



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

(43) Date of publication:
16.10.2024 Bulletin 2024/42

(21) Application number: **22904727.9**

(22) Date of filing: **12.12.2022**

(51) International Patent Classification (IPC):
C22C 38/38 ^(2006.01) **C22C 38/32** ^(2006.01)
C22C 38/28 ^(2006.01) **C22C 38/26** ^(2006.01)
C22C 38/24 ^(2006.01) **B21D 22/02** ^(2006.01)

(52) Cooperative Patent Classification (CPC):
B21D 22/02; C22C 38/24; C22C 38/26;
C22C 38/28; C22C 38/32; C22C 38/38

(86) International application number:
PCT/KR2022/020148

(87) International publication number:
WO 2023/106898 (15.06.2023 Gazette 2023/24)

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

(30) Priority: **10.12.2021 KR 20210176999**

(71) Applicant: **Hyundai Steel Company**
Incheon 22525 (KR)

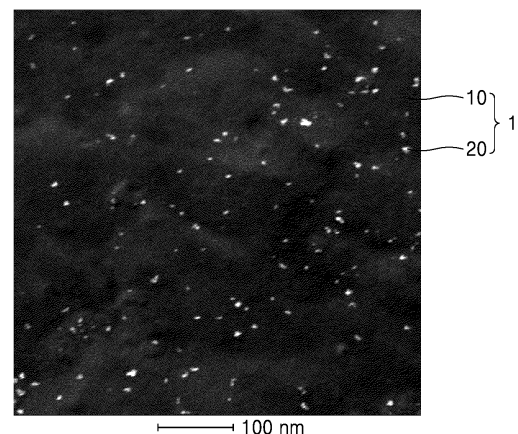
(72) Inventors:
• **SHIN, Nu Ri**
Incheon 22525 (KR)
• **SEO, Yong Ki**
Incheon 22525 (KR)
• **SON, Ji Hee**
Incheon 22525 (KR)
• **JUNG, Sang Bae**
Incheon 22525 (KR)

(74) Representative: **Viering, Jentschura & Partner**
mbB
Patent- und Rechtsanwälte
Am Brauhaus 8
01099 Dresden (DE)

(54) **MATERIAL FOR HOT STAMPING**

(57) The present disclosure provides a material for hot stamping including: a steel sheet including carbon (C) in an amount of 0.19 to 0.25 wt%, silicon (Si) in an amount of 0.1 to 0.6 wt%, manganese (Mn) in an amount of 0.8 to 1.6 wt%, phosphorus (P) in an amount of 0.03 wt% or less, sulfur (S) in an amount of 0.015 wt% or less, chromium (Cr) in an amount of 0.1 to 0.6 wt%, boron (B) in an amount of 0.001 to 0.005 wt%, an additive in an amount of 0.1 wt% or less, a remainder of iron (Fe), and other inevitable impurities; fine precipitates distributed inside the steel sheet, wherein the additive includes at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates include nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates trap hydrogen, and a mean diameter variation coefficient, which is a value obtained by dividing a standard deviation of a mean diameter of the fine precipitates by the mean diameter of the fine precipitates, is 0.8 or less.

FIG. 1



Description

Technical Field

5 **[0001]** Embodiments of the present disclosure relate to a material for hot stamping, and more particularly, a material for hot stamping capable of providing a hot stamping part with high-quality mechanical characteristics and hydrogen-delayed fracture characteristics, and a method of manufacturing the material.

Background Art

10 **[0002]** High-strength steel is applied to lightweight and strong parts for automobiles, etc. High-strength steel may provide high strength characteristics compared to its weight, however, as the strength increases, press formability decreases, and thus, a material may break or a spring back phenomenon may occur during a manufacturing process, making it difficult to precisely form a product having a complex shape.

15 **[0003]** A representative method for addressing these issues is the hot stamping method, and as interest in this method increases, research on materials for hot stamping has been actively conducted. For example, as disclosed in Korean Patent Publication No. 10-2017-0076009, the hot stamping method is molding technology in which a boron steel sheet is heated to an appropriate temperature, formed in a press mold, and then rapidly cooled to manufacture a high-strength part. According to Korean Patent Publication No. 10-2017-0076009, cracks, poor shape freezing, or the like occurring
20 in a high-strength steel sheet during forming may be suppressed, making it possible to manufacture a part with high precision.

[0004] However, in a hot stamping steel sheet, hydrogen-delayed fracture occurs due to hydrogen and residual stress introduced in a hot stamping process. In relation to this, Korean Patent Publication No. 10-2020-0061922 discloses that preheating is performed before heating a hot stamping blank to a high temperature so as to form a thin oxide layer on
25 a surface of the blank, thereby blocking the inflow of hydrogen in a high-temperature heating process to minimize hydrogen-delayed fracture. However, because it is impossible to completely block the inflow of hydrogen, introduced hydrogen may not be controlled, resulting in hydrogen-delayed fracture.

Disclosure

30 **[0005]** Embodiments of the present disclosure are intended to solve various issues including the foregoing, and may provide a material for hot stamping that may secure excellent mechanical characteristics with high strength and high toughness, and improved hydrogen-delayed fracture characteristics of a hot stamping part. However, this objective is merely illustrative, and the scope of the present disclosure is not limited thereto.

Technical Solution

40 **[0006]** A material for hot stamping according to an embodiment of the present disclosure includes: a steel sheet including carbon (C) in an amount of 0.19 to 0.25 wt%, silicon (Si) in an amount of 0.1 to 0.6 wt%, manganese (Mn) in an amount of 0.8 to 1.6 wt%, phosphorus (P) in an amount of 0.03 wt% or less, sulfur (S) in an amount of 0.015 wt% or less, chromium (Cr) in an amount of 0.1 to 0.6 wt%, boron (B) in an amount of 0.001 to 0.005 wt%, an additive in an amount of 0.1 wt% or less, a remainder of iron (Fe), and other inevitable impurities; fine precipitates distributed inside
45 the steel sheet, wherein the additive includes at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates include nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates trap hydrogen, and a mean diameter variation coefficient, which is a value obtained by dividing a standard deviation of a mean diameter of the fine precipitates by the mean diameter of the fine precipitates, is 0.8 or less.

[0007] The material after hot stamping may exhibit a tensile strength of 1,350 MPa or greater, a bending angle of 50
50 degrees or greater, and an amount of activated hydrogen of 0.8 wppm or less.

[0008] The mean diameter of the fine precipitates may be 0.007 μm or less.

[0009] 60 % or greater of the fine precipitates may have a diameter of 0.01 μm or less.

[0010] 25 % or greater of the fine precipitates may have a diameter of 0.005 μm or less.

[0011] The number of the fine precipitates per unit area (100 μm^2) may be 7,000 to 16,500.

55 **[0012]** The number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.01 μm or less may be 4,500 to 16,000.

[0013] The number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.005 μm or less may be 1,755 to 16,000.

[0014] A number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of the fine precipitates by the mean number of the fine precipitates, may be 0.95 or less.

[0015] A material for hot stamping according to an embodiment of the present disclosure includes: a steel sheet including carbon (C) in an amount of 0.19 to 0.25 wt%, silicon (Si) in an amount of 0.1 to 0.6 wt%, manganese (Mn) in an amount of 0.8 to 1.6 wt%, phosphorus (P) in an amount of 0.03 wt% or less, sulfur (S) in an amount of 0.015 wt% or less, chromium (Cr) in an amount of 0.1 to 0.6 wt%, boron (B) in an amount of 0.001 to 0.005 wt%, an additive in an amount of 0.1 wt% or less, a remainder of iron (Fe), and other inevitable impurities; fine precipitates distributed inside the steel sheet, wherein the additive includes at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates include nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates trap hydrogen, and a number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of the fine precipitates by the mean number of the fine precipitates, is 0.95 or less.

[0016] The material after hot stamping may exhibit a tensile strength of 1,350 MPa or greater, a bending angle of 50 degrees or greater, and an amount of activated hydrogen of 0.8 wppm or less.

[0017] A first number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of the fine precipitates having a diameter of 0.01 μm or less from among the fine precipitates, by the mean number of the fine precipitates having a diameter of 0.01 μm or less, may be 0.95 or less.

[0018] A second number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of the fine precipitates having a diameter of 0.005 μm or less from among the fine precipitates, by the mean number of the fine precipitates having a diameter of 0.005 μm or less, may be 0.95 or less.

[0019] The number of the fine precipitates per unit area (100 μm^2) may be 7,000 to 16,500.

[0020] The number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.01 μm or less may be 4,500 to 16,000.

[0021] The number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.005 μm or less may be 1,755 to 16,000.

[0022] The mean diameter of the fine precipitates may be 0.007 μm or less.

[0023] 60 % or greater of the fine precipitates may have a diameter of 0.01 μm or less.

[0024] 25 % or greater of the fine precipitates may have a diameter of 0.005 μm or less.

Advantageous Effects

[0025] According to embodiments of the present disclosure, it is possible to implement a material for hot stamping that may secure excellent mechanical characteristics with high strength and high toughness, and improved hydrogen-delayed fracture characteristics of a hot stamping part. However, the scope of the present disclosure is not limited by the above effect.

Description of Drawings

[0026]

FIG. 1 is a transmission electron microscopy (TEM) image of a portion of a material for hot stamping according to an embodiment of the present disclosure.

FIGS. 2A and 2B are diagrams schematically illustrating a portion of a state in which fine precipitates are dispersed, according to an embodiment of the present disclosure.

FIGS. 3A and 3B are example diagrams schematically illustrating a portion of a state in which hydrogen is trapped in fine precipitates.

FIG. 4 is a flowchart schematically showing a method of manufacturing a material for hot stamping, according to an embodiment of the present disclosure.

FIG. 5 is a graph showing a comparison of tensile strength and bending stress of an embodiment and a comparative example according to coiling temperature.

FIGS. 6A and 6B are images showing results of a 4-point bending test on an embodiment and a comparative example according to coiling temperature.

Mode for Invention

[0027] As the present disclosure allows for various changes and numerous embodiments, particular embodiments will be illustrated in the drawings and described in detail. Advantages and features of the present disclosure and a method of achieving the same should become clear with embodiments described below in detail with reference to the drawings. However, the present disclosure is not limited to the embodiments disclosed below, but may be implemented in various

forms.

[0028] Hereinafter, embodiments will be described in detail with reference to the accompanying drawings, and the same or corresponding components will be denoted by the same reference numerals when described with reference to the accompanying drawings, and thus, their descriptions that are already provided will be omitted.

[0029] In the following embodiments, terms such as "first," "second," etc., are used only to distinguish one component from another, and such components must not be limited by these terms.

[0030] In the following embodiments, the singular expression also includes the plural meaning as long as it is not inconsistent with the context.

[0031] In the following embodiments, the terms "comprises," "includes," "has", and the like used herein specify the presence of stated features or components, but do not preclude the presence or addition of one or more other features or components.

[0032] In the following embodiments, when a layer, region, or component is referred to as being "on" another layer, region, or component, it may be directly or indirectly on the other layer, region, or component, that is, one or more intervening layers, regions, or components may be present therebetween.

[0033] For convenience of description, the magnitude of components in the drawings may be exaggerated or reduced. For example, since the size and thickness of each component illustrated in the drawing are arbitrarily shown for convenience of description, the present disclosure is not necessarily limited to those illustrated in the drawing.

[0034] In a case in which a particular embodiment is realized otherwise, a particular process may be performed out of the order described. For example, two processes, which are successively described herein, may be substantially simultaneously performed, or may be performed in a process sequence opposite to a described process sequence.

[0035] In the present specification, "A and/or B" indicates A, B, or both A and B. In addition, "at least one of A and B" indicates A, B, or both A and B.

[0036] In the following embodiments, when a layer, region, or component is referred to as being connected to another layer, region, or component, they may be directly connected to each other, and/or may be indirectly connected to each other with still another layer, region, or component therebetween. In the present specification, for example, when a layer, region, or component is referred to as being electrically connected to another layer, region, or component, they may be directly electrically connected to each other, and/or may be indirectly electrically connected to each other with still another layer, region, or component therebetween.

[0037] Hereinafter, embodiments of the present disclosure will be described in detail with reference to the accompanying drawings.

[0038] FIG. 1 is a transmission electron microscopy (TEM) image of a portion of a material for hot stamping according to an embodiment of the present disclosure.

[0039] As shown in FIG. 1, a material 1 for hot stamping according to an embodiment of the present disclosure may include a steel sheet 10 and fine precipitates 20 distributed in the steel sheet 10.

[0040] The material 1 for hot stamping may be controlled such that the content of alloy elements included in the steel sheet 10, and the precipitation behavior of the fine precipitates 20 satisfy preset conditions. Accordingly, a formed part after hot stamping may have excellent mechanical characteristics with high strength and high toughness, and improved hydrogen-delayed fracture characteristics. In an embodiment, after hot stamping, the material 1 for hot stamping may exhibit a tensile strength of 1,350 MPa or greater, and preferably, may exhibit a tensile strength of 1,350 MPa or greater but less than 1,650 MPa. In addition, it may exhibit a bending angle of 50 degrees or greater, and an amount of activated hydrogen of 0.8 wppm or less. Here, "bending angle" may refer to a V-bending angle in a rolling direction (RD).

[0041] The steel sheet 10 may be a steel sheet manufactured by performing a hot rolling process and/or a cold rolling process on a slab that is cast to include a certain alloy element in a certain content. The steel sheet 10 may include carbon (C), silicon (Si), manganese (Mn), phosphorus (P), sulfur (S), chromium (Cr), boron (B), the remainder of iron (Fe), and other inevitable impurities. In addition, in an embodiment, the steel sheet 10 may further include, as an additive, at least one of titanium (Ti), niobium (Nb), and vanadium (V). Alternatively, the steel sheet 10 may further include calcium (Ca) in a certain content.

[0042] In an embodiment, the steel sheet 10 may include 0.19 to 0.25 wt% of carbon (C), 0.1 to 0.6 wt% of silicon (Si), 0.8 to 1.6 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P), 0.015 wt% or less of sulfur (S), 0.1 to 0.6 wt% of chromium (Cr), 0.001 to 0.005 wt% of boron (B), 0.1 wt% or less of the sum of one or more of titanium (Ti), niobium (Nb), and vanadium (V) as an additive, the remainder of iron (Fe), and other inevitable impurities.

[0043] Carbon (C) may act as an austenite stabilizing element in the steel sheet 10. Carbon is a major element that determines the strength and hardness of the steel sheet 10, and, after a hot stamping process, may be added to secure the tensile strength of the steel sheet 10 (e.g., a tensile strength of 1,350 MPa or greater) and secure hardenability characteristics. Carbon as described above may be included in an amount of about 0.19 wt% to about 0.25 wt% with respect to the total weight of the steel sheet 10. When the content of carbon is less than about 0.19 wt%, it may be difficult to secure a hard phase (martensite or the like), and thus, it may be difficult to secure the mechanical strength of the steel sheet 10. On the contrary, when the content of carbon is greater than about 0.25 wt%, brittleness may occur

in the steel sheet 10 or bending performance of the steel sheet 10 may be reduced.

[0044] Silicon (Si) may act as a ferrite stabilizing element in the steel sheet 10. Silicon (Si) is a solid solution strengthening element, may improve the ductility of the steel sheet 10, and improve the concentration of carbon in austenite by suppressing the formation of a low-temperature range carbide. In addition, silicon may be a key element in hot rolling, cold rolling, and hot pressing structure homogenization (perlite, manganese segregation control) and ferrite fine dispersion. Silicon may act as a martensitic strength heterogeneity control element to improve crashworthiness. Silicon may be included in an amount of about 0.1 wt% to about 0.6 wt% with respect to the total weight of the steel sheet 10. When the content of silicon is less than about 0.1 wt%, the above effect is difficult to obtain, cementite formation and coarsening may occur in the final hot stamping martensitic structure, and the homogenization effect of the steel sheet 10 is insignificant, and a V-bending angle may not be secured. On the contrary, when the content of silicon is greater than about 0.6 wt%, hot rolling and cold rolling loads increase, a hot-rolling red scale becomes excessive, and plating characteristics of the steel sheet 10 may deteriorate.

[0045] Manganese (Mn) may act as an austenite stabilizing element in the steel sheet 10. Manganese is added to increase hardenability and strength during heat treatment. Manganese may be included in an amount of about 0.8 wt% to about 1.6 wt% with respect to the total weight of the steel sheet 10. When the content of manganese is less than about 0.8 wt%, a grain refinement effect is insufficient, and thus, a hard phase fraction in a formed product after hot stamping may be insufficient due to insufficient hardenability. On the contrary, when the content of manganese is greater than about 1.6 wt%, ductility and toughness may be reduced due to manganese segregation or a pearlite band, causing a decrease in bending performance and generating an inhomogeneous microstructure.

[0046] Phosphorus (P) may be included in an amount of about 0.03 wt% or less with respect to the total weight of the steel sheet 10 to prevent a decrease in the toughness of the steel sheet 10. When the content of phosphorus is greater than about 0.03 wt%, an iron phosphide compound may be formed to reduce the toughness and weldability, and cracks may be generated in the steel sheet 10 during a manufacturing process.

[0047] Sulfur (S) may be included in an amount about 0.015 wt% or less with respect to the total weight of the steel sheet 10. When the content of sulfur is greater than about 0.015 wt %, hot workability, weldability, and impact characteristics may deteriorate, and a surface defect such as cracks may occur due to formation of a large inclusion.

[0048] Chromium (Cr) may be added to improve the hardenability and strength of the steel sheet 10. Chromium may enable grain refinement and strength to be secured through precipitation hardening. Chromium may be included in an amount of about 0.1 wt% to 0.6 wt% with respect to the total weight of the steel sheet 10. When the content of chromium is less than about 0.1 wt %, the precipitation hardening effect is poor, and on the contrary, when the content of chromium is greater than 0.6 wt%, Cr-based precipitates and matrix solid solution increase, and thus, the toughness may deteriorate and the production costs may increase due to an increase in the cost of raw materials.

[0049] Boron (B) may be added to secure the hardenability and strength of the steel sheet 10 by suppressing the transformation of ferrite, pearlite and bainite to secure a martensitic structure. Boron may be segregated at a grain boundary to lower grain boundary energy to increase the hardenability, and increase an austenite grain growth temperature to have a grain refinement effect. Boron may be included in an amount of about 0.001 wt% to 0.005 wt% with respect to the total weight of the steel sheet 10. When boron is included in the above range, the occurrence of hard grain boundary brittleness may be prevented, and high toughness and bendability may be secured. When the content of boron is less than about 0.001 wt%, a hardenability effect may be insufficient, and on the contrary, when the content of boron is greater than about 0.005 wt%, boron has low solid solubility, and thus is easily precipitated at the grain boundary according to heat treatment conditions, thereby deteriorating the hardenability or causing high-temperature embrittlement and causing hard grain boundary brittleness to decrease the toughness and bendability.

[0050] The additive may be a nitride- or carbide-forming element that contributes to the formation of the fine precipitates 20. In detail, the additive may include at least one of titanium (Ti), niobium (Nb), and vanadium (V). Titanium (Ti), niobium (Nb), and vanadium (V) may secure the strength of a hot-stamped and quenched material by forming the fine precipitates 20 in the form of nitride or carbide. In addition, they may be contained in Fe-Mn-based composite oxide, may function as a hydrogen trap site effective for improving delayed fracture resistance characteristics, and may be elements necessary for improving the delayed fracture resistance characteristics. The additive may be included in a total amount of about 0.1 wt% or less with respect to the total weight of the steel sheet 10. When the content of the additive is greater than about 0.1 wt%, the yield strength may excessively increase.

[0051] Titanium (Ti) may be added to strengthen hardenability and improve a material by forming precipitates after hot-pressing heat treatment. In addition, titanium (Ti) may effectively contribute to refinement of austenite grains by forming a precipitated phase such as Ti(C, N) at a high temperature. Titanium may be included in an amount of about 0.010 wt% to about 0.050 wt% with respect to the total weight of the steel sheet 10. When titanium is included in the above content range, poor continuous casting and coarsening of precipitates may be prevented, the physical characteristics of steel may be easily secured, and defects such as the occurrence of cracks in the surface of the steel may be prevented. On the contrary, when the content of titanium is greater than about 0.050 wt%, precipitates may be coarsened, resulting in a decrease in elongation and bendability.

[0052] Niobium (Nb) and vanadium (V) may be added to increase strength and toughness according to a decrease in a martensite packet size. Each of niobium and vanadium may be included in an amount of about 0.010 wt% to about 0.050 wt% with respect to the total weight of the steel sheet 10. When niobium and vanadium are included in the above range, steel has an excellent grain refinement effect in hot rolling and cold rolling processes, the occurrence of cracks in a slab and brittle fracture of a product during steel-making/continuous casting may be prevented, and the formation of steel-making coarse precipitates may be minimized.

[0053] Calcium (Ca) may be added to control the shape of an inclusion. Calcium may be included in an amount of about 0.003 wt% or less with respect to the total weight of the steel sheet 10.

[0054] The fine precipitates 20 may be distributed in the steel sheet 10 to trap hydrogen. That is, the fine precipitates 20 may improve hydrogen-delayed fracture characteristics of a hot stamped product by providing a trap site for hydrogen introduced during or after manufacturing of the material 1 for hot stamping. In an embodiment, the fine precipitates 20 may include nitride or carbide of the additive. In detail, the fine precipitates 20 may include nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V).

[0055] A precipitation behavior of the fine precipitates 20 may be controlled by adjusting process conditions. For example, a precipitation behavior such as the number of fine precipitates 20, a mean distance between the fine precipitates 20 or the diameters of the fine precipitates 20 may be controlled by adjusting a coiling temperature (CT) range from among the process conditions. The process conditions will be described in detail below with reference to FIG. 4.

[0056] The precipitation behavior of the fine precipitates 20 may be controlled to satisfy preset conditions. In addition, a precipitation behavior of the fine precipitates 20 may be controlled through process conditions (e.g., a coiling temperature (CT) range). For example, the number of fine precipitates 20 per unit area, a number variation coefficient C1 indicating the uniformity of the distribution of the numbers of fine precipitates 20 per unit area, a mean distance between the fine precipitates 20, the diameters of the fine precipitates 20, mean diameter variation coefficients C2, C21, and C22 indicating the uniformity of the distribution of diameters per unit area, and the like may be controlled to satisfy preset conditions. A detailed description of the process conditions will be described below with reference to FIGS. 4 and 5. Precipitation behavior conditions regarding the number variation coefficient C1 and the mean diameter variation coefficients C2, C21, and C22 will be described in more detail below with an embodiment and a comparative example.

[0057] Meanwhile, a precipitation behavior of the fine precipitates 20 may be measured by analyzing a TEM image. In detail, TEM images for arbitrary regions as many as a predetermined number may be obtained for a specimen, the fine precipitates 20 may be extracted from the obtained images through an image analysis program or the like, and the number of fine precipitates 20, a mean distance between the fine precipitates 20, the diameter of the fine precipitates 20, and the like may be measured for the extracted fine precipitates 20.

[0058] In an embodiment, a surface replication method may be applied as pretreatment to a specimen to be measured to measure the precipitation behavior of the fine precipitates 20. For example, a first-step replica method, a second-step replica method, an extraction replica method, or the like may be applied, but the present disclosure is not limited to the above-described examples.

[0059] Alternatively, when measuring the diameters of the fine precipitates 20, by considering the nonuniformity of the shapes of the fine precipitates 20, the shapes of the fine precipitates 20 may be converted into a circle to calculate the diameter of the fine precipitates 20. In detail, the area of the fine precipitates 20 extracted by using a unit pixel having a particular area may be measured, the fine precipitates 20 may be converted into a circle having the same area as the measured area, and then the diameter of the fine precipitates 20 may be calculated.

[0060] Alternatively, the mean distance between the fine precipitates 20 may be measured through a mean free path. In detail, the mean distance between the fine precipitates 20 may be calculated by using a particle area fraction and the number of particles per unit length. For example, the mean distance between the fine precipitates 20 may have a correlation as in Equation 1 below.

[Equation 1]

$$\lambda = (1 - AA) / NL$$

[0061] In Equation 1, λ denotes a mean distance between particles, AA denotes a particle area fraction, and NL denotes the number of particles per unit length.

[0062] The method of measuring a precipitation behavior of the fine precipitates 20 is not limited to the above-described example, and various methods may be applied.

[0063] The precipitation behavior of the fine precipitates 20 has a significant impact on the mechanical characteristics and hydrogen-delayed fracture characteristics of a formed part after hot stamping. Hereinafter, a difference in the effect of improving mechanical characteristics and hydrogen-delayed fracture characteristics of a formed part after hot stamping according to the precipitation behavior of the fine precipitates 20 will be described with reference to FIGS. 2A to 3B.

[0064] FIGS. 2A and 2B are diagrams schematically illustrating a portion of a state in which fine precipitates are dispersed, according to an embodiment of the present disclosure.

[0065] In detail, FIG. 2A illustrates a case in which the sizes and distribution of the fine precipitates 20 dispersed inside the steel sheet 10 are relatively nonuniform, and FIG. 2B illustrates a case in which the sizes and distribution of the fine precipitates 20 dispersed inside the steel sheet 10 are relatively uniform.

[0066] Referring to FIG. 2A, the fine precipitates 20 are dispersed nonuniformly and biasedly inside the steel sheet 10. Accordingly, there may be a region inside the steel sheet 10 where a relatively large number of fine precipitates 20 are aggregated. In addition, relatively more defects (e.g., dislocations) may be aggregated in a region where a relatively large number of fine precipitates 20 are aggregated. In addition, when the sizes of the fine precipitates 20 are not uniform as illustrated in FIG. 2A, relatively more defects (e.g., dislocations) may be aggregated in relatively large fine precipitates 20. That is, defects may also be distributed nonuniformly and biasedly inside the steel sheet 10.

[0067] As such, when relatively more defects (e.g., dislocations) are aggregated in a particular region, the region may act as a fracture notch, causing nonuniform stress distribution and stress concentration, and thus deteriorate mechanical characteristics such as strength and bendability.

[0068] On the contrary, referring to FIG. 2B, fine precipitates 20 that are relatively uniform in size are evenly dispersed inside the steel sheet 10. Accordingly, defects (e.g., dislocations) may be relatively uniformly distributed inside the steel sheet 10, and the occurrence of a region acting as the above-mentioned notch may be minimized or prevented.

[0069] In an embodiment, the number of fine precipitates 20 per unit area dispersed inside the steel sheet 10 may be controlled to satisfy a preset range. In detail, the number of fine precipitates 20 per unit area ($100 \mu\text{m}^2$) dispersed inside the steel sheet 10 may be 7,000 to 16,500. That is, the fine precipitates 20 may be formed inside the steel sheet 10 in an amount of 7,000 pieces/ $100 \mu\text{m}^2$ to 16,500 pieces/ $100 \mu\text{m}^2$.

[0070] In addition, from among the fine precipitates 20 dispersed inside the steel sheet 10, the number of fine precipitates 20 per unit area ($100 \mu\text{m}^2$) having a diameter of $0.01 \mu\text{m}$ or less may be 4,500 to 16,000. That is, the fine precipitates 20 may be formed inside the steel sheet 10 in an amount of 4,500 pieces/ $100 \mu\text{m}^2$ to 16,000 pieces/ $100 \mu\text{m}^2$.

[0071] In addition, from among the fine precipitates 20 dispersed inside the steel sheet 10, the number of fine precipitates 20 per unit area ($100 \mu\text{m}^2$) having a diameter of $0.005 \mu\text{m}$ or less may be 1,755 to 16,000. That is, the fine precipitates 20 may be formed inside the steel sheet 10 in an amount of 1,755 pieces/ $100 \mu\text{m}^2$ to 16,000 pieces/ $100 \mu\text{m}^2$.

[0072] When the number of fine precipitates 20 per unit area satisfies the above-described ranges, a tensile strength required after hot stamping (e.g., about 1,350 MPa or greater) may be secured and formability or bendability may be improved. For example, when the number of fine precipitates 20 is less than 7,000/ $100 \mu\text{m}^2$, when the number of fine precipitates 20 having a diameter of $0.01 \mu\text{m}$ or less is less than 4,500/ $100 \mu\text{m}^2$, or when the number of fine precipitates 20 having a diameter of $0.005 \mu\text{m}$ or less is less than 1,755/ $100 \mu\text{m}^2$, the strength may deteriorate. On the contrary, when the number of fine precipitates 20 is greater than 16,500/ $100 \mu\text{m}^2$, when the number of fine precipitates 20 having a diameter of $0.01 \mu\text{m}$ or less is greater than 16,000/ $100 \mu\text{m}^2$, or when the number of fine precipitates 20 having a diameter of $0.005 \mu\text{m}$ or less is greater than 116,000/ $100 \mu\text{m}^2$, formability or bendability may deteriorate.

[0073] Hereinafter, a variation coefficient of a mean number indicating the uniformity of the distribution of the numbers of all fine precipitates per unit area ($100 \mu\text{m}^2$), and numbers of fine precipitates by size (diameter) may be referred to as a second variation coefficient C2. The second variation coefficient C2 may be defined as the standard deviation of the mean number divided by the mean number. In an embodiment, the second variation coefficient C2 may be about 0.95 or less. When the second variation coefficient C2 is greater than about 0.95, bendability may deteriorate. In detail, when the distribution of the numbers of fine precipitates is nonuniform, the increase in density of block boundaries through refinement of a prior austenite grain size (PAGS) in a region where fine precipitates are less distributed is reduced, and accordingly, it is difficult to secure a sufficient slip band. Thus, when the second variation coefficient C2 is greater than about 0.95, formability and bendability may deteriorate. A precipitation behavior regarding the number distribution through the second variation coefficient C2 will be explained in more detail through a comparative example and an embodiment to be described below.

[0074] In an embodiment, the mean distance between adjacent fine precipitates 20 may be controlled to satisfy a preset range. Here, "mean distance" may refer to a mean free path of the fine precipitates 20, and a method of measuring a mean distance will be described in detail below.

[0075] In detail, the mean distance between the fine precipitates 20 may be about $0.4 \mu\text{m}$ to about $0.8 \mu\text{m}$. When the mean distance between the fine precipitates 20 is less than about $0.4 \mu\text{m}$, formability or bendability may deteriorate, whereas when the mean distance is greater than about $0.8 \mu\text{m}$, strength may deteriorate.

[0076] The diameter of the fine precipitates 20 described above may have a significant impact on improvement of hydrogen-delayed fracture characteristics. Hereinafter, a difference in the effect of improving hydrogen-delayed fracture characteristics according to the diameter of the fine precipitates 20 will be described with reference to FIGS. 3A and 3B.

[0077] FIGS. 3A and 3B are example diagrams schematically illustrating a portion of a state in which hydrogen is trapped in the fine precipitates 20.

[0078] In detail, FIG. 3A illustrates that hydrogen is trapped in the fine precipitates 20 having relatively large diameters,

and FIG. 3B illustrates that hydrogen is trapped in the fine precipitates 20 having relatively small diameters.

[0079] When the diameters of the fine precipitates 20 are relatively large as illustrated in FIG. 3A, the number of hydrogen atoms trapped in one fine precipitate 20 may increase. That is, hydrogen atoms introduced into the steel sheet 10 may not be evenly dispersed, and the probability of a plurality of hydrogen atoms being trapped in one hydrogen trap site may increase. A plurality of hydrogen atoms trapped in one hydrogen trap site may be combined with each other to form a hydrogen molecule (H_2). The formed hydrogen molecule may increase the probability of generating internal pressure, and accordingly, may deteriorate hydrogen-delayed fracture characteristics of a hot stamped product.

[0080] On the contrary, when the diameters of the fine precipitates 20 are relatively small as illustrated in FIG. 3B, the probability of a plurality of hydrogen atoms being trapped in one fine precipitate 10 may decrease. That is, hydrogen atoms introduced into the steel sheet 10 may be trapped in different hydrogen trap sites and thus relatively evenly dispersed. Accordingly, the hydrogen atoms may not be combined with each other, and thus, the probability of generating internal pressure due to a hydrogen molecule may decrease, improving hydrogen-delayed fracture characteristics of a hot stamped product.

[0081] In order to improve hydrogen-delayed fracture characteristics, the material 1 for hot stamping according to an embodiment of the present disclosure may be controlled such that the mean diameter of the fine precipitates 20 dispersed inside the steel sheet 10 satisfies a preset range. In detail, the mean diameter of the fine precipitates 20 dispersed inside the steel sheet 10 may be about $0.007\ \mu m$ or less. In addition, about 60 % or more of the fine precipitates 20 dispersed inside the steel sheet 10 may have a diameter of about $0.01\ \mu m$ or less. In addition, about 25 % or more of the fine precipitates 20 dispersed inside the steel sheet 10 may have a diameter of about $0.005\ \mu m$ or less.

[0082] Hereinafter, a variation coefficient of the sizes (diameters) of all fine precipitates per unit area ($100\ \mu m^2$) may be referred to as a first variation coefficient C1. The first variation coefficient C1 may be defined as the standard deviation of the mean diameter of all fine precipitates divided by the mean diameter. In an embodiment, the first variation coefficient C1 may be about 0.8 or less. When the first variation coefficient C1 is greater than about 0.8, tensile strength and hydrogen-delayed fracture characteristics may deteriorate. In detail, when the distribution of the sizes (diameters) of the fine precipitates is nonuniform, the nonuniform diameter distribution may act as an obstacle to dislocation movement, resulting in a decrease in strength. That is, when an external impact is applied to the steel sheet after hot stamping, a portion where fine precipitates having large sizes (diameters) concentrate may act as a fracture notch due to the accumulation of dislocations. In addition, because the amount of hydrogen trapped in the fine precipitates is nonuniform, hydrogen-delayed fracture characteristics may deteriorate due to an increase in local hydrogen partial pressure due to hydrogen bonding. A precipitation behavior regarding the diameter distribution through the first variation coefficient C1 will be explained in more detail through a comparative example and an embodiment to be described below.

[0083] Meanwhile, refinement of the fine precipitates 20 may improve bending characteristics of a formed part after hot stamping. In an embodiment, the refined fine precipitates 20 may act as an obstacle to grain growth to refine the prior austenite grain size (PAGS). As the prior austenite grain size (PAGS) is refined, the martensite packet size and the martensite lath size may decrease. Accordingly, the interval between block boundaries in a packet may decrease and the density of blocks may increase. The block boundaries may act as slip bands when the martensitic structure is deformed by an external impact, and thus, the refinement of the fine precipitates 20 may contribute to improving bending characteristics by securing more slip bands.

[0084] FIG. 4 is a flowchart schematically showing a method of manufacturing a material for hot stamping, according to an embodiment of the present disclosure.

[0085] As shown in FIG. 4, the method of manufacturing a material for hot stamping according to an embodiment of the present disclosure may include a reheating operation S100, a hot rolling operation S200, a cooling/coiling operation S300, a cold rolling operation S400, an annealing heat treatment operation S500, and a plating operation S600.

[0086] For reference, operations S100 to S600 are shown as independent operations in FIG. 4, but some of operations S100 to S600 may be performed in one process, and some of operations S100 to S600 may be omitted if necessary.

[0087] First, a slab, which is a semi-finished product, to be subjected to a process of forming the material 1 for hot stamping may be prepared. The slab may include 0.19 to 0.25 wt% of carbon (C), 0.1 to 0.6 wt% of silicon (Si), 0.8 to 1.6 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P), 0.015 wt% or less of sulfur (S), 0.1 to 0.6 wt% of chromium (Cr), 0.001 to 0.005 wt% of boron (B), 0.1 wt% or less of an additive, the remainder of iron (Fe), and other inevitable impurities. Here, the additive may include at least one of titanium (Ti), niobium (Nb), and vanadium (V). For example, the content of each of titanium (Ti), niobium (Nb), and/or vanadium (V) may be about 0.010 wt% to about 0.050 wt%.

[0088] The reheating operation S100 may be an operation of reheating the slab for hot rolling. In the reheating operation S100, components segregated during casting may be resolved by reheating, within a certain temperature range, the slab secured through a continuous casting process.

[0089] A slab reheating temperature (SRT) may be controlled within a preset temperature range to significantly improve the effect of austenite refinement and precipitation hardening. Here, the range of the slab reheating temperature (SRT) may be included in a temperature range (about $1,000\ ^\circ C$ or higher) in which an additive (Ti, Nb, and/or V) is fully resolved

on the basis of an equilibrium precipitation amount of the fine precipitates 20 when reheating the slab. When the slab reheating temperature (SRT) is less than the temperature range in which the additive (Ti, Nb, and/or V) is fully resolved, a driving force necessary for microstructure control is not sufficiently reflected during hot rolling, and thus, an effect of securing high-quality mechanical characteristics through required precipitation control may not be obtained.

[0090] In an embodiment, the slab reheating temperature (SRT) may be controlled to be about 1,200 °C to about 1,250 °C. When the slab reheating temperature (SRT) is less than 1,200 °C, the components segregated during casting are not sufficiently resolved, thus, a homogenization effect of an alloy element may not be significantly achieved, and a solid solution effect of titanium (Ti) may not be significantly achieved. On the contrary, when the slab reheating temperature (SRT) is high, the slab reheating temperature (SRT) is favorable for homogenization, whereas when the slab reheating temperature (SRT) is greater than about 1,280 °C, an austenite grain size may increase, making it difficult to secure strength and increasing the manufacturing cost of a steel sheet due to an excessive heating process.

[0091] The hot rolling operation S200 may be an operation of manufacturing a steel sheet by hot-rolling, within a certain range of finishing delivery temperature (FDT), the slab reheated in the operation S100. In an embodiment, the range of finishing delivery temperature (FDT) may be controlled to be about 840 °C to about 920 °C. When the finishing delivery temperature (FDT) is less than about 840 °C, it may be difficult to secure the workability of the steel sheet due to the occurrence of a duplex grain structure due to rolling over an abnormal area, the workability may deteriorate due to the microstructure unevenness, and a passing ability may occur during hot rolling due to a rapid phase change. On the contrary, when the finishing delivery temperature (FDT) is greater than about 920 °C, austenite grains may be coarsened. In addition, TiC precipitates may be coarsened, and thus, the performance of a final part may deteriorate.

[0092] In addition, in the reheating operation S100 and the hot rolling operation S200, some of the fine precipitates 20 may be precipitated at grain boundaries at which energy is unstable. Here, the fine precipitates 20 precipitated at the grain boundaries may act as factors that interfere with the growth of austenite grains, thereby providing an effect of enhancing the strength through austenite refinement. Meanwhile, the fine precipitates 20 precipitated in the operations S100 and S200 may be at a level of about 0.007 wt% on the basis of the equilibrium precipitation amount, but the present disclosure is not limited thereto.

[0093] The cooling/coiling operation S300 may be an operation of cooling and coiling, within a certain range of coiling temperature (CT), the steel sheet hot-rolled in the operation S200 and forming the fine precipitates 20 inside the steel sheet. That is, in the operation S300, the fine precipitates 20 are formed by forming nitride or carbide of the additive (Ti, Nb, and/or V) included in the slab. In addition, coiling may be performed in a ferrite zone such that the equilibrium precipitation amount of the fine precipitates 20 reaches the maximum. After grain recrystallization is completed as described above, when a structure is transformed into ferrite, the fine precipitates 20 may be precipitated such that the particle size is uniform not only at the grain boundaries but also in the grains.

[0094] In an embodiment, the coiling temperature (CT) may be about 700 °C to about 780 °C. The coiling temperature (CT) may affect redistribution of carbon (C). When the coiling temperature (CT) is less than about 700 °C, a low-temperature phase fraction may increase due to subcooling, thus, the strength may increase, a rolling load may increase during cold rolling, and the ductility may rapidly deteriorate. On the contrary, when the coiling temperature (CT) is greater than about 780 °C, the formability and strength may deteriorate due to abnormal grain growth or excessive grain growth.

[0095] According to the present embodiment as described above, the precipitation behavior of the fine precipitates 20 may be controlled by controlling the range of coiling temperature (CT). An experimental example for a change in characteristics of the material 1 for hot stamping according to the range of coiling temperature (CT) will be described below with reference to FIGS. 5, 6A, and 6B.

[0096] The cold rolling operation S400 may be an operation of uncoiling the steel sheet coiled in the operation S300 to pickle the steel sheet, and then cold-rolling the steel sheet. Here, pickling is performed to remove scale of the coiled steel sheet, that is, a hot-rolled coil manufactured through the hot rolling process described above. In addition, in an embodiment, a reduction ratio during cold rolling may be controlled to be about 30 % to about 70 %, but is not limited thereto.

[0097] The annealing heat treatment operation S500 may be an operation of performing annealing heat treatment on the steel sheet cold-rolled in the operation S400 at a temperature of about 700 °C or higher. In an embodiment, annealing heat treatment may include heating a cold-rolled sheet material and cooling the heated cold-rolled sheet material at a certain cooling rate.

[0098] The plating operation S600 may be an operation of forming a plating layer on the annealing-heat-treated steel sheet. In an embodiment, in the plating operation S600, an Al-Si plating layer may be formed on the steel sheet annealing-heat-treated in the operation S500.

[0099] In detail, the plating operation S600 may include an operation of forming a hot-dip plating layer on a surface of the steel sheet by immersing the steel sheet in a plating bath having a temperature of about 650 °C to about 700 °C, and a cooling operation of forming a plating layer by cooling the steel sheet on which the hot-dip plating layer is formed. Here, the plating bath may include, as an additional element, Si, Fe, Al, Mn, Cr, Mg, Ti, Zn, Sb, Sn, Cu, Ni, Co, In, Bi, or the like, but is not limited thereto.

[0100] A hot stamping part satisfying the conditions on the precipitation behavior of the fine precipitates 20 described above and thus satisfying required strength and bendability may be manufactured by performing a hot stamping process on the material 1 for hot stamping that is manufactured through the operations S100 to S600 as described above. In an embodiment, the material 1 for hot stamping manufactured to satisfy the above-described content conditions and process conditions may have a tensile strength of about 1,350 MPa or greater, a bendability of about 50 degrees or greater, and an amount of activated hydrogen of about 0.8 wppm or greater, after hot stamping.

[0101] Hereinafter, the present disclosure will be described in more detail through an embodiment and a comparative example. However, the following embodiment and comparative example are intended to describe the present disclosure in more detail, and the scope of the present disclosure is not limited by the following embodiment and comparative example. The following embodiment and comparative example may be appropriately modified and changed by those skill in the art within the scope of the present disclosure.

[0102] FIG. 5 is a graph showing a comparison of tensile strength and bending stress of an embodiment and a comparative example according to coiling temperature, and FIGS. 6A and 6B are images showing results of a 4-point bending test on an embodiment and a comparative example according to coiling temperature.

[0103] An embodiment CT700 and a comparative example CT800 are specimens that are manufactured by hot-stamping the material 1 for hot stamping manufactured by performing the operations S100 to S600 on a slab having a composition as shown in Table 1 below. Here, the embodiment CT700 and the comparative example CT800 are specimens that are manufactured by applying the same content conditions and process conditions in a process of manufacturing the material 1 for hot stamping but differentially applying only the coiling temperature (CT) as a variable. In detail, the embodiment CT700 and the comparative example CT800 are specimens manufactured by heating a hot stamping material at 950 °C for 270 seconds and then hot-stamping the hot stamping material, wherein the hot stamping material is manufactured from a slab having the composition as shown in Table 1, under conditions of a slab reheating temperature (SRT) of 1,230 °C, a finishing delivery temperature (FDT) of 900 °C, a reduction ratio during hot rolling of 95 %, an annealing heat treatment temperature of 780 °C, and a plating immersion temperature of 660 °C.

[Table 11]

Component (wt%)							
C	Si	Mn	P	S	Cr	B	Ti
0.22	0.3	1.5	0.02 or less	0.015 or less	0.25	0.0025	0.05

[0104] In detail, the embodiment CT700 is a specimen manufactured by hot-stamping the material 1 for hot stamping manufactured by applying a coiling temperature (CT) of 700 °C, and the comparative example CT800 is a specimen manufactured by hot-stamping the material 1 for hot stamping manufactured by applying a coiling temperature (CT) of 800 °C.

[0105] Hereinafter, descriptions will be provided with reference to FIG. 5. FIG. 5 is a graph showing tensile strength and bending stress measured in the embodiment CT700 and the comparative example CT800.

[0106] Referring to FIG. 5, it may be confirmed that, regarding tensile strength, the tensile strength of the embodiment CT700 was greater than the tensile strength of the comparative example CT800, and regarding bending stress that affects impact characteristics, the bending stress of the embodiment CT700 was improved compared to the bending stress of the comparative example CT800.

[0107] This is because, as shown in Table 2 below, in the embodiment CT700, the precipitation amount of the fine precipitates 20 increased and the hydrogen trapping ability was improved accordingly, compared to the comparative example CT800.

[0108] Table 2 below shows measurements of the equilibrium precipitation amount and the amount of activated hydrogen of the embodiment CT700 and the comparative example CT800, and results of a bent-beam stress corrosion test on the embodiment CT700 and the comparative example CT800. Here, the equilibrium precipitation amount refers to the maximum number of precipitates that may be precipitated when thermodynamic equilibrium is achieved, and as the equilibrium precipitation amount increases, the number of precipitated precipitates increases. In addition, the amount of activated hydrogen refers to the amount of hydrogen, excluding hydrogen trapped in the fine precipitates 20, from among hydrogen introduced into the steel sheet 10.

[0109] The amount of activated hydrogen as described above may be measured by using a thermal desorption spectroscopy method. In detail, while heating a specimen at a preset heating rate to raise its temperature, the amount of hydrogen released from the specimen at a temperature lower than or equal to a particular temperature may be measured. Here, hydrogen released from the specimen at the temperature lower than or equal to the particular temperature may be understood as activated hydrogen that is not trapped and affects hydrogen-delayed fracture, from among hydrogen introduced into the specimen.

[Table 2]

Sample name	Equilibrium precipitation amount (wt%)	Result of 4-point bending test	Amount of activated hydrogen (wppm)
CT700	0.028	Not fractured	0.780
CT800	0.009	Fractured	0.801

[0110] Table 2 shows results of the 4-point bending test performed on samples having different equilibrium precipitation amounts of fine precipitates, and amounts of activated hydrogen measured by using the thermal desorption spectroscopy method.

[0111] Here, the 4-point bending test refers to a test method for checking whether a stress corrosion crack occurs while applying, to a particular point of a specimen manufactured by reproducing a state of exposing the specimen to a corrosive environment, stress at a level lower than or equal to an elastic limit. Here, the stress corrosion crack refers to a crack occurring when corrosion and continuous tensile stress act simultaneously.

[0112] In detail, the results of the 4-point bending test in Table 2 are results of checking whether fracture occurs by applying, to the respective samples, stress of 1,000 MPa for 100 hours in air. In addition, the amounts of activated hydrogen were measured by using the thermal desorption spectroscopy method, and were values obtained by measuring the amount of hydrogen released from the specimen at a temperature of about 350 °C or lower, while raising the temperature from room temperature to about 500 °C at a heating rate of about 20 °C/min for each of the samples.

[0113] Referring to Table 2, regarding the equilibrium precipitation amount of the fine precipitates 20, the equilibrium precipitation amount of the embodiment CT700 was measured as 0.028 wt%, and the equilibrium precipitation amount of the comparative example CT800 was measured as 0.009 wt%. That is, it may be confirmed that the embodiment CT700 may provide more hydrogen trap sites by forming more fine precipitates 20 compared to the comparative example CT800.

[0114] Meanwhile, regarding the results of the 4-point bending test, the embodiment CT 700 was not fractured, and the comparative example CT800 was fractured. In addition, regarding the amounts of activated hydrogen, the amount of activated hydrogen of the embodiment CT700 was measured as about 0.780 wppm, and the amount of activated hydrogen of the comparative example CT800 was measured as about 0.801 wppm. In this regard, it may be confirmed that the embodiment CT700 having a relatively lower amount of activated hydrogen was not fractured, and the comparative example CT800 having a relatively higher amount of activated hydrogen was fractured. This may indicate that the embodiment CT700 had improved hydrogen-delayed fracture characteristics compared to the comparative example CT800.

[0115] That is, in the embodiment CT700, the precipitation amount of fine precipitates 20 increased compared to the comparative example CT800, and accordingly, the amount of activated hydrogen decreased. This may indicate that the amount of hydrogen trapped in the embodiment CT700 increased compared to the comparative example CT800, and accordingly, the hydrogen-delayed fracture characteristics were improved.

[0116] FIGS. 6A and 6B are images respectively showing results of performing a 4-point bending test on the embodiment CT700 and the comparative example CT800. In detail, FIG. 6A shows a result of performing a 4-point bending test on the embodiment CT700, and FIG. 6B corresponds to a result of performing the 4-point bending test on the comparative example CT800 by applying the same conditions as in the embodiment CT700.

[0117] As shown in FIGS. 6A and 6B, it may be confirmed that the results of the 4-point bending test show that the specimen of the embodiment CT700 was not fractured, whereas the specimen of the comparative example CT800 was fractured.

[0118] The embodiment CT700 of FIG. 6A is a specimen manufactured by hot-stamping the material 1 for hot stamping manufactured by applying a coiling temperature (CT) of 700 °C, wherein fine precipitates 20 having a diameter of 0.01 μm or less may be formed in an amount of 4,500 pieces to 16,000 pieces per unit area (100 μm²), and a mean distance between the fine precipitates 20 may be 0.4 μm to 0.8 μm. Thus, it may be confirmed that, in the embodiment CT700, hydrogen-delayed fracture characteristics were improved by efficiently dispersing and trapping hydrogen introduced into the steel sheet 10, and the tensile strength and the bending characteristics were improved.

[0119] On the contrary, the comparative example CT800 of FIG. 6B is a specimen manufactured by hot-stamping the material 1 for hot stamping manufactured by applying a coiling temperature (CT) of 800 °C, wherein the precipitation amount of the fine precipitates 20 may be insufficient, the diameter of the fine precipitates 20 may be coarsened, and thus, the probability of generating internal pressure due to hydrogen bonding may increase. Thus, it may be confirmed that, in the comparative example CT800, hydrogen introduced into the steel sheet 10 was not efficiently dispersed and trapped, and the tensile strength, the bending characteristics, and the hydrogen-delayed fracture characteristics deteriorated.

[0120] That is, although the material 1 for hot stamping is made of the same components, due to the difference in the coiling temperature (CT), differences occur in the strength, bendability, and hydrogen-delayed fracture characteristics of the material 1 for hot stamping after a hot stamping process. This is because a difference occurs in the precipitation behavior of the fine precipitates 20 according to the coiling temperature (CT). Thus, when the content conditions and the process conditions according to the above-described embodiments are applied, high strength may be secured, and bendability and hydrogen-delayed fracture characteristics may be improved.

[0121] Table 3 to Table 6 below show numerical representations of tensile strength, bendability, and hydrogen-delayed fracture characteristics of a plurality of specimens according to a difference in the precipitation behavior of fine precipitates 20. In detail, Table 3 to Table 6 show, for the plurality of specimens, measurements of a precipitation behavior (the number of fine precipitates 20, the mean distance between the fine precipitates 20, the diameters of the fine precipitates 20, and the like) and measurements of characteristics (tensile strength, bendability, and the amount of activated hydrogen) after hot stamping.

[0122] In addition, each of the plurality of specimens was heated to a temperature of 950 °C, then cooled to a temperature of about 300 °C at a cooling rate of about 30 °C/s or higher, and then the tensile strength, bendability, and amount of activated hydrogen of the specimen were measured.

[0123] Here, the tensile strength and the amount of activated hydrogen were measured based on the 4-point bending test and the thermal desorption spectroscopy method described above, and the bendability was obtained by measuring a V-bending angle according to VDA238-100, which is the standard of Verband Der Automobilindustrie (VDA).

[0124] In addition, the precipitation behavior of fine precipitates (the number of fine precipitates, the mean distance between the fine precipitates, the diameters of the fine precipitates, and the like) was measured through TEM image analysis as described above. In addition, the precipitation behavior of the fine precipitates was measured by measuring a precipitation behavior of fine precipitates for arbitrary regions having an area of 0.5 μm *0.5 μm , and converting the precipitation behavior on the basis of a unit area (100 μm 2).

[Table 3]

Specimen	Component (wt%)							
	C	Si	Mn	P	S	Cr	B	Ti
A	0.25	0.30	1.2	0.02 or less	0.01 or less	0.20	0.002 6	0.030
B	0.23	0.30	1.4	0.02 or less	0.01 or less	0.15	0.002 8	0.033
C	0.25	0.25	1.1	0.02 or less	0.01 or less	0.16	0.002 0	0.033
D	0.24	0.20	1.2	0.02 or less	0.01 or less	0.16	0.002 7	0.033
E	0.24	0.25	1.3	0.02 or less	0.01 or less	0.21	0.002 1	0.035
F	0.24	0.30	1.3	0.02 or less	0.01 or less	0.17	0.002 2	0.031
G	0.24	0.30	1.2	0.02 or less	0.01 or less	0.16	0.002 1	0.035
H	0.23	0.25	1.2	0.02 or less	0.01 or less	0.20	0.002 0	0.033
I	0.24	0.20	1.2	0.02 or less	0.01 or less	0.18	0.002 5	0.031
J	0.23	0.30	1.3	0.02 or less	0.01 or less	0.18	0.002 7	0.035

EP 4 446 453 A1

[Table 4]

S P e c i m e n	All fine precipitates			Fine precipitate s having a diameter of 0.01 μm or less	Fine precipitate s having a diameter of 0.005 μm or less	Characteristics after hot stamping		
	Number of fine precipitate s (pieces/100 μm^2)	Mean distanc e (μm)	Mean diamet er (μm)	Number of fine precipitate s (pieces/100 μm^2) / proportion (%)	Number of fine precipitate s (pieces/100 μm^2) / proportion (%)	Tensile strengt h (MPa)	Bendi ng angle ($^\circ$)	Amoun t of activat ed hydrog en (wppm)
A	7,020	0.69	0.0064	4,577 / 65.2 %	1,755 / 25.0 %	1382	54	0.789
B	7,026	0.65	0.0068	6,513 / 92.7 %	2,677 / 38.1 %	1400	57	0.798
C	8,375	0.55	0.0050	5,313 / 63.4 %	2,500 / 29.9 %	1396	60	0.791
D	11,313	0.52	0.0044	10,625 / 93.9 %	7,250 / 64.1 %	1418	60	0.778
E	15,280	0.52	0.0042	14,680 / 96.1 %	12,000 / 78.5 %	1439	58	0.762
F	16,490	0.59	0.0056	9,910 / 60.1 %	4,172 / 25.3 %	1502	57	0.721
G	16,478	0.42	0.0048	15,967 / 96.9 %	4,136 / 25.1 %	1510	64	0.788
H	9,736	0.8	0.0047	7,652 / 78.6 %	4,225 / 43.4 %	1416	55	0.782
I	13,921	0.4	0.0043	13,698 / 98.4 %	11,387 / 81.8 %	1422	59	0.754
J	10,521	0.61	0.0070	8,911 / 84.7 %	5,513 / 52.4 %	1420	55	0.782

[Table 5]

Spe cim en	Component (wt%)							
	C	Si	Mn	P	S	Cr	B	Ti
K	0.25	0.30	1.2	0.02 or less	0.01 or less	0.20	0.002 6	0.030
L	0.23	0.30	1.4	0.02 or less	0.01 or less	0.15	0.002 8	0.033
M	0.25	0.25	1.1	0.02 or less	0.01 or less	0.16	0.002 0	0.033
N	0.24	0.20	1.2	0.02 or less	0.01 or less	0.16	0.002 7	0.033
O	0.24	0.25	1.3	0.02 or less	0.01 or less	0.21	0.002 1	0.035
P	0.24	0.30	1.3	0.02 or less	0.01 or less	0.17	0.002 2	0.031
Q	0.24	0.30	1.2	0.02 or less	0.01 or less	0.16	0.002 1	0.035
R	0.23	0.25	1.2	0.02 or less	0.01 or less	0.20	0.002 0	0.033
S	0.24	0.20	1.2	0.02 or less	0.01 or less	0.18	0.002 5	0.031
T	0.23	0.30	1.3	0.02 or less	0.01 or less	0.18	0.002 7	0.035
U	0.25	0.30	1.2	0.02 or less	0.01 or less	0.20	0.002 6	0.030

[Table 6]

Specimen	all fine precipitates			Fine precipitates having a diameter of 0.01 μm or less	Fine precipitates having a diameter of 0.005 μm or less	Characteristics after hot stamping		
	Number of fine precipitates (pieces/100 μm^2)	Mean distance (μm)	Mean diameter (μm)	Number of fine precipitates (pieces/100 μm^2)	Number of fine precipitates (pieces/100 μm^2)	Tensile strength (MPa)	Bending angle ($^\circ$)	Amount of activated hydrogen (wppm)
				/ proportion (%)	/ proportion (%)			
K	7,011	0.77	0.0068	4,494 / 64.1 %	1,774 / 25.3 %	1331	51	0.795
L	6,991	0.74	0.0061	4,544 / 65.0 %	1,762 / 25.2 %	1322	52	0.779
M	16,200	0.5	0.0041	16,038 / 99.0 %	13,939 / 86.0 %	1523	43	0.758
N	16,521	0.41	0.0046	10,408 / 63.0 %	4,279 / 25.9 %	1478	40	0.796
O	14,612	0.43	0.0071	12,917 / 88.4 %	4,647 / 31.8 %	1437	55	0.881
P	16,490	0.72	0.0059	9,861 / 59.8 %	4,353 / 26.4 %	1505	63	0.828
Q	7,052	0.74	0.0060	4,809 / 68.2 %	1,756 / 24.9 %	1380	52	0.815
R	16,500	0.45	0.0059	5,691 / 95.1 %	4,092 / 24.8 %	1513	66	0.845
S	16,455	0.39	0.0040	15,994 / 97.2 %	14,925 / 90.7 %	1484	45	0.784
T	12,996	0.81	0.0046	12,346 / 95.0 %	11,437 / 88 %	1344	56	0.785
U	7,008	0.68	0.0065	4,555 / 64.9 %	1,752 / 25.0 %	1342	54	0.781

[0125] Table 3 to Table 6 show, for specimens A to U, measurements of a precipitation behavior of fine precipitates (the number of fine precipitates, the mean distance between the fine precipitates, the diameters of the fine precipitates, and the like) and measurements of characteristics (tensile strength, bendability, and the amount of activated hydrogen) after hot stamping.

[0126] The specimens A to J are specimens manufactured by hot-stamping a material for hot stamping manufactured through the operations S100 to S600 by applying the above-described process conditions to a slab satisfying the content conditions in Table 3. Here, the specimens A to J are specimens manufactured by heating a hot stamping material at a temperature of 950 °C for 270 seconds and then hot-stamping the hot stamping material, wherein the hot stamping material is manufactured under conditions of a slab reheating temperature (SRT) of 1230 °C, a finishing delivery temperature (FDT) of 900 °C, a reduction ratio during hot rolling of 95 %, a coiling temperature (CT) of 780 °C, an annealing heat treatment temperature of 780 °C, and a plating immersion temperature of 660 °C. That is, the specimens A to J are specimens that satisfy the precipitation behavior conditions of the fine precipitates described above.

[0127] In detail, in the specimens A to J, fine precipitates are formed in a steel sheet in an amount of 7,000 pieces/100 μm^2 to 16,500 pieces/100 μm^2 , the mean diameter of all fine precipitates is 0.007 μm or less, and the mean distance between all fine precipitates is 0.4 μm to 0.8 μm . In addition, 60 % or more of the fine precipitates formed inside the steel sheet have a diameter of 0.01 μm or less, and the number of fine precipitates having a diameter of 0.01 μm or less is 4,500/100 μm^2 to 16,000/100 μm^2 . In addition, 25 % or more of the fine precipitates formed inside the steel sheet have a diameter of 0.005 μm or less, and the number of fine precipitates having a diameter of 0.005 μm or less is 1,755/100 μm^2 to 16,000/100 μm^2 .

[0128] It may be confirmed that the specimens A to J of the present disclosure satisfying the precipitation behavior conditions as described above had improved tensile strength, bendability, and hydrogen-delayed fracture characteristics. In detail, in the specimens A to J, the tensile strength after hot stamping is 1,350 MPa or greater, the bendability after hot stamping is 50 degrees or greater, and the amount of activated hydrogen after hot stamping is 0.8 wppm or less.

[0129] On the contrary, specimens K to U are specimens manufactured by hot-stamping a material for hot stamping manufactured through the operations S100 to S600 by applying the above-described process conditions to a slab satisfying the content conditions in Table 5. Here, the specimens K to U are specimens manufactured by heating a hot stamping material at a temperature of 950 °C for 270 seconds and then hot-stamping the hot stamping material, wherein the hot stamping material is manufactured under conditions of a slab reheating temperature (SRT) of 1230 °C, a finishing

delivery temperature (FDT) of 900 °C, a reduction ratio during hot rolling of 95 %, a coiling temperature (CT) of 790 °C, an annealing heat treatment temperature of 780 °C, and a plating immersion temperature of 660 °C. That is, the specimens K to U are specimens that do not satisfy at least some of the precipitation behavior conditions of the fine precipitates described above, and it may be confirmed that they have lower tensile strength, bendability, and/or hydrogen-delayed fracture characteristics compared to the specimens A to J.

[0130] In the specimen K, the number of fine precipitates having a diameter of 0.01 μm or less is 4,494. This is less than the lower limit of the condition for the number of fine precipitates having a diameter of 0.01 μm or less. Accordingly, it may be confirmed that the tensile strength of the specimen K is only 1,331 MPa, which is relatively low.

[0131] In the specimen L, the total number of fine precipitates is 6,991. This is less than the lower limit of the condition for the total number of fine precipitates. Accordingly, it may be confirmed that the tensile strength of the specimen L is only 1,322 MPa, which is relatively low.

[0132] In the specimen M, the number of fine precipitates having a diameter of 0.01 μm or less is 16,038. This is greater than the upper limit of the condition for the number of fine precipitates having a diameter of 0.01 μm or less. Accordingly, it may be confirmed that the bendability of the specimen M is only 43 degrees, which is relatively low.

[0133] In the specimen N, the total number of fine precipitates is 16,521. This is greater than the upper limit of the condition for the total number of fine precipitates. Accordingly, it may be confirmed that the bendability of the specimen N is only 40 degrees, which is relatively low.

[0134] In the specimen O, the mean diameter of all fine precipitates is 0.0071 μm . This is greater than the upper limit of the condition for the mean diameter of all fine precipitates. Accordingly, it may be confirmed that the amount of activated hydrogen in the specimen O was measured as 0.881 wppm, which is relatively high, and thus, the hydrogen-delayed fracture characteristics relatively deteriorated.

[0135] In the specimen P, the proportion of fine precipitates having a diameter of 0.01 μm or less is 59.8 %. This is less than the lower limit of the condition for the proportion of fine precipitates having a diameter of 0.005 μm or less. Accordingly, it may be confirmed that the amount of activated hydrogen in the specimen P was measured as 0.828 wppm, which is relatively high, and thus, the hydrogen-delayed fracture characteristics relatively deteriorated.

[0136] In the specimen Q, the proportion of fine precipitates having a diameter of 0.005 μm or less is 24.9 %. This is less than the lower limit of the condition for the proportion of fine precipitates having a diameter of 0.005 μm or less. Accordingly, it may be confirmed that the amount of activated hydrogen in the specimen Q was measured as 0.815 wppm, which is relatively high, and thus, the hydrogen-delayed fracture characteristics relatively deteriorated.

[0137] In the specimen R, the proportion of fine precipitates having a diameter of 0.005 μm or less is 24.8 %. This is less than the lower limit of the condition for the proportion of fine precipitates having a diameter of 0.005 μm or less. Accordingly, it may be confirmed that the amount of activated hydrogen in the specimen R was measured as 0.845 wppm, which is relatively high, and thus, the hydrogen-delayed fracture characteristics relatively deteriorated.

[0138] In the specimen S, the mean distance of all fine precipitates is 0.39 μm . This is less than the lower limit of the condition for the mean distance of all fine precipitates. Accordingly, it may be confirmed that the bendability of the specimen S is only 45 degrees, which is relatively low.

[0139] In the specimen T, the mean distance between all fine precipitates is 0.81 μm . This is greater than the upper limit of the condition for the mean distance between all fine precipitates. Accordingly, it may be confirmed that the tensile strength of the specimen T is only 1,344 MPa, which is relatively low.

[0140] In the specimen U, the number of fine precipitates having a diameter of 0.005 μm or less is 1,752. This is less than the lower limit of the condition for the number of fine precipitates having a diameter of 0.005 μm or less. Accordingly, it may be confirmed that the tensile strength is only 1,342 MPa, which is relatively low.

[0141] Hereinafter, a difference in the effect of improving the tensile strength and hydrogen-delayed fracture characteristics of a formed part after hot stamping according to the precipitation behavior of the fine precipitates 20 will be described with reference to Table 7. The following precipitation behavior of fine precipitates was measured through TEM image analysis described above. The precipitation behavior of the fine precipitates was measured by measuring a precipitation behavior of fine precipitates for 10 arbitrary regions having an area of 0.5 μm × 0.5 μm , and converting the precipitation behavior on the basis of a unit area (100 μm^2), and hereinafter, 'mean' refers to the mean of precipitation behavior values for the arbitrary regions. The total number of precipitates in the above arbitrary regions was calculated, and their mean value was referred to as 'mean number of all precipitates'. Similarly, the mean distance between fine precipitates was calculated through a mean free path in the above arbitrary regions, and the mean value thereof was referred to as 'mean distance between precipitates'. The number of fine precipitates having a diameter of 10 nm or less and the number of fine precipitates having a diameter of 5 nm or less in the above arbitrary regions were converted on the basis of a unit area (100 μm^2), the mean value of the numbers was calculated, and then their proportions with respect to the 'mean number of all precipitates' were referred to as 'mean 10-nm-or-less proportion' and 'mean 5-nm-or-less proportion'.

[0142] The mean of the diameters of all fine precipitates in the above arbitrary regions was referred to as 'mean diameter of all precipitates', and the standard deviation of these values was referred to as 'standard deviation of mean

diameter'. A mean diameter variation coefficient, that is, the first variation coefficient C1, was defined as the standard deviation of the mean diameter divided by the mean diameter. In the present disclosure, the first variation coefficient C1 may be 0.8 or less.

[Table 7]

Specimen	Mean number of all precipitates (pieces/ μm^2)	Mean distance between precipitates (μm)	Mean 10-nm-or-less proportion (%)	Mean 5-nm-or-less proportion (%)	Mean diameter of all precipitates (μm)	Standard deviation of mean diameter	Mean diameter variation coefficient (C1)	Tensile strength after H/S (MPa)	Amount of activated hydrogen after H/S (wppm)
X1	7,249	0.79	64.1	30.1	0.0052	0.0041	0.80	1410	0.658
X2	8,292	0.76	60.7	27.85	0.0033	0.0016	0.47	1411	0.661
X3	10,082	0.50	66.4	27.25	0.0036	0.0025	0.70	1427	0.651
X4	11,025	0.47	61.2	28.15	0.0068	0.0053	0.77	1430	0.642
X5	9,936	0.51	98.1	65.95	0.0037	0.0019	0.51	1414	0.64
X6	12,943	0.48	93.5	86.2	0.0031	0.0009	0.30	1445	0.635
X7	13,999	0.43	90.4	55.3	0.0040	0.0016	0.40	1499	0.636
X8	15,439	0.40	86.9	42.7	0.0067	0.0051	0.76	1489	0.637
X9	7,148	0.75	65.9	31.45	0.0053	0.0044	0.82	1355	0.781
X10	10,819	0.50	62.4	31.3	0.0058	0.0047	0.81	1371	0.779
X11	11,201	0.49	60.3	25.9	0.0068	0.0057	0.84	1379	0.783
X12	14,963	0.41	88.3	83.8	0.0031	0.0026	0.85	1380	0.754

[0143] Table 7 shows numerical representations of the tensile strength and hydrogen-delayed fracture characteristics of a plurality of specimens according to a precipitation behavior of fine precipitates. In detail, Table 7 shows, for a plurality of specimens X1 to X12, as a precipitation behavior of fine precipitates, measurements of the mean number of all fine precipitates, the mean distance between fine precipitates, the mean proportion of fine precipitates having a particular diameter or less, the mean diameter of all fine precipitates, the standard deviation of the mean diameter, and the first variation coefficient C1, and as resulting characteristics after hot stamping, measurements of tensile strength and the amount of activated hydrogen. In particular, descriptions will be provided in terms of tensile strength and hydrogen-delayed fracture characteristics according to the first variation coefficient C1, which is the variation coefficient of the mean diameter.

[0144] The specimens X1 to X12 are specimens manufactured by hot-stamping a material for hot stamping that is manufactured through the operations S100 to S600 by applying the above-described process conditions to a slab including 0.19 to 0.25 wt% of carbon (C), 0.1 to 0.6 wt% of silicon (Si), 0.8 to 1.6 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P), 0.015 wt% or less of sulfur (S), 0.1 to 0.6 wt% of chromium (Cr), 0.001 to 0.005 wt% of boron (B), 0.1 wt% or less of an additive (including at least one of titanium (Ti), niobium (Nb), and vanadium (V)), the remainder of iron (Fe), and other inevitable impurities. Here, the specimens X1 to X12 are specimens manufactured by heating a hot stamping material at a temperature of 950 °C for 270 seconds and then hot-stamping the hot stamping material, wherein the hot stamping material is manufactured under conditions of a slab reheating temperature (SRT) of 1230 °C, a finishing delivery temperature (FDT) of 900 °C, a reduction ratio during hot rolling of 95 %, a coiling temperature (CT) of 780 °C, an annealing heat treatment temperature of 780 °C, and a plating immersion temperature of 660 °C. Meanwhile, the specimens X1 to X12 may satisfy not only the precipitation behavior for the first variation coefficient C1 but also the precipitation behavior for the second variation coefficient C2 described above. That is, the specimens X1 to X12 are specimens that satisfy the precipitation behavior conditions of the fine precipitates described above.

[0145] In detail, in specimens X1 to X12, the total number of fine precipitates is 7,000 to 16,500/ μm^2 , the mean distance between adjacent fine precipitates is 0.4 μm to 0.8 μm , the proportion of fine precipitates having a diameter of 0.01 μm or less is 60 % or greater, the proportion of fine precipitates having a diameter of 0.005 μm or less is 25 % or

greater, and the mean diameter of all fine precipitates is 0.007 μm or less.

[0146] However, the specimens X1 to X8 satisfy the condition that the first variation coefficient is 0.8 or less, and the specimens X9 to X12 have a first variation coefficient being greater than 0.8 and thus does not satisfy the precipitation behavior condition for the first variation coefficient of the present disclosure. It may be confirmed that the specimens X1 to X8 having a first variation coefficient being 0.8 or less are superior, in tensile strength and hydrogen-delayed fracture characteristics, to the specimens X9 to X12 having a first variation coefficient being greater than 0.8. In detail, the specimens X1 to X8 have a tensile strength after hot stamping of 1400 MPa or greater and an amount of activated hydrogen of 0.7 wppm or less, whereas the specimens X9 to X12 have a tensile strength after hot stamping of 1,350 MPa to 1,400 MPa (less than 1,400 MPa) and an amount of activated hydrogen of 0.7 wppm to 0.8 wppm, and thus, the specimens X1 to X8 are superior to the specimens X9 to X12 in tensile strength and hydrogen-delayed fracture characteristics.

[0147] In particular, in the specimens X1 to X4, the mean number of all precipitates is 7,000 to 12,000, and the mean proportion of fine precipitates having a diameter of 10 nm or less is 60 % to 70 %, and the mean proportion of fine precipitates having a diameter of 5 nm or less is 25 % to 35 %, which means that the total number of precipitates and the proportion of fine precipitates having a diameter of 10 nm or less, or 5 nm or less are also small, and thus, it may be significantly difficult to secure tensile strength after hot stamping or hydrogen-delayed fracture characteristics. Nevertheless, the specimens X1 to X4 satisfy the precipitation behavior condition of the present disclosure that the first variation coefficient is 0.8 or less, and thus have relatively high tensile strength and hydrogen-delayed fracture characteristics compared to the specimens X9 to X12.

[0148] Meanwhile, in the specimen X12, the mean number of all precipitates is 14,963, which is large, and the proportion of fine precipitates having a diameter of 10 nm or less, and the proportion of fine precipitates having a diameter of 5 nm or less are respectively 88.3 % and 83.8 %, which are high, and thus, the specimen X12 may be relatively advantageous for securing tensile strength and hydrogen-delayed fracture characteristics. Nevertheless, the specimen X12 does not satisfy the precipitation behavior condition of the present disclosure that the first variation coefficient is 0.8 or less, and thus have relatively low tensile strength and hydrogen-delayed fracture characteristics compared to the specimens X1 to X8.

[0149] Hereinafter, a difference in the effect of improving the bendability of a formed part after hot stamping according to the precipitation behavior of the fine precipitates 20 will be described with reference to Table 8. The following precipitation behavior of fine precipitates was measured through TEM image analysis described above. The precipitation behavior of the fine precipitates was measured by measuring a precipitation behavior of fine precipitates for 10 arbitrary regions having an area of 0.5 μm *0.5 μm , and converting the precipitation behavior on the basis of a unit area (100 μm^2), and hereinafter, 'mean' refers to the mean of precipitation behavior values for the arbitrary regions. The total number of precipitates, the number of fine precipitates having a diameter of 10 nm or less, and the number of fine precipitates having a diameter of 5 nm or less in the above arbitrary regions were measured and converted on the basis of a unit area (100 μm^2), their mean values were referred to as 'mean diameter of all precipitates', 'mean number of precipitates of 10 nm or less', and 'mean number of precipitates of 5 nm or less', and the standard deviation of each of them was measured. The mean distance between fine precipitates was calculated through a mean free path in the above arbitrary regions, and the mean value thereof was referred to as 'mean distance between precipitates'.

[0150] A number variation coefficient, that is, the second variation coefficient C2, was defined as the standard deviation of the mean number divided by the mean number. In the present disclosure, the second variation coefficient C2 may be 0.95 or less. The second variation coefficient C2 includes a 2-1st variation coefficient C21, which is a variation coefficient for the number of fine precipitates having a diameter of 10 nm or less, and a 2-2nd variation coefficient C22, which is a variation coefficient for the number of fine precipitates having a diameter of 5 nm or less.

[0151] The 2-1 st variation coefficient C21 is defined as the standard deviation of the mean number of fine precipitates having a diameter of 0.01 μm or less from among all fine precipitates divided by the mean number of fine precipitates having a diameter of 0.01 μm or less, and the 2-1 st variation coefficient C21 may be 0.95 or less. Hereinafter, the 2-1 st variation coefficient C21 may also be referred to as 'first number variation coefficient'. The 2-2nd variation coefficient C22 is defined as the standard deviation of the mean number of fine precipitates having a diameter of 0.005 μm or less from among all fine precipitates divided by the mean number of fine precipitates having a diameter of 0.005 μm or less, and the 2-2nd variation coefficient C22 may be 0.95 or less. Hereinafter, the 2-2nd variation coefficient C22 may also be referred to as 'second number variation coefficient'.

[Table 8]

Specimen	All precipitates				Precipitates of 10 nm or less			Precipitates of 5 nm or less			Bendability after H/S (°)
	Mean number (piece s/μm ²)	Standard deviation of mean number	Number variation coefficient (C2)	Mean distance between precipitates (μm)	Mean number (piece s/μm ²)	Standard deviation of mean number	Number variation coefficient (C21)	Mean number (piece s/μm ²)	Standard deviation of mean number	Number variation coefficient (C22)	
Y1	7,094	6,643	0.94	0.47	4,585	7,821	0.95	1,844	5,775	0.91	62
Y2	10,245	6,674	0.65	0.57	9,679	10,576	0.67	6,758	9,682	0.77	63
Y3	12,641	7,034	0.56	0.57	10,659	13,444	0.77	11,861	18,392	0.94	62
Y4	15,629	10,818	0.69	0.57	11,457	17,147	0.92	15,199	23,088	0.95	61
Y5	14,184	13,475	0.95	0.46	13,477	18,780	0.87	10,929	16,179	0.88	64
Y6	16,254	13,897	0.86	0.43	15,494	21,752	0.88	12,686	19,190	0.92	65
Y7	16,039	14,149	0.88	0.45	15,193	21,681	0.90	13,854	21,304	0.95	64
Y8	16,373	15,333	0.94	0.42	15,977	23,772	0.94	14,599	22,292	0.95	62
Y9	7,051	6,889	0.98	0.49	6,370	10,375	0.96	5,616	10,375	0.96	55
Y10	10,217	9,910	0.97	0.55	9,693	12,751	0.80	6,930	7,098	0.56	54
Y11	15,614	14,989	0.96	0.40	15,241	14,168	0.58	10,840	12,608	0.69	52
Y12	7,245	6,981	0.96	0.77	4,581	7,369	0.90	2,195	5,420	0.88	53
Y13	9,278	8,058	0.87	0.73	5,949	10,051	0.98	3,585	7,462	0.92	52
Y14	11,343	9,852	0.87	0.76	7,919	12,050	0.91	4,392	9,002	0.98	51

[0152] Table 8 shows numerical representations of the bending angle of a plurality of specimens according to a precipitation behavior of fine precipitates. In detail, Table 8 shows, for a plurality of specimens Y1 to Y14, as a precipitation behavior of fine precipitates, measurements of the mean numbers of all fine precipitates, fine precipitates having a diameter of 10 nm or less, and fine precipitates having a diameter of 5 nm or less, the standard deviations of the mean numbers, and the second variation coefficient C2, which is a variation coefficient of the number of fine precipitates, and as resulting characteristics after hot stamping, measurements of a bending angle. In particular, descriptions will be provided in terms of bendability according to the second variation coefficient C2, which is the variation coefficient of the mean number.

[0153] The specimens Y1 to Y14 are specimens manufactured by hot-stamping a material for hot stamping that is manufactured through the operations S100 to S600 by applying the above-described process conditions to a slab including 0.19 to 0.25 wt% of carbon (C), 0.1 to 0.6 wt% of silicon (Si), 0.8 to 1.6 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P), 0.015 wt% or less of sulfur (S), 0.1 to 0.6 wt% of chromium (Cr), 0.001 to 0.005 wt% of boron (B), 0.1 wt% or less of an additive (including at least one of titanium (Ti), niobium (Nb), and vanadium (V)), the remainder of iron (Fe), and other inevitable impurities. Here, the specimens Y1 to Y14 are specimens manufactured by heating a hot stamping material at a temperature of 950 °C for 270 seconds and then hot-stamping the hot stamping material, wherein the hot stamping material is manufactured under conditions of a slab reheating temperature (SRT) of 1230 °C, a finishing delivery temperature (FDT) of 900 °C, a reduction ratio during hot rolling of 95 %, a coiling temperature (CT) of 780 °C, an annealing heat treatment temperature of 780 °C, and a plating immersion temperature of 660 °C. Meanwhile, the specimens Y1 to Y14 may satisfy not only the precipitation behavior for the second variation coefficient C2 to be described below but also the precipitation behavior for the first variation coefficient C1 described above. That is, the specimens Y1 to Y14 are specimens that satisfy the precipitation behavior conditions of the fine precipitates described above.

[0154] In detail, in specimens Y1 to Y14, the total number of fine precipitates is 7,000 to 16,500/ μm^2 , the mean distance between adjacent fine precipitates is 0.4 μm to 0.8 μm , the number of fine precipitates having a diameter of 10 nm or less is 4,500 to 16,000/ μm^2 , and the number of fine precipitates having a diameter of 5 nm or less is 1,755 to 16,000/ μm^2 . Although not shown in Table 8, in the specimens Y1 to Y14, the proportion of fine precipitates having a diameter of 0.01 μm or less is 60 % or greater, the proportion of fine precipitates having a diameter of 0.005 μm or less is 25 % or greater, and the mean diameter of all fine precipitates is 0.007 μm or less.

[0155] However, the specimens Y1 to Y8 satisfy the condition that the second variation coefficient is 0.95 or less, and the specimens Y9 to Y14 have a second variation coefficient being greater than 0.95 and thus does not satisfy the precipitation behavior condition for the second variation coefficient of the present disclosure. It may be confirmed that the specimens Y1 to Y8 having a second variation coefficient being 0.95 or less are superior, in bendability, to the specimens Y9 to Y14 having a second variation coefficient being greater than 0.95. In detail, the specimens Y1 to Y8 have a bending angle (°) after hot stamping of 60 degrees to 70 degrees, whereas the specimens Y9 to Y14 have a bending angle after hot stamping of 50 degrees to 60 degrees, and thus, the specimens Y1 to Y8 are superior to the specimens Y9 to Y14 in bendability.

[0156] In the specimen Y9, the second variation coefficient C2, the 2-1st variation coefficient C21, and the 2-2nd variation coefficient C22 are 0.98, 0.96, and 0.96, respectively, and thus are greater than the upper limits (0.95) of the conditions for the number variation coefficients C2, C21, and C22. Accordingly, it may be confirmed that the bendability of the specimen Y9 is only 55 degrees, which is relatively low.

[0157] The second variation coefficients C2 of the specimens Y10 to Y12 are 0.97 or 0.96, which is greater than the upper limit of the condition for the second variation coefficient C2. Accordingly, it may be confirmed that the bendabilities of the specimen Y10 to Y12 are only 55 degrees to 54 degrees, which are relatively low.

[0158] The second variation coefficient C2 of the specimen Y13 is 0.98, which is greater than the upper limit of the condition for the 2-1st variation coefficient C21. Accordingly, it may be confirmed that the bendability of the specimen Y13 is only 52 degrees, which is relatively low. The second variation coefficient C2 of the specimen Y14 is 0.98, which is greater than the upper limit of the condition for the 2-2nd variation coefficient C22. Accordingly, it may be confirmed that the bendability of the specimen Y14 is only 51 degrees, which is relatively low.

[0159] In particular, in the specimens Y5 to Y8, the mean number of all precipitates per unit area (100 μm^2) is 14,000 to 16,500, which is large, the numbers of fine precipitates having a diameter of 10 nm or less and fine precipitates having a diameter of 5 nm or less are relatively large, and thus, it may be difficult to secure bendability. Nevertheless, the specimens Y5 to Y8 satisfy the precipitation behavior condition of the present disclosure that the second variation coefficient is 0.95 or less, and thus have relatively high bendability compared to the specimens Y9 to Y14.

[0160] On the contrary, the specimens Y9 to Y14 have relatively large numbers of all precipitates, fine precipitates having a diameter of 10 nm or less, and fine precipitates having a diameter of 5 nm or less, and thus may be relatively advantageous for securing bendability. Nevertheless, the specimens Y9 to Y14 does not satisfy the precipitation behavior condition of the present disclosure that the second variation coefficient is 0.95 or less, and thus have relatively low bendability compared to the specimens Y1 to Y8.

[0161] As a result, it was confirmed that a material for hot stamping manufactured by the method of manufacturing a material for hot stamping by applying the content conditions and the process conditions of the present disclosure described above satisfied the above-described precipitation behavior conditions of fine precipitates after hot stamping, and a hot stamping product that satisfies the precipitation behavior conditions of fine precipitates had improved tensile strength, bendability, and hydrogen-delayed fracture characteristics. In particular, it may be confirmed that a material for hot stamping according to the embodiments of the present disclosure satisfied the mean diameter variation coefficient and/or the number variation coefficient of the precipitation behavior conditions, and thus, the tensile strength, bendability, and hydrogen-delayed fracture characteristics of a formed part after hot stamping were further improved as the numbers and sizes (diameters) of fine precipitates are uniformly distributed.

[0162] Although the present disclosure has been described with reference to the embodiments illustrated in the drawings, they are merely exemplary, and it will be understood by one of skill in the art that various modifications and equivalent embodiments may be made therefrom. Therefore, the true technical protection scope of the present disclosure should be determined by the appended claims.

Claims

1. A material for hot stamping, the material comprising:

a steel sheet comprising carbon (C) in an amount of 0.19 to 0.25 wt%, silicon (Si) in an amount of 0.1 to 0.6 wt%, manganese (Mn) in an amount of 0.8 to 1.6 wt%, phosphorus (P) in an amount of 0.03 wt% or less, sulfur (S) in an amount of 0.015 wt% or less, chromium (Cr) in an amount of 0.1 to 0.6 wt%, boron (B) in an amount of 0.001 to 0.005 wt%, an additive in an amount of 0.1 wt% or less, a remainder of iron (Fe), and other inevitable impurities; and

fine precipitates distributed inside the steel sheet, wherein the additive comprises at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates comprise nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V), the fine precipitates trap hydrogen, and a mean diameter variation coefficient, which is a value obtained by dividing a standard deviation of a mean diameter of the fine precipitates by the mean diameter of the fine precipitates, is 0.8 or less.

2. The material of claim 1, wherein the material after hot stamping exhibits a tensile strength of 1,350 MPa or greater, a bending angle of 50 degrees or greater, and an amount of activated hydrogen of 0.8 wppm or less.

3. The material of claim 1, wherein the mean diameter of the fine precipitates is 0.007 μm or less.

4. The material of claim 3, wherein 60 % or greater of the fine precipitates have a diameter of 0.01 μm or less.

5. The material of claim 4, wherein 25 % or greater of the fine precipitates have a diameter of 0.005 μm or less.

6. The material of claim 1, wherein the number of the fine precipitates per unit area (100 μm^2) is 7,000 to 16,500.

7. The material of claim 6, wherein the number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.01 μm or less is 4,500 to 16,000.

8. The material of claim 7, wherein the number of the fine precipitates per unit area (100 μm^2) having a diameter of 0.005 μm or less is 1,755 to 16,000.

9. The material of claim 1, wherein a number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of the fine precipitates by the mean number of the fine precipitates, is 0.95 or less.

10. A material for hot stamping, the material comprising:

a steel sheet comprising carbon (C) in an amount of 0.19 to 0.25 wt%, silicon (Si) in an amount of 0.1 to 0.6 wt%, manganese (Mn) in an amount of 0.8 to 1.6 wt%, phosphorus (P) in an amount of 0.03 wt% or less, sulfur (S) in an amount of 0.015 wt% or less, chromium (Cr) in an amount of 0.1 to 0.6 wt%, boron (B) in an amount of 0.001 to 0.005 wt%, an additive in an amount of 0.1 wt% or less, a remainder of iron (Fe), and other inevitable impurities; and

fine precipitates distributed inside the steel sheet,
 wherein the additive comprises at least one of titanium (Ti), niobium (Nb), and vanadium (V),
 the fine precipitates comprise nitride or carbide of at least one of titanium (Ti), niobium (Nb), and vanadium (V),
 the fine precipitates trap hydrogen, and
 a number variation coefficient, which is a value obtained by dividing a standard deviation of a mean number of
 the fine precipitates by the mean number of the fine precipitates, is 0.95 or less.

11. The material of claim 10, wherein the material after hot stamping exhibits a tensile strength of 1,350 MPa or greater,
 a bending angle of 50 degrees or greater, and an amount of activated hydrogen of 0.8 wppm or less.

12. The material of claim 10, wherein a first number variation coefficient, which is a value obtained by dividing a standard
 deviation of a mean number of the fine precipitates having a diameter of 0.01 μm or less from among the fine
 precipitates, by the mean number of the fine precipitates having a diameter of 0.01 μm or less, is 0.95 or less.

13. The material of claim 12, wherein a second number variation coefficient, which is a value obtained by dividing a
 standard deviation of a mean number of the fine precipitates having a diameter of 0.005 μm or less from among
 the fine precipitates, by the mean number of the fine precipitates having a diameter of 0.005 μm or less, is 0.95 or less.

14. The material of claim 10, wherein the number of the fine precipitates per unit area ($100 \mu\text{m}^2$) is 7,000 to 16,500.

15. The material of claim 14, wherein the number of the fine precipitates per unit area ($100 \mu\text{m}^2$) having a diameter of
 0.01 μm or less is 4,500 to 16,000.

16. The material of claim 15, wherein the number of the fine precipitates per unit area ($100 \mu\text{m}^2$) having a diameter of
 0.005 μm or less is 1,755 to 16,000.

17. The material of claim 10, wherein the mean diameter of the fine precipitates is 0.007 μm or less.

18. The material of claim 17, wherein 60 % or greater of the fine precipitates have a diameter of 0.01 μm or less.

19. The material of claim 18, wherein 25 % or greater of the fine precipitates have a diameter of 0.005 μm or less.

FIG. 1

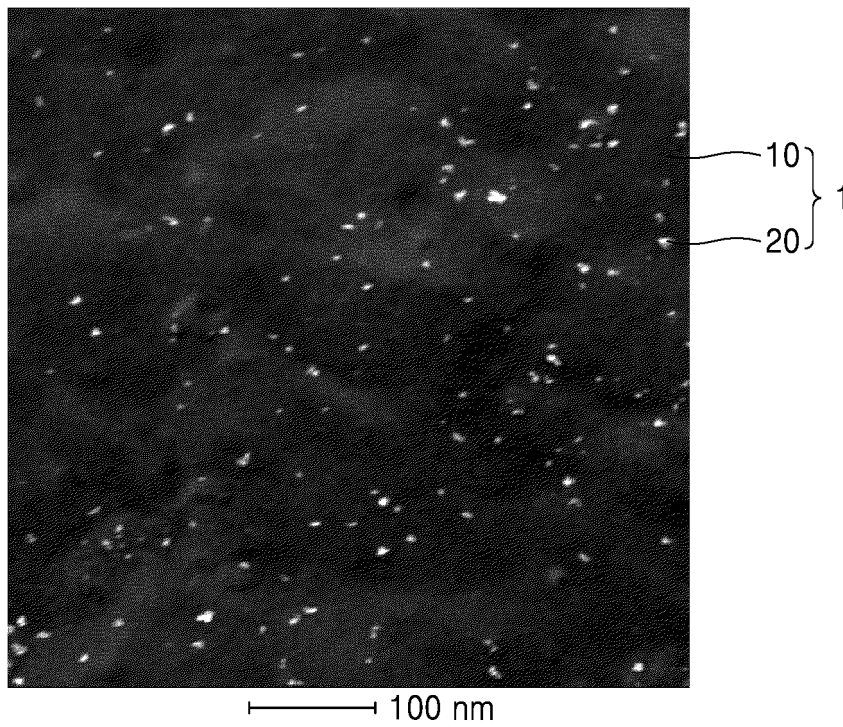


FIG. 2A

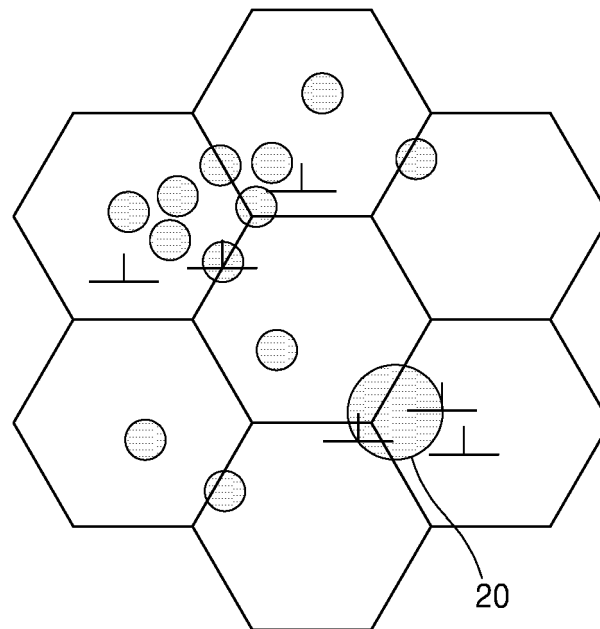


FIG. 2B

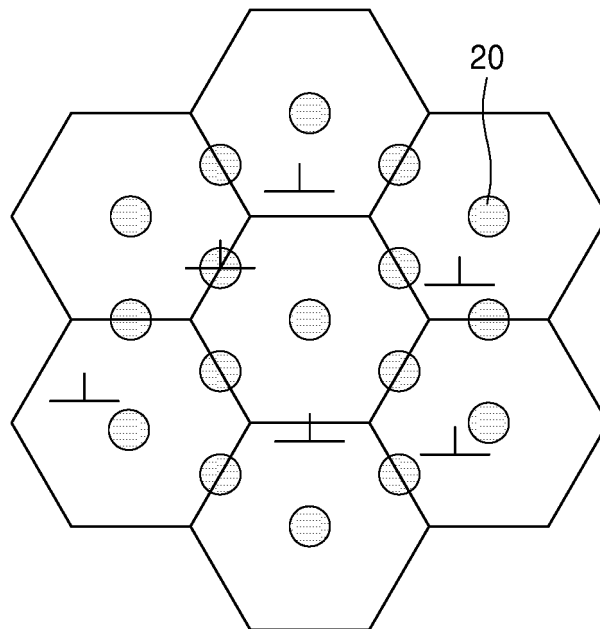


FIG. 3A

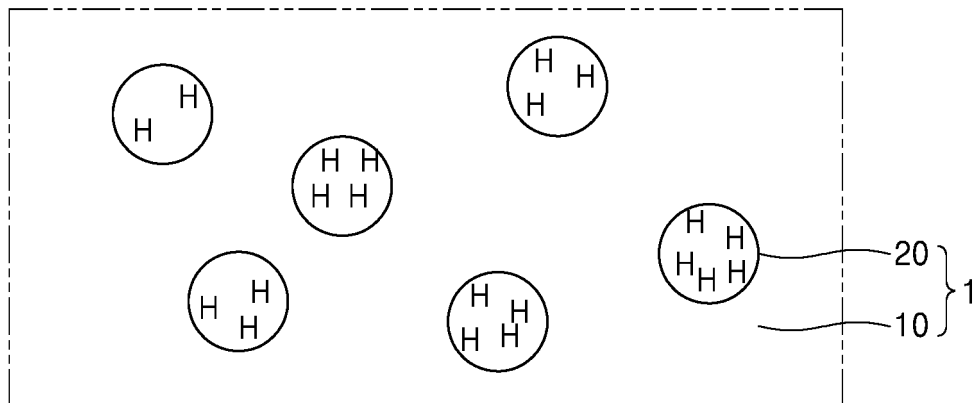


FIG. 3B

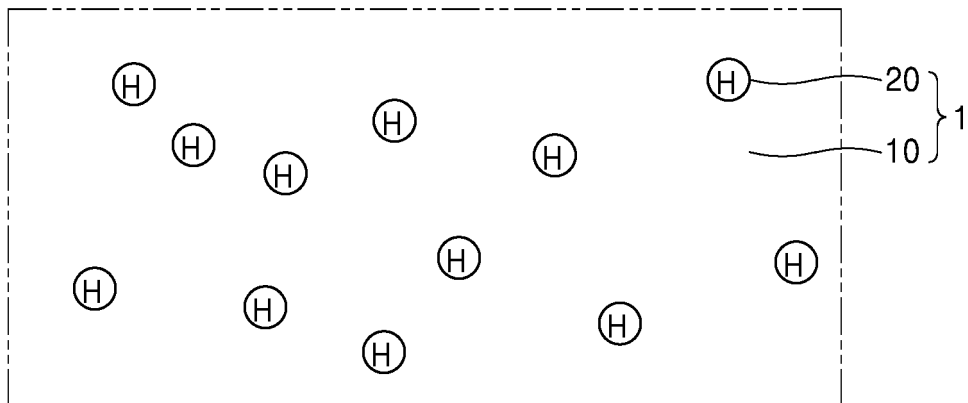


FIG. 4

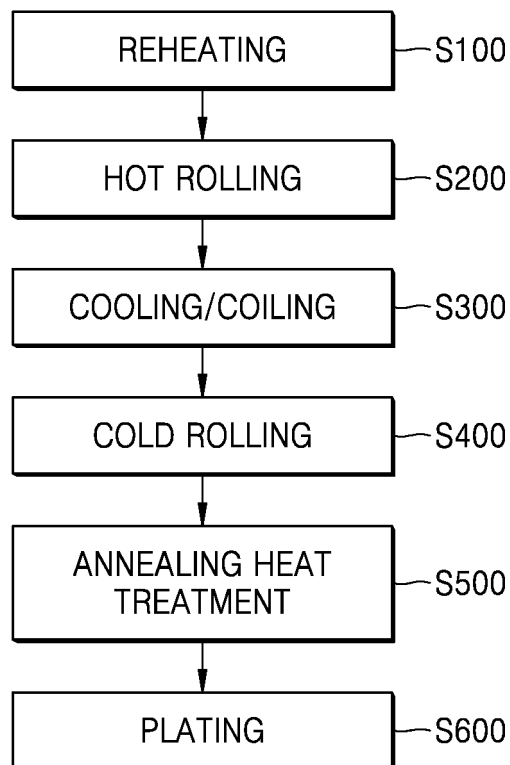


FIG. 5

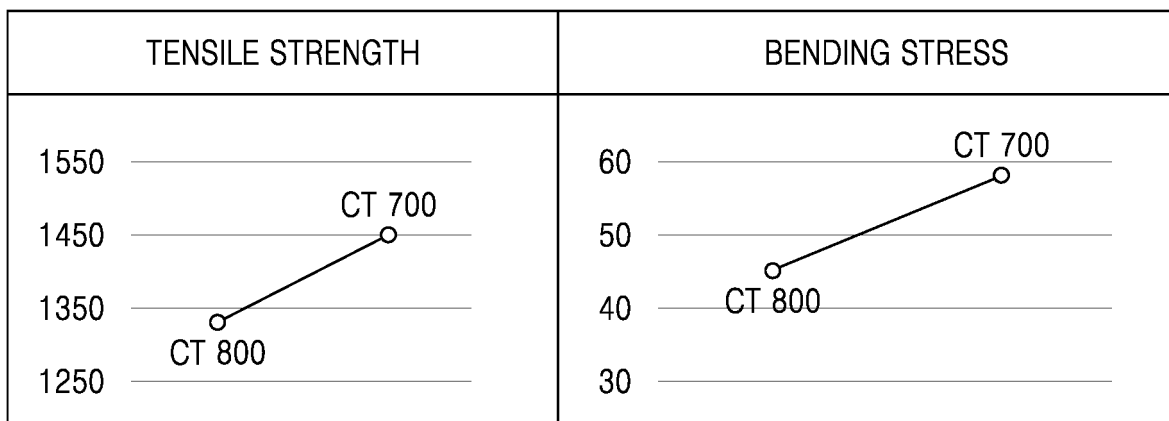


FIG. 6A

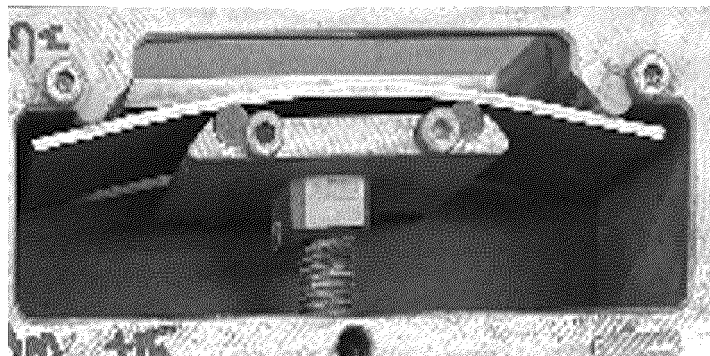
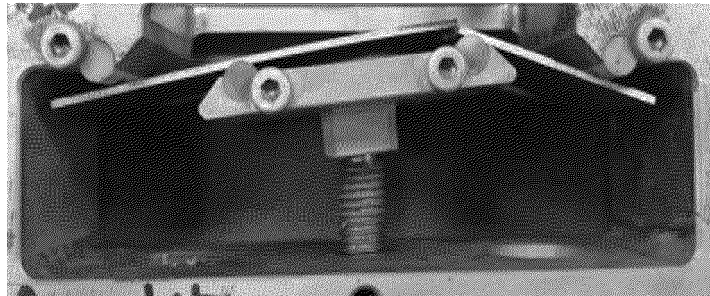


FIG. 6B



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/020148

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/38(2006.01)i; C22C 38/32(2006.01)i; C22C 38/28(2006.01)i; C22C 38/26(2006.01)i; C22C 38/24(2006.01)i;
B21D 22/02(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C 38/38(2006.01); B21B 3/00(2006.01); B21B 3/02(2006.01); B21D 35/00(2006.01); C21D 1/18(2006.01);
C21D 8/02(2006.01); C21D 9/46(2006.01); C21D 9/48(2006.01); C22C 38/00(2006.01); C22C 38/58(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 핫 스탬핑 소재(hot stamping material), 석출물(precipitation), 평균 직경(average diameter), 표준편차(standard deviation), 평균 개수(average number), 티타늄(titanium), 니오븀(niobium), 바나듐(vanadium)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2005-068548 A (NIPPON STEEL CORP.) 17 March 2005 (2005-03-17) See paragraphs [0002] and [0049]; and claims 1 and 4.	1,3
Y		2,4-8
A		9-19
Y	KR 10-2019-0001493 A (HYUNDAI STEEL COMPANY) 04 January 2019 (2019-01-04) See paragraphs [0082] and [0086]; and claim 1.	2,4-8
Y	JP 2005-126733 A (NIPPON STEEL CORP.) 19 May 2005 (2005-05-19) See paragraph [0037].	4-8
A	KR 10-2014-0102310 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 21 August 2014 (2014-08-21) See paragraphs [0009]-[0041].	1-19

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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

“D” document cited by the applicant in the international application

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

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

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

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

23 February 2023

Date of mailing of the international search report

24 February 2023

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208

Facsimile No. +82-42-481-8578

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/020148

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-1533164 B1 (NIPPON STEEL & SUMITOMO METAL CORPORATION et al.) 01 July 2015 (2015-07-01) See claims 1-4.	1-19

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2022/020148

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2005-068548 A	17 March 2005	JP 4167587 B2	15 October 2008
KR 10-2019-0001493 A	04 January 2019	CN 110799281 A	14 February 2020
		CN 110799281 B	03 December 2021
		DE 112017007697 T5	26 March 2020
		KR 10-2021200 B1	11 September 2019
		US 11390929 B2	19 July 2022
		US 2021-0147955 A1	20 May 2021
		WO 2019-004540 A1	03 January 2019
JP 2005-126733 A	19 May 2005	None	
KR 10-2014-0102310 A	21 August 2014	BR 112014017113 A2	13 June 2017
		BR 112014017113 A8	04 July 2017
		BR 112014017113 B1	26 March 2019
		CA 2863218 A1	18 July 2013
		CA 2863218 C	18 July 2017
		CN 104040008 A	10 September 2014
		CN 104040008 B	24 August 2016
		EP 2803746 A1	19 November 2014
		EP 2803746 A4	16 March 2016
		EP 2803746 B1	01 May 2019
		ES 2733320 T3	28 November 2019
		JP 5382278 B1	08 January 2014
		KR 10-1660144 B1	26 September 2016
		MX 2014008429 A	06 October 2014
		PL 2803746 T3	30 September 2019
		RU 2014-129326 A	10 March 2016
		RU 2581333 C2	20 April 2016
		TW 201343932 A	01 November 2013
		TW I468532 B	11 January 2015
		US 2015-0050519 A1	19 February 2015
		US 9725782 B2	08 August 2017
		WO 2013-105631 A1	18 July 2013
		ZA 201404811 B	27 January 2016
KR 10-1533164 B1	01 July 2015	BR 112013009515 A2	26 July 2016
		BR 112013009515 B1	07 August 2018
		BR 112013009517 A2	26 July 2016
		BR 112013009517 B1	24 April 2019
		BR 112013009520 A2	25 July 2017
		BR 112013009520 B1	07 May 2019
		CA 2813915 A1	26 April 2012
		CA 2813915 C	08 March 2016
		CA 2814630 A1	26 April 2012
		CA 2814630 C	26 April 2016
		CA 2814646 A1	26 April 2012
		CA 2814646 C	08 March 2016
		CN 103168106 A	19 June 2013
		CN 103168106 B	12 November 2014
		CN 103261452 A	21 August 2013
		CN 103261452 B	19 November 2014
		CN 103314120 A	18 September 2013
		CN 103314120 B	05 November 2014

Form PCT/ISA/210 (patent family annex) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR2022/020148

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
		EP 2631306 A1	28 August 2013
		EP 2631306 A4	07 September 2016
		EP 2631306 B1	11 December 2019
		EP 2631307 A1	28 August 2013
		EP 2631307 A4	02 November 2016
		EP 2631307 B1	03 April 2019
		EP 2631308 A1	28 August 2013
		EP 2631308 A4	02 November 2016
		EP 2631308 B1	28 November 2018
		ES 2711649 T3	06 May 2019
		ES 2729056 T3	30 October 2019
		JP 2013-151708 A	08 August 2013
		JP 5224010 B2	03 July 2013
		JP 5293902 B2	18 September 2013
		JP 5547287 B2	09 July 2014
		JP 5752409 B2	22 July 2015
		KR 10-1509362 B1	07 April 2015
		KR 10-1513378 B1	17 April 2015
		KR 10-2013-0055020 A	27 May 2013
		KR 10-2013-0063541 A	14 June 2013
		MX 2013004355 A	28 June 2013
		MX 2013004356 A	24 June 2013
		MX 2013004357 A	24 June 2013
		MX 348196 B	05 June 2017
		MX 359051 B	13 September 2018
		MX 361834 B	18 December 2018
		PL 2631307 T3	30 September 2019
		PL 2631308 T3	31 May 2019
		US 10030280 B2	24 July 2018
		US 2013-0199676 A1	08 August 2013
		US 2013-0220490 A1	29 August 2013
		US 2013-0292009 A1	07 November 2013
		US 2017-0051372 A1	23 February 2017
		US 2017-0145531 A1	25 May 2017
		US 9512499 B2	06 December 2016
		US 9598745 B2	21 March 2017
		US 9840751 B2	12 December 2017
		US 9896736 B2	20 February 2018
		WO 2012-053636 A1	26 April 2012
		WO 2012-053637 A1	26 April 2012
		WO 2012-053642 A1	26 April 2012

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- KR 1020170076009 [0003]
- KR 1020200061922 [0004]