heating speed of more than 100°C/s from 600°C to the above heat treatment temperature, it is possible to avoid a temperature region in which recrystallization proceeds, and therefore it is possible to keep the austenite nucleation sites formed in the steps up to then from being reduced or eliminated due to progression of recrystallization. Therefore, due to the martensite transformation in the subsequent cooling process, in the finally obtained hot stamped body, it is possible to obtain a metallographic structure containing former austenite grains increased in fineness and uniformity and remarkably reduced in variation of hardness in the sheet thickness direction. Along with the increasing higher strength of steel materials, sometimes a relatively large amount of Mn is added so as to improve the hardenability of the steel material. In such a case, sometimes the Mn segregation becomes remarkable and it is impossible to suitably suppress variation in former austenite grains. However, according to the present method of production, by rapid heating by a more than 100°C/s high average heating speed, even if the Mn content is relatively high, it is possible to reduce the variation in grain size and hardness of the austenite grains and obtain the desired metallographic structure. On the other hand, if the average heating speed is 100°C/s or less or the heating start temperature by an average heating speed of more than 100°C/s is higher than 600°C, recrystallization proceeds and the austenite nucleation sites are reduced or eliminated and it becomes impossible to achieve the desired increased fineness and increased uniformity at the metallographic structure. From the viewpoint of achieving the desired increased fineness and increased uniformity, the average heating speed is preferably 120°C/s or more. Further, if rapidly heating by a high average heating speed such as more than 100°C/s, in general, there is a tendency for the A3 point to rise. Therefore, to sufficiently austenize the metallographic structure to obtain the desired hard structures and to achieve the desired increased fineness and increased uniformity, the rapid heating has to be heating up to a temperature 50 to 150°C higher than the A3 point (°C) of the following formula 3 found by approximation from the chemical composition of the hot stamped body:

$$A3=850+10\times([C]+[N])\times[Mn]+350\times[Nb]+250\times[Ti]+40\times[B]+10\times[Cr]+100\times[Mo]$$
 ...

formula 3

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where, [C], [N], [Mn], [Nb], [Ti], [B], [Cr], and [Mo] are contents (mass%) of elements in hot stamped body. [0097] If the above heat treatment temperature is lower than A3+50°C, the austenization will become insufficient and the desired hard structures will not be obtained and/or the desired increased fineness and increased uniformity will become impossible to achieve. On the other hand, if the above heat treatment temperature is more than A3+150°C, the austenite will excessively grow in size and similarly the desired increased fineness and increased uniformity will become impossible to achieve and, as a result, the desired Vickers hardness distribution in the sheet thickness direction will become impossible to obtain. Further, even if the holding time at the above heat treatment temperature is more than 30 seconds, the austenite will excessively grow in size and the desired increased fineness and increased uniformity will become impossible

to achieve. Therefore, the holding time at the above heat treatment temperature is preferably 10 seconds or less, more preferably 3 seconds or less. The lower limit is not particularly prescribed, but the holding time may also be 1 second or more.

[0098] The heating atmosphere is not particularly limited. Usual conditions are enough. For example, it may be an air atmosphere, a gas combustion atmosphere controlled in ratio of air and fuel, and a nitrogen atmosphere. The dew points may also be controlled in these gases. Further, as the heating method, for example, furnace heating by an electric furnace, gas furnace, etc., flame heating, ohmic heating, high frequency heating, induction heating, etc. The steel sheet is held at that heat treatment temperature, then starts to be hot stamped in the period until the temperature becomes 550°C. If starting the hot stamping at a temperature lower than 550°C, bainite transformation, etc., will proceed. In such a case, it will become impossible to obtain the martensite 90 vol% or more desired hard structures. After hot stamping, to obtain the desired hard structures of martensite 90 vol% or more, the steel sheet may be cooled down to a temperature region of 250°C or less by an average cooling speed of 10°C/s or more. Further, it is also possible to perform bake hardening treatment (BH treatment) after hot stamping and after painting, for example, perform BH treatment at 170 to 200°C for 20 to 30 minutes.

**[0099]** Below, examples will be used to explain the present invention in more detail, but the present invention is not limited to these examples in any way.

#### **EXAMPLES**

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**[0100]** In the following examples, hot stamped bodies according to an embodiment of the present invention were produced under various conditions and the obtained tensile strength, yield strength, and hydrogen embrittlement resistance of the hot stamped bodies were investigated.

**[0101]** First, molten steels having the chemical compositions shown in Table 1 were cast by continuous casting to produce slabs. The balances besides the constituents shown in Table 1 were Fe and impurities. These slabs were heated to a 1100°C or more temperature and rough rolled under predetermined conditions, then were finish rolled, cooled, coiled, tempered, and cold rolled under the conditions shown in Table 2. Next, the obtained cold rolled steel sheets were heated by the average heating speeds shown in Table 3 from 600°C to the heat treatment temperatures shown in Table 3 and held there, then started to be hot stamped in the period up to the temperature becoming 550°C and cooled by the average cooling speed shown in Table 3 down to a temperature region of 250°C or less. In Comparative Examples 42, 44, and 46 and Invention Examples 43 and 45, the cold rolled steel sheets obtained by cold rolling were heated by the average heating speeds shown in Table 4 from the temperature T1 similarly shown in Table 4 to the heat treatment temperatures and held there, then started to be hot stamped in the period until the temperature became 550°C, and were cooled by the average cooling speeds shown in Table 4 down to a temperature region of 250°C or less. The heating atmosphere and heating method in the hot stamping step were a gas combustion atmosphere (air-fuel ratio 0.85) and ohmic heating. Further, from the viewpoint of evaluating the performances under conditions closer to actual products, the obtained hot stamped bodies were heat treated at 170°C for 20 minutes (no painting) as post-painting bake hardening treatment (BH treatment).

[Table 1]

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	Table	1																								
	Steel							Chemica	l comp	ositior	ı (mass	%, bala	nce: F	e and in	ipuriti	es)							A3	Ms	Mf	Remarks
	type	С	Si	Mn	P	S	N	О	Al	Cr	Nb	Ti	Mo	В	Co	Ni	Cu	V	W	REM	Sn	As	(°C)	(°C)	(°C)	Remarks
	Α	0.46	0.40	0.39	0.009	0.0006	0.0029	0.0022	0.033	0.29	0.020	0.025	0.20	0.0021									888	363	199	Inv. steel
	В					0.0006					0.019			0.0014									865	369	206	Inv. steel
	С					0.0005											0.05				0.030		893	368	204	Inv. steel
5	D					0.0006							0.10		0.06								879	359	194	Inv. steel
	E					0.0008								0.0019									874	349	186	Inv. steel
	F					0.0010					0.020		0.22	0.0021				0.29					890	353	199	Inv. steel
	G	$\overline{}$		_		0.0020			0.033			0.020		0.0015									860	424	274	Comp.steel
	Н					0.0029		0.0024						0.0022									878	387	232	Comp.steel
	I					0.0011							_	0.0019	_								876		218	Comp.steel
	J					0.0003								0.0014		0.07						0.002	887		212	Inv. steel
10	K					0.0003					0.077			0.0014						0.001			892	325	167	Inv. steel
10	L					0.0005																	917		201	Inv. steel
	M					0.0005																	887	363	199	Inv. steel
	N					0.0005					0.018	0.026	0.19	0.0020					0.38				886	361	199	Inv. steel
	0					0.0004			0.028		-		-										854	361	197	Inv. steel
	P					0.0009																	885	290	115	Inv. steel
	Q			_		0.0009				_			_										887	346	183	Inv. steel
	R					0.0011																	891	326	160	Inv. steel
15	S			_		0.0008																	887	374	209	Inv. steel
	T					0.0009		0.0018															899	268	107	Inv. steel
	U					0.0010		0.0020															885	356	192	Inv. steel
						0.0010																	910	375	197	Inv. steel
	W					0.0008								0.0021									900	386	199	Inv. steel
	X					0.0010			0.120	0.27	0.019	0.024	0.22	0.0022									889	363	196	Inv. steel

Underlines indicate outside scope of present invention

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[Table 2]

[0102]

25 Table 2

				Hot roll	ing step		Temper	ing step	Cold rolling step	
30	Ex. no.	Steel type	Heating temp. (°C)	Finish rolling end temp.	Average cooling speed (°C/s)	Coiling temp. (°C)	Tempering temp. (°C)	Tempering time (s)	Rolling reduction (%)	Remarks
35	1	Α	1272	904	115	322	520	3600	43	Inv. ex.
	2	Α	1272	912	112	322	520	3600	43	Comp. ex.
40	3	Α	1275	910	119	343	None	None	42	Comp. ex.
	4	Α	1254	908	118	336	500	3600	None	Comp. ex.
	5	Α	1242	905	115	324	500	3600	45	Inv. ex.
45	6	Α	1272	899	115	322	520	3600	44	Comp. ex.
	7	Α	1258	910	123	<u>498</u>	450	3600	43	Comp. ex.
50	8	В	1263	896	123	326	450	3600	52	Inv. ex.
	9	В	1245	907	119	334	<u>740</u>	3600	42	Comp. ex.
55	10	В	1223	907	115	334	<u>250</u>	3600	45	Comp. ex.
	11	С	1266	912	117	320	480	3600	38	Comp. ex.

(continued)

5				Hot roll	ing step		Temper	ng step	Cold rolling step	
10	Ex. no.	Steel type	Heating temp. (°C)	Finish rolling end temp.	Average cooling speed (°C/s)	Coiling temp. (°C)	Tempering temp. (°C)	Tempering time (s)	Rolling reduction (%)	Remarks
	12	D	1255	915	125	322	500	3600	50	Comp. ex.
	13	D	1254	908	124	331	480	3600	45	Inv. ex.
15	14	D	1249	906	120	336	480	3600	44	Comp. ex.
	15	D	1255	903	118	338	500	3600	44	Comp. ex.
20	16	E	1246	899	116	341	500	3600	43	Inv. ex.
	17	F	1272	906	119	335	500	3600	43	Inv. ex.
	18	G	1248	926	122	399	450	1200	51	Comp. ex.
25	19	Н	1252	896	115	364	450	1200	44	Comp. ex.
	20	Ι	1244	908	119	335	500	1200	43	Comp. ex.
30	21	J	1264	923	123	355	450	1800	48	Inv. ex.
	22	J	1255	933	121	<u>620</u>	450	1800	49	Comp. ex.
	23	K	1277	924	118	319	450	1800	48	Inv. ex.
35	24	К	1272	909	120	313	450	1800	48	Comp. ex.
	25	L	1246	924	119	323	500	1200	37	Inv. ex.
	26	М	1273	930	126	331	500	1200	36	Inv. ex.
40	27	N	1272	904	117	314	500	1200	36	Inv. ex.
	28	0	1249	905	123	322	450	1800	42	Inv. ex.
	29	Р	1248	912	115	272	480	1800	43	Inv. ex.
45	30	Q	1273	921	121	324	480	1800	38	Inv. ex.
	31	R	1255	908	119	322	470	1800	41	Inv. ex.
	32	S	1246	910	115	354	470	1800	51	Inv. ex.
	33	T	1273	911	123	249	480	1800	42	Inv. ex.
50	34	U	1273	908	124	321	450	1800	44	Inv. ex.
	35	V	1259	904	118	336	470	1800	38	Inv. ex.
	36	W	1244	912	119	355	450	1800	36	Inv. ex.
55	37	Х	1256	903	115	343	480	1800	41	Inv. ex.
	38	С	1272	908	20	322	480	1800	43	Comp. ex.

(continued)

5				Hot roll	ing step		Temper	ing step	Cold rolling step	
10	Ex. no.	Steel type	Heating temp. (°C)	Finish rolling end temp.	Average cooling speed (°C/s)	Coiling temp. (°C)	Tempering temp. (°C)	Tempering time (s)	Rolling reduction (%)	Remarks
	39	С	1263	912	117	324	480	1800	43	Comp. ex.
15	40	F	1261	903	125	336	500	1800	5	Comp. ex.
	41	F	1248	901	124	334	500	1800	42	Inv. ex.
	42	Α	1252	924	116	343	500	1800	46	Comp. ex.
20	43	С	1244	914	121	351	500	1800	43	Inv. ex.
	44	С	1244	914	121	351	500	1800	43	Comp. ex.
	45	F	1258	909	124	333	500	1800	48	Inv. ex.
25	46	F	1258	909	124	333	500	1800	48	Comp. ex.
	Unde	rlines ind	icate produc	ction condit	ions not pref	erable.				

<sup>30</sup> [Table 3]

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Remarks Inv. ex. Inv. ex. Inv. ex. Inv. ex. Comp. Comp. Comp. Comp. Comp. Comp. Comp. Comp. Comp. eX. e×. ex ex. e×. ë. e×. 5 Properties of hot stamped body atmosphere load in hydrogen Fracture (MPa) 902 519 435 672 636 699 538 565 653 392 747 644 431 10 TS (MPa) 2104 2320 2205 2346 2403 2328 2323 2302 2402 2383 2387 2421 2391 YS (MPa) 1946 1786 1905 2068 1952 2099 2111 1656 1887 1994 1977 1667 1701 15 Hardness provision Metallo graphic structure of hot stamped body %) 9 53 9 38 37 4 24 77 37 4 34 47 24 20 distribution deviation (μm) Grain size standard 2.3 <del>1</del>.3 1.2 4.8 <del>1</del>.3 2.3 <del>1</del>. 1.2 2.5 2.2 2.8 25 grain average Former y grain size (µm) 2.3 3.4 2.7 2.5 4.5 2.2 3.4 4.5 2.4 5.1 4. 47 6.1 Table 3 30 Martensite vol. ratio %) 96 86 96 86 86 95 98 98 86 97 97 97 97 35 BH treatment Yes cooling Average speed (°C/s) 140 125 255 125 153 155 130 300 28 65 85 62 59 40 Hot stamping ste Holding time (s) 120 90 4 က က  $^{\circ}$ 9  $^{\circ}$ 4 9 က 45 treatment temp. (°C) Heat 945 972 948 947 890 940 952 944 959 944 967 951 931 50 Average heating speed (°C/s) 150 150 150 150 150 150 150 150 150 150 150 က 4 Steel type 55 C ⋖ ⋖ ⋖ ⋖ ⋖ ⋖ ⋖ Ω Ω Ω  $\Box$  $\Box$ [0103] . E 13 ω 9 7 12 4 2 တ 2 က 9 \_

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5			Remarks	Comp. ex.	Comp. ex.	Inv. ex.	Inv. ex.	Comp. ex.	Comp. ex.	Comp. ex.	Inv. ex.	Comp. ex.	Inv. ex.	Comp. ex.	Inv. ex.					
		Properties of hot stamped body	Fracture load in hydrogen atmosphere (MPa)	373	865	702	969	1274	852	665	689	1421	726	1094	692	704	723	612	605	664
10		es of hot st	TS (MPa)	2322	892	2385	2443	1690	2026	2104	2208	1662	2240	1119	2415	2387	2379	2411	2648	2339
15		Properti	YS (MPa)	1927	669	1974	2089	1557	1752	1797	1937	1142	1953	927	2098	2022	2036	2028	2444	1988
20	•	ped body	Hardness provision (%)	43	1	26	22	27	34	26	23	21	27	99	31	28	25	28	33	23
25		Metallo graphic structure of hot stamped body	Grain size distribution standard deviation (µm)	6.9		1.1	1.2	1.3	0.8	1.3	1.4	1.0	1.2	0.7	1.3	1.2	1.2	1.3	1.2	1.2
	(continued)	aphic structu	Former γ grain average grain size (μm)	12.5	1	2.5	2.4	2.9	2.7	2.9	2.9	2.8	2.6	1.7	2.8	2.4	2.5	2.8	2.3	2.5
30	(conti	Metallo gra	Martensite vol. ratio (%)	86	<del>&lt;30</del>	26	86	86	98	26	86	72	86	53	96	86	86	97	86	86
35			BH treat- ment	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
40		6	Average cooling speed (°C/s)	320	81	173	124	325	143	65	295	306	322	342	86	77	79	294	85	105
45		Hot stamping ste	Holding time (s)	4	8	4	2	1	1	3	1	1	1	1	2	2	2	2	1	1
		Hot s	Heat treatment temp. (°C)	1095	942	945	944	922	935	933	951	096	953	763	970	945	941	949	978	948
50			Average heating speed (°C/s)	150	150	150	150	200	200	150	200	200	200	200	150	150	150	200	150	150
55			Steel	D	D	Ш	ъ	Ŋ	T	_	ſ	ſ	×	×	Γ	Σ	z	0	Ь	Ø
			ë. ë	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30

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			Remarks	Inv. ex.	Comp. ex.	Comp. ex.	Comp. ex.	Inv. ex.							
5		Properties of hot stamped body	Fracture load in hydrogen atmosphere (MPa)	662	704	621	613	652	674	644	438	522	571	625	
10		es of hot st	TS (MPa)	2274	2322	2322	2293	2344	2337	2344	2393	2381	2334	2432	
15		Propertie	YS (MPa)	2044	2015	2033	2023	1975	1983	2042	1985	2004	1822	2071	
20		ped body	Hardness provision (%)	26	24	22	28	28	25	23	46	43	41	24	
25		Metallo graphic structure of hot stamped body	Grain size distribution standard deviation (µm)	1.2	1.2	1.1	1.4	1.4	1.2	1.3	2.8	2.5	2.5	1.3	
	nued)	phic structu	Former $\gamma$ grain average grain size $(\mu m)$	2.4	2.3	2.2	2.6	2.8	2.3	2.4	4.6	5.3	4.8	2.5	referable.
30	(continued)	Metallo gra	Martensite vol. ratio (%)	86	26	94	93	96	96	66	86	26	86	86	production conditions not preferable.
35			BH treat- ment	Yes	Yes	Yes	Yes	duction co							
40		6	Average cooling speed (°C/s)	234	225	18	125	133	124	119	98	115	145	113	
45		Hot stamping ste	Holding time (s)	1	2	2	1	2	2	-	1	2	1	1	resent inver
		Hot s	Heat treatment temp. (°C)	953	947	996	942	972	928	922	949	096	948	946	e scope of p
50			Average heating speed (°C/s)	150	150	150	150	150	125	125	150	85	150	150	Underlines indicate outside scope of present invention or
55			Steel	2	S	_	n	>	×	×	С	C	ш	ш	rlines ind
				31	32	33	34	35	36	37	38	39	40	41	Unde

[Table 4]

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		Remarks	Comp. ex.	Inv. ex.	Comp. ex.	Inv. ex.	Comp. ex.	
5	Properties of hot stamped body	Fracture load in hydrogen atmo- sphere (MPa)	488	624	265	641	461	
10	rties of hot body	TS (MPa)	2281	2342	2338	2322	2342	
	Prope	YS (MPa)	2012	2087	2091	1997	2111	
15	stamped	Hardness provision (%)	<u>78</u>	24	32	21	<u>98</u>	
20	Metallographic structure of hot stamped body	Grain size distribution tion standard deviation (µm)	2.4	1.3	2.2	1.2	2.7	
25	raphic struc bc	Former   y grain  average  grain  size  (µm)	4.2	2.6	3.9	2.4	5.1	
78 os a de 4	Metallog	Martensite vol.	63	26	26	86	26	oreferable.
<u> </u>		BH treat- ment	Yes	Yes	Yes	Yes	Yes	ditions not p
35		Average cooling speed (°C/s)	92	89	88	91	63	oduction conditions not preferable.
40	step	Holding time (s)	2	~	7	2	2	on or prod
	Hot stamping step	Heat treatment Holdii temp.	964	964	862	296	977	ent inventic
45	<u>9</u>	Average heating speed from T1 to heat treatment temp. (°C/s)	150	200	200	200	150	Underlines indicate outside scope of present invention or pr
50		Speed change temp. T1 (°C)	008	450	082	300	720	utside sco
		Average heating speed from room temp. to T1 (°C/s)	15	15	5	2	10	indicate ou
55		Steel	Α	C	С	F	F	rlines
[0104]		no .	42	43	44	45	46	Unde

[0105] The properties of the obtained hot stamped body were measured and evaluated by the following methods:

[Tensile Strength (TS) and Yield Strength (YS)]

**[0106]** The tensile strength (TS) and (YS) of the hot stamped body were obtained from any position of the hot stamped body by preparing a No. 5 test piece and conducting a tensile test based on JIS Z 2241: 2011. The crosshead speed was 1 mm/min.

[Hydrogen Embrittlement Resistance]

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[0107] The hydrogen embrittlement resistance of the hot stamped body was evaluated as follows by the slow strain rate technique (SSRT). First, a  $1.0t \times 9.0W \times 140L$  (mm) test piece was prepared. The test piece was made one of a parallel part length of 25 mm and a diameter of the parallel part of 2.0 mm. At the two sides of the center of the parallel part, U-notches each having a notch depth of 0.35 mm and a notch bottom radius of 0.1 mm were provided. This test piece was dipped in a 3% NaCl solution. Hydrogen was charged using a galvanostat as a power source and controlling the current density of a dipping portion of the test piece surface to become 0.1 mA/cm $^2$ . Next, the test piece charged with hydrogen was subjected to a slow strain rate test by a tensile rate of 0.0060 mm/min and the load at the time of fracture was investigated. Cases where such a fracture load in a hydrogen environment was 600 MPa or more were evaluated as passing and cases where the fracture load was less than 600 MPa were evaluated as failing.

**[0108]** Cases where the tensile strength (TS) was 2200 MPa or more, the yield strength (YS) was 1800 MPa or more, and the hydrogen embrittlement resistance was evaluated as passing were evaluated as a hot stamped body which is high in strength and able to suppress hydrogen embrittlement. The results are shown in Table 3. In Table 3, the volume ratio of martensite at a region of the hot stamped body centered about the 1/4 depth position of the sheet thickness and the average grain size and the standard deviation in the grain size distribution of the former austenite grains (former  $\gamma$  grains) are shown. Further, in Table 3, the ratio of the difference of the maximum value and minimum value in the Vickers hardness distribution in a sheet thickness direction with respect to the average value (hardness provision) is shown. In the hot stamped body shown in Table 3, the remaining structures besides the martensite were bainite, ferrite, retained austenite, and/or pearlite.

[0109] Referring to Tables 1 to 4, in Comparative Example 2, the average heating speed in the hot stamping step was slow, and therefore it is believed that recrystallization proceeded and the austenite nucleation sites were reduced. As a result, the desired increased fineness and increased uniformity could not be realized in the metallographic structure. In relation to this, the desired average grain size and standard deviation in the grain size distribution of the  $\gamma$  grains and the hardness provision could not be obtained and the hydrogen embrittlement resistance fell. In Comparative Example 3, the tempering step was not performed, and therefore it is believed austenite nucleation sites by precipitation of carbides could not be sufficiently formed. As a result, it was not possible to obtain the desired average grain size of the  $\gamma$  grains and hardness provision in the metallographic structure and the TS and the hydrogen embrittlement resistance fell. In Comparative Example 4, the cold rolling step was not performed, and therefore it was not possible to randomize the relative orientations of the austenite formed using the interfaces of carbides and substructures of martensite as nucleation sites and it is believed the austenite became easily connected. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the YS fell. In Comparative Example 6, the heat treatment temperature at the hot stamping step was low, and therefore the austenization became insufficient, the desired hard structures and hardness provision could not be realized, and the YS and hydrogen embrittlement resistance fell. In Comparative Example 7, the coiling temperature was high, and therefore it is believed it was not possible to form a metallographic structure mainly comprised of martensite at the hot rolled steel sheet after coiling. As a result, it was not possible to achieve the desired increased fineness and increased uniformity in the metallographic structure of the finally obtained hot stamped body and the YS fell.

**[0110]** In Comparative Example 9, the tempering temperature was high, and therefore it is believed the precipitated carbides became coarser. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the YS fell. On the other hand, in Comparative Example 10, the tempering temperature was low, and therefore it is believed that carbides could not be made to sufficiently precipitate. As a result, similarly, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In Comparative Example 11, the holding time at the hot stamping step was long, and therefore it is believed the austenite excessively grew in size. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In Comparative Example 12, the average heating speed at the hot stamping step was slow and the holding time was also long, and therefore it is believed recrystallization proceeded and austenite nucleation sites were reduced and further the austenite formed excessively grew in size. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In

Comparative Example 14, the heat treatment temperature at the hot stamping step was high, and therefore it is believed that the austenite excessively grew in size. As a result, it was not possible to realize the desired increased fineness and uniformity of grains in the metallographic structure and the hydrogen embrittlement resistance fell. In Comparative Example 15, the average cooling speed at the hot stamping step was slow, and therefore the volume ratio of the martensite in the metallographic structure greatly fell. For this reason, it was not possible to suitably measure the average grain size of the  $\gamma$  grains, the standard deviation in the grain size distribution, and the hardness provision by the methods prescribed in the Description. Further, the YS and TS also greatly fell. In each of Comparative Examples 18 to 20, the C content was low, and therefore the YS and TS fell. In Comparative Example 22, the coiling temperature was high, and therefore it is believed that it was not possible to form a metallographic structure mainly comprised of martensite in the hot rolled steel sheet after coiling. As a result, in the finally obtained hot stamped body, it was not possible to realize the desired hard structures and prescribed hardness in the metallographic structure and the YS and TS fell. In Comparative Example 24, the heat treatment temperature at the hot stamping step was low, and therefore the austenization became insufficient, the desired hard structures and hardness provision could not be realized, and the YS and TS fell.

[0111] In Comparative Example 38, the average cooling speed after finish rolling at the hot rolling step was slow, and therefore it is believed it was not possible to form a metallographic structure mainly comprised of martensite in the hot rolled steel sheet after coiling. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In Comparative Example 39, the average heating speed at the hot stamping step was low, and therefore it is believed that recrystallization proceeded and austenite nucleation sites were reduced or eliminated. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In Comparative Example 40, the rolling reduction of the cold rolling was low, and therefore it is believed that it was not possible to randomize the relative orientations of the austenite formed using interfaces between the carbides and substructures of martensite as nucleation sites and it is believed the austenite became easily connected. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell. In each of Comparative Examples 42, 44, and 46, the heating start temperature at an average heating speed of more than 100°C/s at the hot stamping step (speed change temperature T1 in Table 4) was higher than 600°C, and therefore it is believed that recrystallization proceeded and austenite nucleation sites were reduced or eliminated. As a result, it was not possible to realize the desired increased fineness and increased uniformity in the metallographic structure and the hydrogen embrittlement resistance fell.

[0112] In contrast to this, in the hot stamped bodies according to all of the invention examples, by having the desired chemical composition and a metallographic structure comprised of 90 vol% or more of martensite and making the former austenite grains finer to reduce the average grain size to 3.0  $\mu$ m or less and controlling the standard deviation in grain size distribution to 1.5  $\mu$ m or less to make the grains more uniform and, in relation to this, controlling the difference of the maximum value and minimum value in the Vickers hardness distribution in the sheet thickness direction to 35% or less of the average value of the Vickers hardness distribution, regardless of having a 2200 MPa or more high tensile strength and a 1800 MPa or more high yield strength due to the high C content and martensite volume ratio, etc., it was possible to achieve a 600 MPa or more high fracture load and therefore possible to realize an excellent hydrogen embrittlement resistance.

Claims

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1. A hot stamped body having a chemical composition comprising, by mass%,

45 C: 0.40 to 0.70%. Si: 0.01 to 1.30%, Mn: 0.05 to 3.00%, P: 0.100% or less, S: 0.0100% or less, 50 N: 0.0200% or less, O: 0.0200% or less. Al: 0.001 to 1.000%, Cr: 0.01 to 1.00%. Nb: 0 to 0.200%, 55 Ti: 0 to 0.200%. Mo: 0 to 1.00%, B: 0 to 0.1000%,

Co: 0 to 4.00%,

Ni: 0 to 3.00%, Cu: 0 to 3.00%, V: 0 to 3.00%, W: 0 to 1.00%, Ca: 0 to 1.000%, 5 Mg: 0 to 1.000%, REM: 0 to 1.000%, Sb: 0 to 1.000%, Zr: 0 to 1.000%, 10 Sn: 0 to 1.000%, As: 0 to 0.100%, and balance: Fe and impurities, and a metallographic structure comprising, by volume ratio, martensite in 90% or more, wherein an average grain size of former austenite grains is 3.0 μm or less, 15 a standard deviation in grain size distribution of former austenite grains is 1.5 μm or less, and a difference of a maximum value and a minimum value in a Vickers hardness distribution in a sheet thickness direction is 35% or less of an average value of the Vickers hardness distribution. 2. The hot stamped body according to claim 1, wherein the chemical composition contains, by mass%, one or more 20 selected from the group consisting of Nb: 0.001 to 0.200%, Ti: 0.001 to 0.200%, Mo: 0.001 to 1.00%, 25 B: 0.0001 to 0.1000%, Co: 0.001 to 4.00%. Ni: 0.001 to 3.00%, Cu: 0.001 to 3.00%, V: 0.001 to 3.00%, 30 W: 0.001 to 1.00%, Ca: 0.0001 to 1.000%, Mg: 0.0001 to 1.000%, REM: 0.0001 to 1.000%, Sb: 0.001 to 1.000%, 35 Zr: 0.001 to 1.000%, Sn: 0.001 to 1.000%, and As: 0.001 to 0.100%. 40 45 50

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/003401

	SSIFICATION OF SUBJECT MATTER				
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	<b>9/00</b> (2006.01)i; <b>C21D 9/46</b> (2006.01)i; <b>C22C 38/00</b> (2 C22C38/00 301Z; C22C38/60; C21D1/18 C; C21D9/0		<b>/18</b> (2006.01)i		
According to	International Patent Classification (IPC) or to both na	ational classification and IPC			
B. FIEL	DS SEARCHED				
Minimum de	ocumentation searched (classification system followed	by classification symbols)			
C21D	9/00; C21D9/46; C22C38/00; C22C38/60; C21D1/18				
Documentat	on searched other than minimum documentation to th	e extent that such documents are included	in the fields searched		
Publis Regist	hed examined utility model applications of Japan 192, hed unexamined utility model applications of Japan 19 ered utility model specifications of Japan 1996-2023 hed registered utility model applications of Japan 199	971-2023			
Electronic da	ata base consulted during the international search (nan	ne of data base and, where practicable, sear	ch terms used)		
C. DOC	UMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where	appropriate, of the relevant passages	Relevant to claim No.		
A	WO 2021/162084 A1 (NIPPON STEEL CORP.) 19	August 2021 (2021-08-19)	1-2		
A	WO 2020/158285 A1 (JFE STEEL CORP.) 06 Aug	ust 2020 (2020-08-06)	1-2		
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	locuments are listed in the continuation of Box C.	See patent family annex.			
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# INTERNATIONAL SEARCH REPORT Information on patent family members Description of the publication date (day/month/year) Patent family member(s) International application No. PCT/JP2023/003401 Publication date (day/month/year)

Pat cited	ent document in search report		Publication date (day/month/year)	P	atent family member	r(s)	Publication date (day/month/year)
WO	2021/162084	A1	19 August 2021	KR	10-2022-0124789	A	
				CN	115087755	Α	
WO	2020/158285	A1	06 August 2020	US	2022/0118741	A1	
				EP	3919645	A1	
				CN	113366135	A	
				KR	10-2021-0107806	A	

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#### REFERENCES CITED IN THE DESCRIPTION

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## Patent documents cited in the description

- JP 2020012173 A [0007]
- WO 2019186928 A [0007]

• WO 2019186927 A [0007]

## Non-patent literature cited in the description

Acta Materialia, 2010, vol. 58, 6393-6403 [0077]