



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

(43) Date of publication:  
**06.10.2021 Bulletin 2021/40**

(21) Application number: **19888281.3**

(22) Date of filing: **29.11.2019**

(51) Int Cl.:  
**C22C 38/44** (2006.01) **C22C 38/46** (2006.01)  
**C22C 38/42** (2006.01) **C22C 38/48** (2006.01)  
**C22C 38/50** (2006.01) **C22C 38/54** (2006.01)  
**C22C 38/00** (2006.01) **C22C 38/06** (2006.01)  
**C22C 38/02** (2006.01) **C22C 38/04** (2006.01)

(86) International application number:  
**PCT/KR2019/016694**

(87) International publication number:  
**WO 2020/111857 (04.06.2020 Gazette 2020/23)**

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

(30) Priority: **29.11.2018 KR 20180150819**

(71) Applicant: **POSCO**  
**Pohang-si, Gyeongsangbuk-do 37859 (KR)**

(72) Inventors:  
• **SUNG, Hyun-Je**  
**Pohang-si, Gyeongsangbuk-do 37877 (KR)**  
• **KIM, Dae-Woo**  
**Pohang-si, Gyeongsangbuk-do 37877 (KR)**

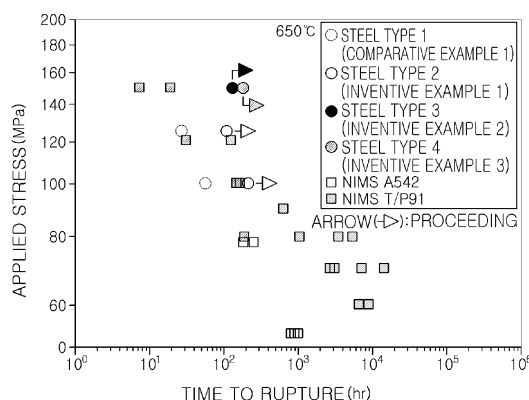
(74) Representative: **Zech, Stefan Markus**  
**Meissner Bolte Patentanwälte**  
**Rechtsanwälte Partnerschaft mbB**  
**Postfach 86 06 24**  
**81633 München (DE)**

(54) **CHROMIUM-MOLYBDENUM STEEL PLATE HAVING EXCELLENT CREEP STRENGTH AND METHOD FOR MANUFACTURING SAME**

(57) Provided are a chromium-molybdenum steel plate having excellent creep strength and a method for manufacturing same. The chromium-molybdenum steel plate of the present invention comprises, by weight%, 0.11-0.15% of C, 0.10% or less of Si (exclusive of 0%), 0.3-0.6% of Mn, 0.010% or less of S (exclusive of 0%), 0.015% or less of P (exclusive of 0%), 2.0-2.5% of Cr,

0.9-1.1% of Mo, 0.65-1.0% of V, 0.25% or less of Ni (exclusive of 0%), 0.20% or less of Cu (exclusive of 0%), 0.07% or less of Nb (exclusive of 0%), 0.03% or less of Ti (exclusive of 0%), 0.015% or less of N (exclusive of 0%), 0.025% or less of Al (exclusive of 0%), 0.002% or less of B (exclusive of 0%), and the remainder of Fe and unavoidable impurities.

【FIG. 1】



**Description**

[Technical Field]

**[0001]** The present disclosure relates to manufacturing of a chromium-molybdenum steel plate having excellent creep properties, and more particularly, to a chromium-molybdenum steel plate which may have an excellent creep strength by forming only fine carbonitrides in the inside and the grain boundary of a martensite matrix of a composed phase of a steel material to interrupt dislocation movement at a high temperature and secure stability of sub-crystal grains, and a method for manufacturing the same.

[Background Art]

**[0002]** Power generation and oil refinery/refining industries should consider the construction of environmentally friendly facilities and greater efficiency in energy use.

**[0003]** First, an increase in temperature and pressure of steam supplied to a turbine for increasing power generation efficiency is required, and thus, improvement of thermal resistance of boiler materials to produce steam at a higher temperature is essential.

**[0004]** In addition, in the oil refinery/refining industries, steel materials having excellent properties at raised temperature and pressure are being developed for higher efficiency due to recent strengthening of environmental regulation.

**[0005]** Since an austenite stainless steel contains a large amount of high-priced alloying elements, it is expensive and its use is limited due to poor physical properties (low thermal conductivity and high coefficient of thermal expansion) and a difficulty in manufacture of large parts. However, a chromium steel is often used due to its excellent creep strength, weldability, corrosion resistance, oxidation resistance, and the like.

**[0006]** For maintaining the creep strength at a high temperature of the thermal resistant chromium steel for a long time, solid solution strengthening and precipitation strengthening methods are applied. For this, molybdenum and vanadium, niobium, and titanium which are elements forming M(C,N) carbonitrides (M = metal element, C = carbon, N = nitrogen) are mainly alloyed. Also, a thermal resistant steel in which formation of  $(Fe,Cr)_{23}C_6$  carbides which are thermodynamically unstable and easily coarsened to deteriorate creep properties is suppressed by extremely decreasing a carbon content to 0.002 wt%, and fine carbonitrides are precipitated to greatly improve creep properties, was suggested, but it is currently almost impossible to commercially mass-produce the thermal resistant steel having a lowered carbon content as described above.

[Disclosure]

[Technical Problem]

**[0007]** An aspect of the present disclosure is to provide a chromium-molybdenum steel plate having excellent creep properties by completely suppressing formation of coarse precipitates such as  $(Fe,Cr)_{23}C_6$  carbides and forming only fine carbonitrides without extremely lowering a carbon content, unlike the conventional technologies described above, using alloy design and heat treatment, and a method for manufacturing the same.

**[0008]** However, the object of the present disclosure is not limited to the object described above, and other objects which are not described above may be clearly understood by those skilled in the art from the following description.

[Technical Solution]

**[0009]** According to an aspect of the present disclosure, a chromium-molybdenum steel plate having excellent creep strength includes, by weight: 0.11 to 0.15% of C, 0.10% or less (exclusive of 0%) of Si, 0.3 to 0.6% of Mn, 0.010% or less (exclusive of 0%) of S, 0.015% or less (exclusive of 0%) of P, 2.0 to 2.5% of Cr, 0.9 to 1.1% of Mo, 0.65 to 1.0% of V, 0.25% or less (exclusive of 0%) of Ni, 0.20% or less (exclusive of 0%) of Cu, 0.07% or less (exclusive of 0%) of Nb, 0.03% or less (exclusive of 0%) of Ti, 0.015% or less (exclusive of 0%) of N, 0.025% or less (exclusive of 0%) of Al, and 0.002% or less (exclusive of 0%) of B, with a balance of Fe and unavoidable impurities.

**[0010]** The steel plate may have a microstructure including tempered martensite.

**[0011]** It is preferable that the number of precipitates having a diameter of 200 nm or more including  $(Fe,Cr)_{23}C_6$  is in a range of one/ $\mu m^2$  or less in the microstructure of the steel plate.

**[0012]** It is preferable that the number of precipitates having a diameter of 20 nm or less is in a range of 20/ $\mu m^2$  or more in the microstructure of the steel plate.

**[0013]** The precipitates having a diameter of 20 nm or less may be (V,Mo,Nb,Ti) (C,N).

**[0014]** According to another aspect of the present disclosure, a method for manufacturing a steel plate includes:

hot-rolling a steel slab having the composition described above so that a finish rolling temperature is equivalent to or higher than Ar<sub>3</sub> to manufacture a hot rolled steel plate, and then cooling the hot rolled steel plate;  
 reheating the cooled hot rolled steel plate in a temperature range of 900 to 1200°C for 1t to 3t minutes [t (mm) is a thickness of the hot rolled steel plate] to austenitize the steel plate;  
 quenching the austenitized hot rolled steel plate to room temperature; and  
 tempering the quenched hot rolled steel plate in a temperature range of 675 to 800°C for 30 minutes to 120 minutes.

[Advantageous Effects]

**[0015]** As set forth above, according to an exemplary embodiment in the present disclosure, the chromium-molybdenum steel plate having excellent creep properties of the present disclosure having the configuration described above may have a longer creep life than an ASTM A387 Grade 91 steel containing chromium in a large amount of 9 wt%, with an excellent creep life at a high temperature, by quenching and tempering.

[Description of Drawings]

**[0016]**

FIG. 1 is a drawing illustrating a comparison of the results of a creep test for steel types 1 to 4 and conventional materials used in the experiment of the present disclosure.

FIGS. 2 to 5 are graphs illustrating the results of a dilatometer test representing phase transformation depending on a cooling rate after austenitization in steel types 1 to 4 used in the experiment of the present disclosure.

FIG. 6 is a graph illustrating Gibbs free energy for (Fe,Cr)<sub>23</sub>C<sub>6</sub> carbide formation depending on a content of vanadium in a chromium-molybdenum steel plate.

FIG. 7 is scanning electron microscope (SEM) photographs for steel types 1 to 4 used in the experiment of the present disclosure.

[Best Mode for Invention]

**[0017]** Hereinafter, the present disclosure will be described.

**[0018]** As described above, a conventional thermal resistant chromium steel mainly uses molybdenum and vanadium, niobium, and titanium which are elements forming M(C,N) carbonitrides (M = metal element, C = carbon, N = nitrogen), but the thermal resistant chromium steel as such is thermodynamically unstable and easily coarsened so that formation of (Fe,Cr)<sub>23</sub>C<sub>6</sub> carbides which deteriorate creep properties may not be avoided, and thus, it is difficult to secure excellent creep properties.

**[0019]** In order to solve the problems of the conventional technology, the present inventors repeated studies and experiments, and as a result, confirmed that by optimizing an amount of vanadium added to a thermal resistant chromium steel alloy containing 2.0 to 2.5% of Cr and also properly controlling a tempering temperature, a thermal resistant chromium steel having excellent creep properties may be obtained, thereby suggesting the present disclosure.

**[0020]** The chromium-molybdenum steel plate having excellent creep strength of the present disclosure includes, by weight: 0.11 to 0.15% of C, 0.10% or less (exclusive of 0%) of Si, 0.3 to 0.6% of Mn, 0.010% or less (exclusive of 0%) of S, 0.015% or less (exclusive of 0%) of P, 2.0 to 2.5% of Cr, 0.9 to 1.1% of Mo, 0.65 to 1.0% of V, 0.25% or less (exclusive of 0%) of Ni, 0.20% or less (exclusive of 0%) of Cu, 0.07% or less (exclusive of 0%) of Nb, 0.03% or less (exclusive of 0%) of Ti, 0.015% or less (exclusive of 0%) of N, 0.025% or less (exclusive of 0%) of Al, and 0.002% or less (exclusive of 0%) of B, with a balance of Fe and unavoidable impurities.

**[0021]** Hereinafter, the reason for limiting the components of the chromium-molybdenum steel plate having excellent creep properties will be described, and "%" herein represents "wt%", unless otherwise defined.

• Carbon (C): 0.11 to 0.15%

**[0022]** Carbon is an element for austenite stabilization, which may adjust an Ae<sub>3</sub> temperature and a martensite formation initiation temperature depending on the content and is very effective for applying asymmetric distortion as an interstitial element to a lattice structure of a martensite phase to secure high strength. However, when a carbon content in the steel is more than 0.15%, carbides are excessively formed and weldability is greatly deteriorated.

**[0023]** Therefore, it is preferable to limit the carbon content to a range of 0.11 to 0.15%, more preferably to a range of 0.11 to 0.14% in the present disclosure.

- Silicon (Si): 0.10% or less (exclusive of 0%)

**[0024]** Silicon is added as a deoxidizer during casting as well as for strengthening of solid solution. However, while it is essential to form advantageous carbides such as fine carbides in the chromium-molybdenum steel plate having excellent creep properties according to an exemplary embodiment in the present disclosure, silicon serves to suppress carbide formation.

**[0025]** Therefore, it is preferable to limit a silicon content to 0.10% or less, more preferably to a range of 0.005 to 0.08% in the present disclosure.

- Manganese (Mn): 0.3 to 0.6%

**[0026]** Manganese is an element for austenite stabilization, which greatly increases hardenability of a steel to allow a hard phase such as martensite to be formed. In addition, manganese reacts with sulfur so that MnS is precipitated, which is advantageous for preventing cracks at a high temperature by sulfur segregation. However, as a manganese content increases, an austenite stability degree is excessively increased.

**[0027]** Therefore, it is preferable to limit the manganese content to a range of 0.3 to 0.6%, more preferably to a range of 0.35 to 0.55% in the present disclosure.

- Sulfur (S): 0.010% or less (exclusive of 0%)

**[0028]** Sulfur is an impurity element and when the content is more than 0.010%, ductility and weldability of a steel are deteriorated.

**[0029]** Therefore, it is preferable to limit a sulfur content to 0.010% or less.

- Phosphorus (P): 0.015% or less (exclusive of 0%)

**[0030]** Phosphorus is an element having a solid solution strengthening effect, but an impurity element like sulfur, when the content is more than 0.015%, a steel has brittleness and decreased weldability.

**[0031]** Therefore, it is preferable to limit a phosphorus content to 0.015% or less.

- Chromium (Cr): 2.0 to 2.5%

**[0032]** Chromium is a ferrite stabilization element and an element increasing hardenability, and adjusts an Ae3 temperature and a delta ferrite forming temperature range depending on the amount. In addition, chromium reacts with oxygen to form a dense and stable protective film of Cr<sub>2</sub>O<sub>3</sub> to increase oxidation resistance and corrosion resistance at a high temperature, but increases a delta ferrite forming temperature range. In a process of casting a steel having a high chromium content, delta ferrite may be formed, and remains even after heat treatment to adversely affect steel characteristics.

**[0033]** Therefore, it is preferable to limit the chromium content to a range of 2.0 to 2.5%, more preferably to a range of 2.1 to 2.4% in the present disclosure.

- Molybdenum (Mo): 0.9 to 1.1%

**[0034]** Molybdenum is known as an element which increases hardenability and stabilizes ferrite. Molybdenum increases a creep life at a high temperature by strong solid solution strengthening, participates as a metal element forming M(C, N) carbonitrides to stabilize carbonitrides, and greatly reduces a coarsening speed. However, when a molybdenum content is increased, a delta ferrite forming temperature range may be widened and delta ferrite may be formed and remain in a process of casting a steel. Remaining delta ferrite adversely affects steel characteristics.

**[0035]** Therefore, it is preferable to limit the molybdenum content to a range of 0.9 to 1.1%, more preferably to a range of 0.95 to 1.05%.

- Vanadium (V): 0.65 to 1.0%

**[0036]** Vanadium is one of elements forming M(C,N) carbonitrides, and when a vanadium content is increased, (Fe, Cr)<sub>23</sub>C<sub>6</sub> carbide formation driving force is decreased, resulting in complete suppression of (Fe, Cr)<sub>23</sub>C<sub>6</sub> carbide formation. In order to suppress (Fe, Cr)<sub>23</sub>C<sub>6</sub> carbide formation in a chromium steel having a chromium content of 2.0 to 2.5%, 0.65% or more of a vanadium alloy is needed. However, when the vanadium content is more than 1.0%, there is a difficulty in a production process of materials.

**[0037]** Therefore, it is preferable to limit the vanadium content to a range of 0.65 to 1.0%, more preferably to a range of 0.67 to 0.98%.

• Nickel (Ni): 0.25% or less (exclusive of 0%)

**[0038]** Nickel is an element for improving toughness of a steel and is added for increasing steel strength without deterioration of toughness at a low temperature. When nickel is added at the content of more than 0.25%, a price increase due to nickel addition is caused.

**[0039]** Therefore, it is preferable to limit the nickel content to a range of 0.25% or less, more preferably to a range of 0.005 to 0.24%.

• Copper (Cu): 0.20% or less (exclusive of 0%)

**[0040]** Copper is an element for improving hardenability of materials and is added so that a steel plate has a homogeneous structure after heat treatment. However, the amount added is more than 0.20%, a possibility of crack occurrence for steel plate may be increased.

**[0041]** Therefore, it is preferable to limit a copper content to 0.20% or less, more preferably to a range of 0.005 to 0.18%.

• Niobium (Nb): 0.07% or less (exclusive of 0%)

**[0042]** Niobium is one of elements forming M(C,N) carbonitrides. In addition, it is solid-solubilized when reheating a slab and suppresses austenite crystal grain growth during hot rolling, and then is precipitated to improve steel strength. However, when niobium is excessively added at more than 0.07%, weldability may be deteriorated and crystal grains may be fined than necessary.

**[0043]** Therefore, it is preferable to limit a niobium content to 0.07% or less, more preferably to a range of 0.005 to 0.06%.

• Titanium (Ti): 0.03% or less (exclusive of 0%)

**[0044]** Titanium is also an element effective for suppressing austenite crystal grain growth in a TiN form. However, when titanium is added at more than 0.03%, coarse Ti-based precipitates are formed and there is a difficulty in welding of materials.

**[0045]** Therefore, it is preferable to limit a titanium content to 0.03% or less, more preferably to a range of 0.005 to 0.025%.

• Nitrogen (N): 0.015% or less (exclusive of 0%)

**[0046]** Since it is difficult to industrially completely remove nitrogen from steel, the upper limit of N is 0.015% which is a range allowable in a manufacturing process. Nitrogen is known as an austenite stabilization element, and stability at a high temperature is greatly increased when forming M(C,N) carbonitrides as compared with simple MC carbides, thereby effectively increasing creep strength of a steel material. However, when the content is more than 0.015%, nitrogen is bonded to boron to form BN, thereby increasing a risk of defect occurrence.

**[0047]** Therefore, it is preferable to limit a nitrogen content to 0.015% or less.

• Alumina (Al): 0.025% or less (exclusive of 0%)

**[0048]** Aluminum enlarges a ferrite area, and is added as a deoxidizer during casting. Since in a chromium steel, other ferrite stabilization elements are alloyed much, when an aluminum content is increased, an Ae3 temperature may be excessively raised. In addition, when the amount added is more than 0.025%, an oxide-based inclusion is formed in a large amount to deteriorate the physical properties of a material.

**[0049]** Therefore, it is preferable to limit the aluminum content to 0.025% or less, more preferably to a range of 0.005 to 0.025%.

• Boron (B): 0.002% or less (exclusive of 0%)

**[0050]** Boron is a ferrite stabilization element and contributes much to a hardenability increase only with a little amount. In addition, it is easily segregated in a crystal grain boundary to give a crystal grain boundary strengthening effect. However, when boron is added at more than 0.002%, BN may be formed, which may adversely affect the mechanical properties of materials.

**[0051]** Therefore, it is preferable to limit a boron content to 0.002% or less.

**[0052]** Other than that, a balance of Fe and unavoidable impurities are included. However, since in a common manufacturing process, unintended impurities may be inevitably incorporated from raw materials or a surrounding environment, the impurities may not be excluded. Since these impurities are known to any person with ordinary knowledge in the art, the entire contents thereof are not particularly mentioned herein.

**[0053]** Hereinafter, a microstructure and precipitates of the chromium-molybdenum steel plate of the present disclosure having excellent creep properties will be described in detail.

**[0054]** First, the steel plate of the present disclosure includes a tempered martensite structure as the matrix microstructure. However, a tempered bainite structure may be partly included depending on heat treatment conditions.

**[0055]** It is preferable that the number of precipitates having a diameter of 200 nm or more including  $(\text{Fe,Cr})_{23}\text{C}_6$  is in a range of one/ $\mu\text{m}^2$  or less in the steel plate microstructure of the present disclosure. When the number of precipitates having a diameter of 200 nm or more is more than one/ $\mu\text{m}^2$ , deteriorated creep properties may be caused by coarse carbides.

**[0056]** It is preferable that the number of precipitates having a diameter of 20 nm or less is in a range of 20/ $\mu\text{m}^2$  or more in the steel plate microstructure of the present disclosure. When the number of precipitates having a diameter of 20 nm or less is less than 20/ $\mu\text{m}^2$ , a distance between fine carbonitrides is significantly increased. Therefore, since dislocation movement at a high temperature and movement of sub-crystal grains are not effectively prevented, an effect of improving creep properties may not be large.

**[0057]** The precipitates having a diameter of 20 nm or less in the present disclosure may include  $(\text{V,Mo,Nb,Ti})(\text{C,N})$ .

**[0058]** Next, the method for manufacturing a precipitation hardening type chromium-molybdenum steel plate having excellent creep strength according to an exemplary embodiment in the present disclosure will be described.

**[0059]** The method for manufacturing a precipitation hardening type chromium-molybdenum steel plate having excellent creep strength of the present disclosure includes: hot-rolling a steel slab having the composition described above so that a finish rolling temperature is equivalent to or higher than Ar3 to manufacture a hot rolled steel plate, and then cooling the hot rolled steel plate; reheating the cooled hot rolled steel plate in a temperature range of 900 to 1200°C for 1t to 3t minutes [t (mm) is a thickness of the hot rolled steel plate] to austenitize the steel plate; quenching the austenitized hot rolled steel plate to room temperature; and tempering the quenched hot rolled steel plate in a temperature range of 675 to 800°C for 30 minutes to 120 minutes.

**[0060]** First, in the present disclosure, a steel slab having the composition component described above is hot-rolled so that a finish rolling temperature is equivalent to or higher than Ar3 to obtain a hot rolled steel plate. The reason for performing hot rolling in an austenite single phase region is to increase uniformity of a structure.

**[0061]** Then, in the present disclosure, the hot rolled steel plate manufactured was cooled to room temperature.

**[0062]** Subsequently, in the present disclosure, the cooled hot rolled steel plate is reheated to austenitize the steel plate. Here, it is preferable that a reheating temperature range is 900 to 1200°C and a reheating time is in a range of 1t minute to 3t minutes depending on a thickness t (mm) of the hot rolled steel plate.

**[0063]** When the reheating temperature is lower than 900°C, it is difficult to properly redissolve undesired carbides formed in a process of cooling after hot rolling. However, when the reheating temperature is higher than 1200°C, the characteristics may be deteriorated due to crystal grain coarsening.

**[0064]** It is preferable that the reheating time is in a range of 1t to 3t, in which the thickness of the hot rolled steel plate is t (mm). For example, a hot rolled steel plate having a thickness of 20 mm is reheated to be austenitized, reheating may be performed for 20 to 60 minutes. When the reheating time is less than 1t minute, it is difficult to properly redissolve undesired carbides formed in a process of cooling after hot rolling, but when the reheating time is more than 3t minutes, the characteristics may be deteriorated due to crystal grain coarsening.

**[0065]** Then, in the present disclosure, the hot rolled steel plate austenitized by the reheating is quenched to be cooled down to room temperature, thereby obtaining a martensite structure. Here, when cooling a matrix structure, care should be taken so that ferrite and pearlite structures are not formed to greatly decrease matrix strength.

**[0066]** Subsequently, in the present disclosure, the quenched hot rolled steel plate is tempered. Here, it is preferable that a tempering temperature is 675 to 800°C, a tempering time is 30 minutes to 120 minutes, and then air cooling is performed.

**[0067]** When the tempering temperature is lower than 675°C, precipitation of fine carbonitrides may not be induced in time due to the low temperature. However, when the tempering temperature is higher than 800°C, tempering causes softening of materials to greatly decrease a creep life.

**[0068]** More preferably, the tempering temperature is controlled to a range of 700 to 780°C.

**[0069]** Meanwhile, when the tempering time is less than 30 minutes, precipitates to be formed may not be formed. However, when the tempering time is more than 120 minutes, precipitate coarsening and material softening occur to greatly decrease a creep life.

[Mode for Invention]

**[0070]** Hereinafter, the present disclosure will be described in detail through the following examples.

(Example)

**[0071]** Hot rolled steel plates having alloy compositions of the following Table 1 and a thickness of 20 mm were prepared. Then, the hot rolled steel plate was reheated at 1000°C for 1 hour and quenched to cool down to room temperature. Subsequently, the cooled steel plate was tempered at 730°C for 1 hour and then air-cooled to room temperature to manufacture a Cr-Mo alloy steel. Meanwhile, in the following Table 1, steel type 1 is a composition of ASTM A542D steel and steel types 2 to 4 are steel types satisfying the steel composition components of the present disclosure.

**[0072]** For Cr-Mo alloy steels manufactured as described above, an ASTM E139 standard was utilized in a hot rolling direction to manufacture each of creep specimens having a gauge length of 15 mm and a gauge diameter of 6 mm, and the creep life at a high temperature of these specimens was evaluated using ATS 2320 creep test equipment and the results are shown in FIG. 1. In addition, for comparison, the creep results for ASTM A542 steel material and ASTM A387 Grade 91 steel material provided by National Institute for Materials Science (NIMS) of Japan are also shown together in FIG. 1.

**[0073]** In addition, phase transformation depending on a cooling rate after austenitization was confirmed using a dilatometer, and the results are shown in FIGS. 2 to 5. Also, Gibbs free energy change for  $(\text{Fe,Cr})_{23}\text{C}_6$  carbide formation depending on a vanadium content was calculated using a Thermo-Calc program and a TCFE6 database based on steel type 1, and the results are shown in FIG. 6.

**[0074]** Then, for the alloy steel specimen manufactured, a scanning electron microscope (SEM) was utilized to observe a microstructure, and the results are shown in FIG. 7.

[Table 1]

| Steel type No.                                                                                                                                                                                                  | C     | Si    | Mn    | Cr   | Mo   | Ni    | Cu    | Nb    | Ti    | V     | N     | Al    | Remarks               |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|-------|-------|------|------|-------|-------|-------|-------|-------|-------|-------|-----------------------|
| 1                                                                                                                                                                                                               | 0.127 | 0.053 | 0.490 | 2.28 | 1.04 | 0.206 | 0.081 | 0.016 | 0.012 | 0.308 | 0.014 | 0.017 | Comparative Example 1 |
| 2                                                                                                                                                                                                               | 0.118 | 0.060 | 0.475 | 2.22 | 0.98 | 0.199 | 0.084 | 0.015 | 0.010 | 0.68  | 0.013 | 0.025 | Inventive Example 1   |
| 3                                                                                                                                                                                                               | 0.124 | 0.063 | 0.459 | 2.23 | 1.0  | 0.199 | 0.082 | 0.015 | 0.010 | 0.79  | 0.013 | 0.023 | Inventive Example 2   |
| 4                                                                                                                                                                                                               | 0.126 | 0.065 | 0.455 | 2.20 | 0.99 | 0.199 | 0.03  | 0.015 | 0.010 | 0.89  | 0.013 | 0.017 | Inventive Example 3   |
| * In Table 1, steel types 1 to 4 included P <30ppm, S <30ppm, and B <5ppm, respectively. The unit of amounts of other components added is wt%, and the remaining components were Fe and unavoidable impurities. |       |       |       |      |      |       |       |       |       |       |       |       |                       |

**[0075]** As shown in FIG. 1, it is seen that the chromium-molybdenum steel plate of the present disclosure had a better creep life than the ASTM A387 Grade 91 steel material including 9 wt% of Cr. In addition, it is confirmed that steel types 2 to 4 satisfying the steel composition components of the present disclosure had better creep properties than steel type 1 which did not satisfy the steel composition components of the present disclosure.

**[0076]** It is seen from FIGS. 2 to 5 that when all of steel types 1 to 4 were reheated at 1000°C for 1 hour, quenched, and cooled to room temperature, the matrix microstructure included a martensite structure.

**[0077]** Meanwhile, FIG. 6 shows that when a vanadium content is increased,  $(\text{Fe,Cr})_{23}\text{C}_6$  carbide formation driving force is decreased, resulting in complete suppression of  $(\text{Fe,Cr})_{23}\text{C}_6$  carbide formation. Specifically, it is seen that in order to suppress  $(\text{Fe,Cr})_{23}\text{C}_6$  carbide formation in a chromium steel having a chromium content of 2.0 to 2.5 wt%, 0.65 wt% or more vanadium alloying is needed, when considering the tempering temperature range of 675 to 800°C and the creep temperature mentioned in the present disclosure. That is, it is seen that since steel types 2 to 4 of the present disclosure all included 0.65 wt% or more vanadium unlike steel type 1,  $(\text{Fe,Cr})_{23}\text{C}_6$  carbide formation was able to be completely suppressed.

**[0078]** Then, FIG. 7 is a scanning microscope photograph illustrating the results of observing the microstructure of a steel plate which was reheated at 1000°C for 1 hour, quenched to be cooled down to room temperature, and tempered at 730°C for 1 hour, and steel types 2 to 4 all showed fine carbonitride precipitation along sub-crystal grain boundary. It is seen that the carbonitrides as such effectively interrupt dislocation movement at a high temperature and also effectively prevent movement of sub-crystal grains to secure the stability, thereby greatly improving creep properties as compared with the conventional chromium steel. However, it is seen that steel type 1 formed coarse  $(\text{Fe,Cr})_{23}\text{C}_6$  carbides and the creep properties were not good as compared with steel types 2 to 4.

**[0079]** The present disclosure is not limited to the exemplary embodiments and the examples, but may be made in various forms different from each other, and those skilled in the art will understand that the present disclosure may be implemented in other specific forms without departing from the spirit or essential feature of the present disclosure. Therefore, it should be understood that the above-mentioned exemplary embodiments and examples are illustrative but not restrictive in all aspects.

## Claims

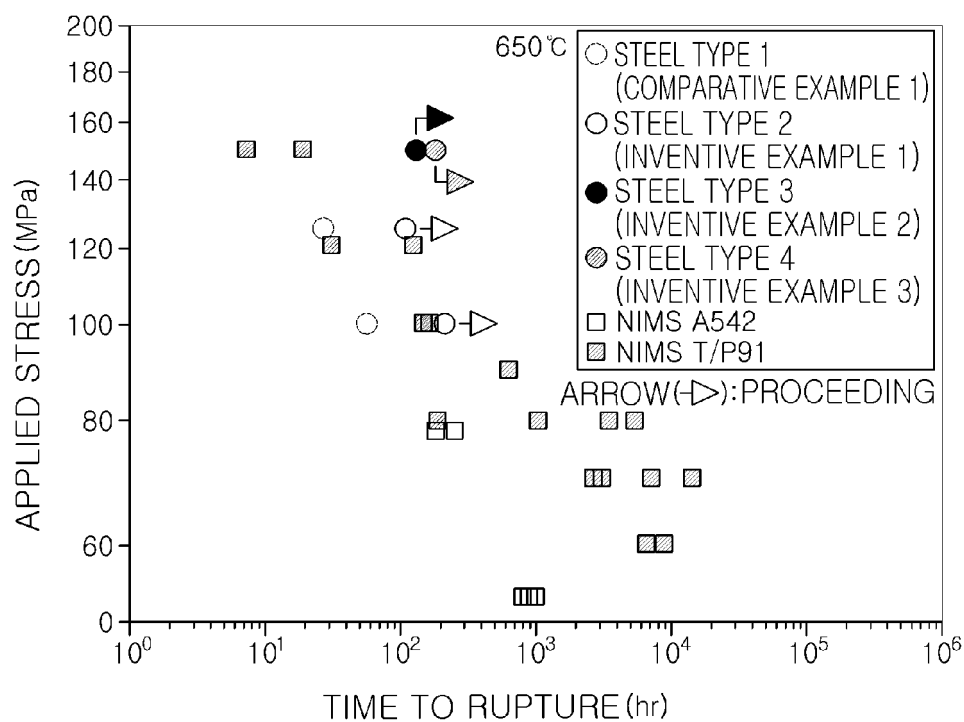
1. A chromium-molybdenum steel plate having excellent creep strength comprising, by weight: 0.11 to 0.15% of C, 0.10% or less (exclusive of 0%) of Si, 0.3 to 0.6% of Mn, 0.010% or less (exclusive of 0%) of S, 0.015% or less (exclusive of 0%) of P, 2.0 to 2.5% of Cr, 0.9 to 1.1% of Mo, 0.65 to 1.0% of V, 0.25% or less (exclusive of 0%) of Ni, 0.20% or less (exclusive of 0%) of Cu, 0.07% or less (exclusive of 0%) of Nb, 0.03% or less (exclusive of 0%) of Ti, 0.015% or less (exclusive of 0%) of N, 0.025% or less (exclusive of 0%) of Al, and 0.002% or less (exclusive of 0%) of B, with a balance of Fe and unavoidable impurities.
2. The chromium-molybdenum steel plate having excellent creep strength of claim 1, wherein the steel plate has a microstructure including tempered martensite.
3. The chromium-molybdenum steel plate having excellent creep strength of claim 2, wherein the number of precipitates having a diameter of 200 nm or more including  $(\text{Fe,Cr})_{23}\text{C}_6$  is in a range of one/ $\mu\text{m}^2$  or less in the microstructure of the steel plate.
4. The chromium-molybdenum steel plate having excellent creep strength of claim 2, wherein the number of precipitates having a diameter of 20 nm or less is in a range of 20/ $\mu\text{m}^2$  or more in the microstructure of the steel plate.
5. The chromium-molybdenum steel plate having excellent creep strength of claim 4, wherein the precipitates having a diameter of 20 nm or less are  $(\text{V,Mo,Nb,Ti})(\text{C,N})$ .
6. A method for manufacturing a chromium-molybdenum steel plate having excellent creep strength, the method comprising:
 

hot-rolling a steel slab including, by weight: 0.11 to 0.15% of C, 0.10% or less (exclusive of 0%) of Si, 0.3 to 0.6% of Mn, 0.010% or less (exclusive of 0%) of S, 0.015% or less (exclusive of 0%) of P, 2.0 to 2.5% of Cr, 0.9 to 1.1% of Mo, 0.65 to 1.0% of V, 0.25% or less (exclusive of 0%) of Ni, 0.20% or less (exclusive of 0%) of Cu, 0.07% or less (exclusive of 0%) of Nb, 0.03% or less (exclusive of 0%) of Ti, 0.015% or less (exclusive of 0%) of N, 0.025% or less (exclusive of 0%) of Al, and 0.002% or less (exclusive of 0%) of B, with a balance of Fe and unavoidable impurities so that a finish rolling temperature is equivalent to or higher than Ar<sub>3</sub> to manu-

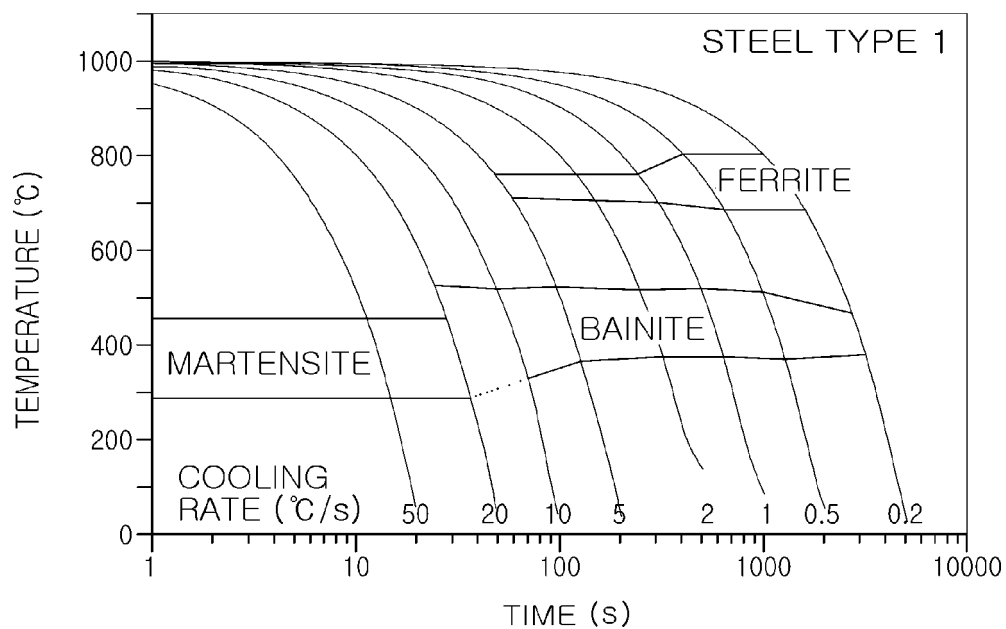
facture a hot rolled steel plate, and then cooling the hot rolled steel plate;  
 reheating the cooled hot rolled steel plate in a temperature range of 900°C to 1200°C for 1t to 3t minutes [t  
 (mm) is a thickness of the hot rolled steel plate] to austenitize the steel plate;  
 quenching the austenitized hot rolled steel plate to room temperature; and  
 tempering the quenched hot rolled steel plate in a temperature range of 675 to 800°C for 30 minutes to 120  
 minutes.

7. The method for manufacturing a chromium-molybdenum steel plate having excellent creep strength of claim 6,  
 wherein the steel plate has a microstructure including tempered martensite and the number of precipitates having  
 a diameter of 200 nm or more including  $(\text{Fe,Cr})_{23}\text{C}_6$  is in a range of one/ $\mu\text{m}^2$  or less in the microstructure of the  
 steel plate.
8. The method for manufacturing a chromium-molybdenum steel plate having excellent creep strength of claim 6,  
 wherein the steel plate has a microstructure including tempered martensite and the number of precipitates having  
 a diameter of 20 nm or less is in a range of 20/ $\mu\text{m}^2$  or more in the microstructure of the steel plate.
9. The method for manufacturing a chromium-molybdenum steel plate having excellent creep strength of claim 8,  
 wherein the precipitates having a diameter of 20 nm or less are (V,Mo,Nb,Ti) (C,N).

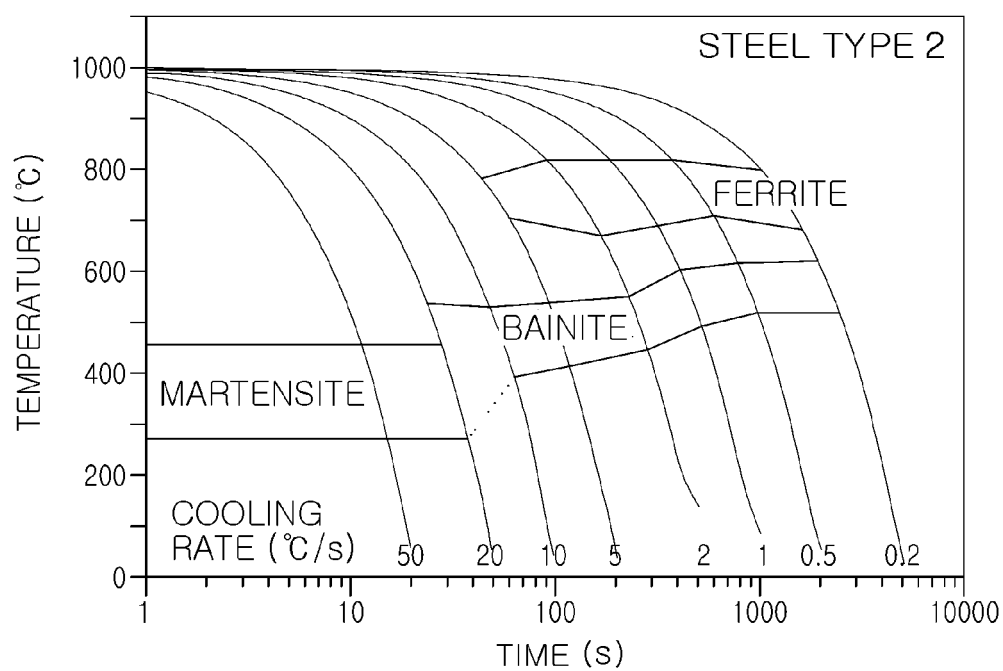
【FIG. 1】



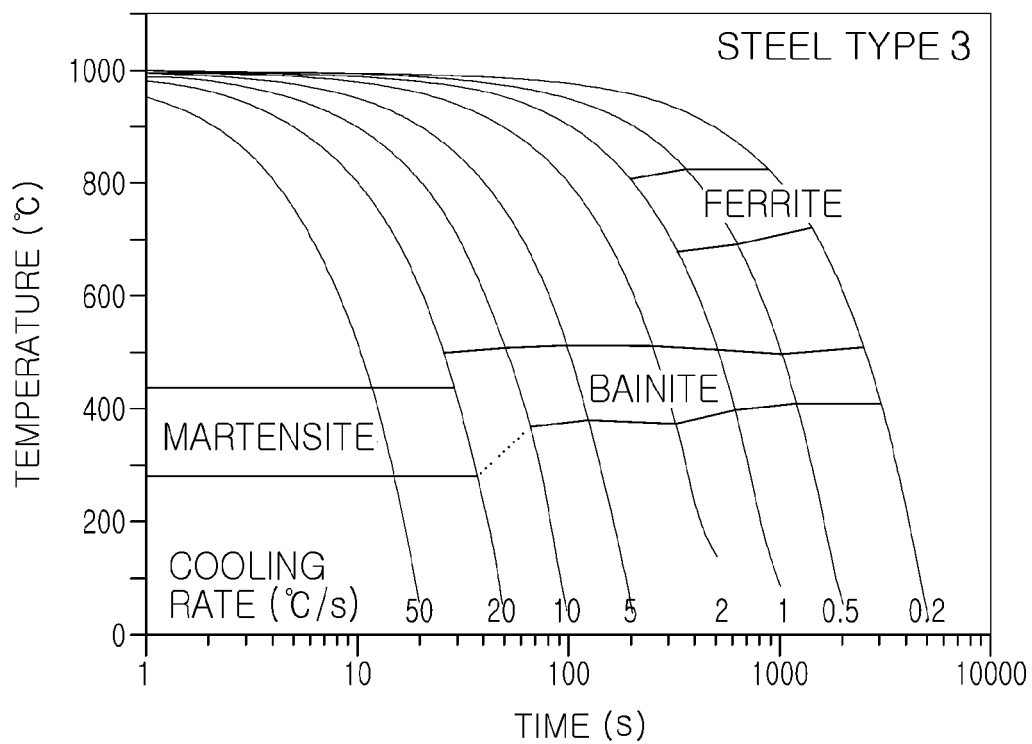
【FIG. 2】



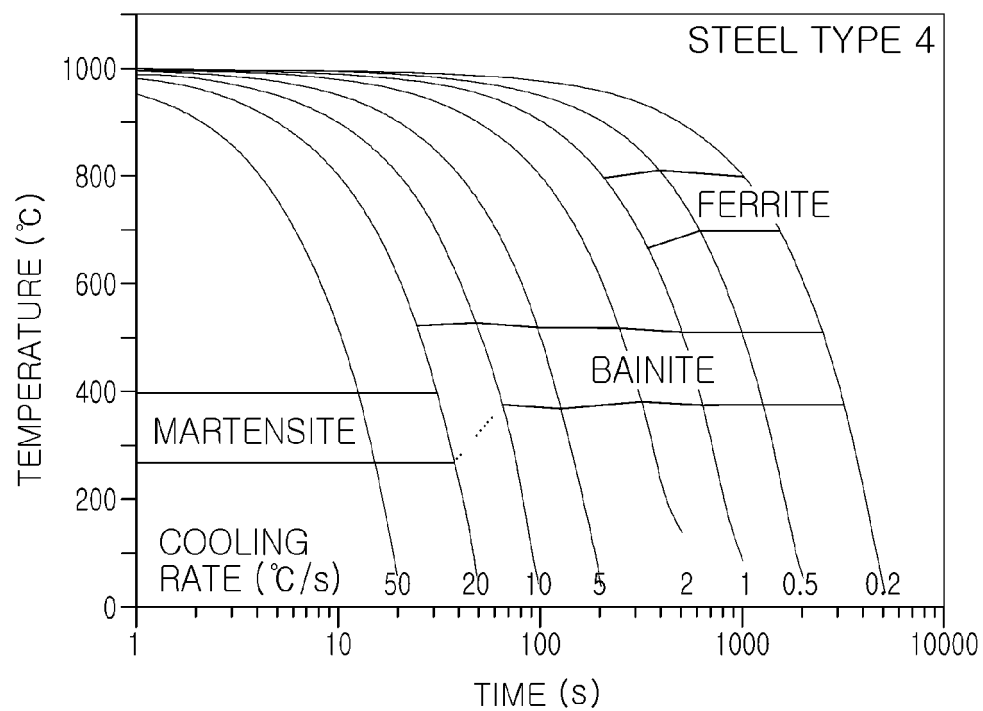
【FIG. 3】



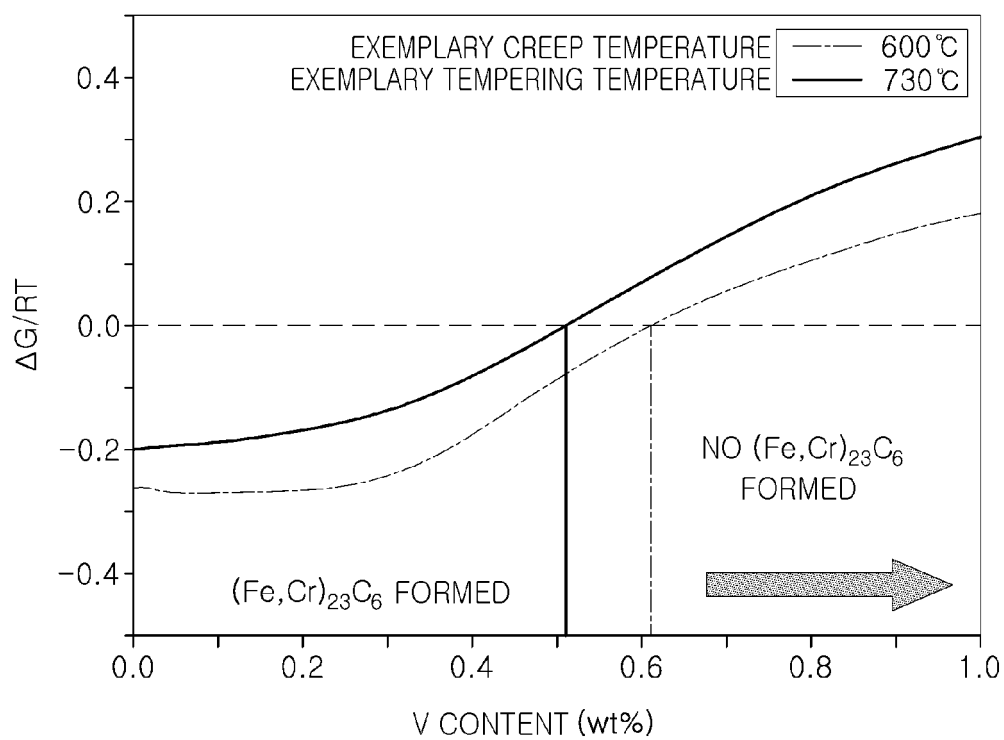
【FIG. 4】



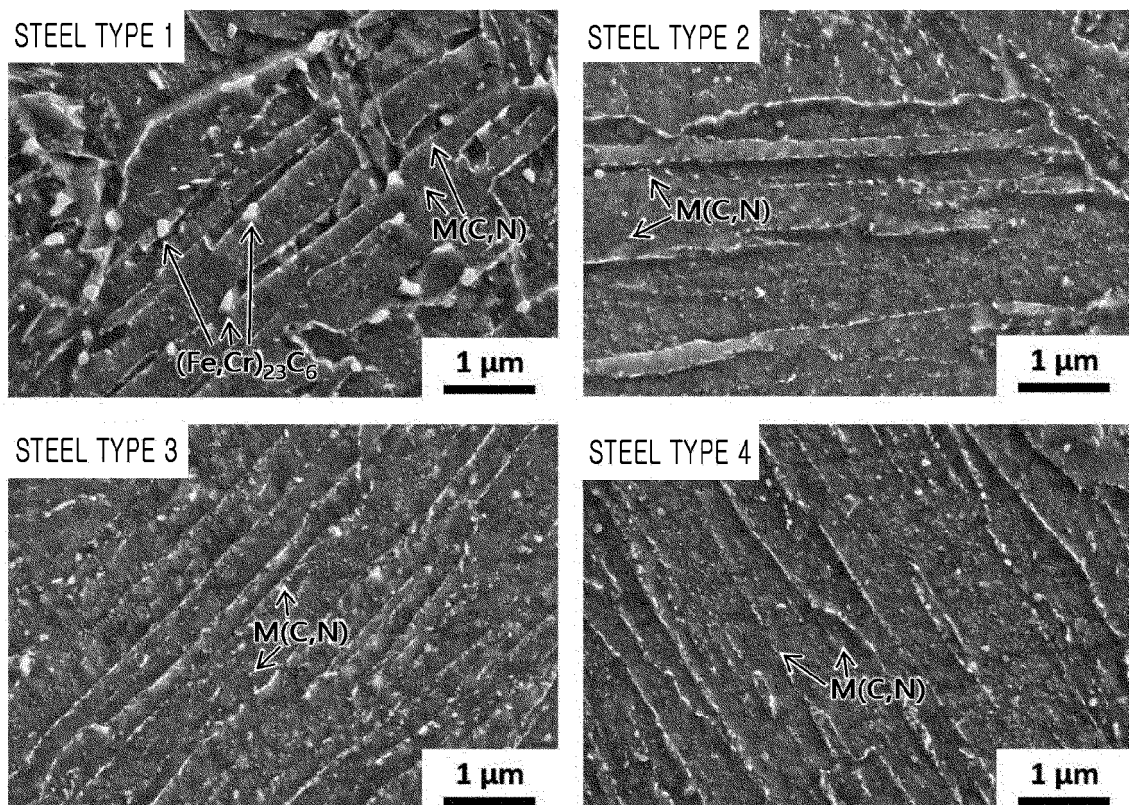
【FIG. 5】



【FIG. 6】



【FIG. 7】



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2019/016694

## A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/44(2006.01)i, C22C 38/46(2006.01)i, C22C 38/42(2006.01)i, C22C 38/48(2006.01)i, C22C 38/50(2006.01)i, C22C 38/54(2006.01)i, C22C 38/00(2006.01)i, C22C 38/06(2006.01)i, C22C 38/02(2006.01)i, C22C 38/04(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 38/44; B21C 37/08; C22C 19/00; C22C 19/05; C22C 33/02; C22C 38/00; C22C 38/18; C22C 38/22; C22C 38/54; C22C 38/46; C22C 38/42; C22C 38/48; C22C 38/50; C22C 38/06; C22C 38/02; C22C 38/04

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) &amp; Key words: creep, chrome(Cr), molybdenum(Mo), hot rolling, cooling, precipitation

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                    | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 2003-286543 A (NIPPON STEEL CORP.) 10 October 2003<br>See paragraphs [0010]-[0043]; and claims 1-8.                                | 1-9                   |
| A         | KR 10-2011-0080965 A (KOREA ATOMIC ENERGY RESEARCH INSTITUTE et al.)<br>13 July 2011<br>See paragraphs [0010]-[0013]; and claims 1-4. | 1-9                   |
| A         | KR 10-2015-0104348 A (KOREA ATOMIC ENERGY RESEARCH INSTITUTE)<br>15 September 2015<br>See paragraph [0012]; and claims 1-6.           | 1-9                   |
| A         | KR 10-2015-0005706 A (VDM METALS GMBH.) 14 January 2015<br>See paragraphs [0025]-[0197]; and claims 1-28.                             | 1-9                   |
| A         | KR 10-2005-0044624 A (ATI PROPERTIES, INC.) 12 May 2005<br>See claims 1-8.                                                            | 1-9                   |

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

☒ See patent family annex.

\* Special categories of cited documents:

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

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

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

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

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

"I" 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

09 MARCH 2020 (09.03.2020)

Date of mailing of the international search report

10 MARCH 2020 (10.03.2020)

Name and mailing address of the ISA/KR

 Korean Intellectual Property Office  
Government Complex Daejeon Building 4, 189, Cheongsa-ro, Seo-gu,  
Daejeon, 35208, Republic of Korea  
Facsimile No. +82-42-481-8578

Authorized officer

Telephone No.

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.

**PCT/KR2019/016694**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member | Publication<br>date |
|-------------------------------------------|---------------------|-------------------------|---------------------|
| JP 2003-286543 A                          | 10/10/2003          | JP 4009124 B2           | 14/11/2007          |
| KR 10-2011-0080965 A                      | 13/07/2011          | KR 10-1140651 B1        | 03/05/2012          |
|                                           |                     | US 2011-0162764 A1      | 07/07/2011          |
| KR 10-2015-0104348 A                      | 15/09/2015          | CN 104894478 A          | 09/09/2015          |
|                                           |                     | JP 2015-168883 A        | 28/09/2015          |
|                                           |                     | JP 5948382 B2           | 06/07/2016          |
|                                           |                     | KR 10-1769745 B1        | 22/08/2017          |
|                                           |                     | KR 10-2016-0079739 A    | 06/07/2016          |
|                                           |                     | KR 10-2017-0057206 A    | 24/05/2017          |
|                                           |                     | US 10011893 B2          | 03/07/2018          |
|                                           |                     | US 2015-0252458 A1      | 10/09/2015          |
| KR 10-2015-0005706 A                      | 14/01/2015          | BR 112014024761 B1      | 26/03/2019          |
|                                           |                     | CN 104245978 A          | 24/12/2014          |
|                                           |                     | CN 104245978 B          | 26/10/2016          |
|                                           |                     | DE 102012011161 A1      | 05/12/2013          |
|                                           |                     | DE 102012011161 B4      | 18/06/2014          |
|                                           |                     | EP 2855723 A1           | 08/04/2015          |
|                                           |                     | EP 2855723 B1           | 05/10/2016          |
|                                           |                     | ES 2605948 T3           | 17/03/2017          |
|                                           |                     | JP 2015-524023 A        | 20/08/2015          |
|                                           |                     | JP 6076472 B2           | 08/02/2017          |
|                                           |                     | KR 10-1668383 B1        | 21/10/2016          |
|                                           |                     | MX 2014014557 A         | 05/03/2015          |
|                                           |                     | MX 362836 B             | 19/02/2019          |
|                                           |                     | RU 2014-153531 A        | 10/08/2016          |
|                                           |                     | RU 2599324 C2           | 10/10/2016          |
|                                           |                     | US 2015-0050182 A1      | 19/02/2015          |
|                                           |                     | US 9657373 B2           | 23/05/2017          |
|                                           |                     | WO 2013-182177 A1       | 12/12/2013          |
| KR 10-2005-0044624 A                      | 12/05/2005          | AT 483038 T             | 15/10/2010          |
|                                           |                     | AU 2002-350227 A1       | 17/06/2003          |
|                                           |                     | BR 0214588 A            | 03/11/2004          |
|                                           |                     | CA 2465604 A1           | 12/06/2003          |
|                                           |                     | CA 2465604 C            | 24/07/2012          |
|                                           |                     | CN 100370049 C          | 20/02/2008          |
|                                           |                     | CN 1599805 A            | 23/03/2005          |
|                                           |                     | EP 1448803 A1           | 25/08/2004          |
|                                           |                     | EP 1448803 A4           | 16/08/2006          |
|                                           |                     | EP 1448803 B1           | 29/09/2010          |
|                                           |                     | EP 2278036 A1           | 26/01/2011          |
|                                           |                     | EP 2278036 B1           | 18/06/2014          |
|                                           |                     | EP 2767607 A1           | 20/08/2014          |
|                                           |                     | ES 2362223 T3           | 29/06/2011          |
|                                           |                     | ES 2487530 T3           | 21/08/2014          |
|                                           |                     | FI 124893 B             | 13/03/2015          |

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR2019/016694

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member | Publication<br>date |
|-------------------------------------------|---------------------|-------------------------|---------------------|
|                                           |                     | FI 20045186 A           | 21/05/2004          |
|                                           |                     | HK 1071774 A1           | 16/05/2008          |
|                                           |                     | HK 1198182 A1           | 13/03/2015          |
|                                           |                     | JP 2005-511892 A        | 28/04/2005          |
|                                           |                     | JP 4510458 B2           | 21/07/2010          |
|                                           |                     | KR 10-0615126 B1        | 22/08/2006          |
|                                           |                     | MX PA04004659 A         | 13/08/2004          |
|                                           |                     | NO 20042641 L           | 23/06/2004          |
|                                           |                     | US 2003-0124019 A1      | 03/07/2003          |
|                                           |                     | US 2004-0050462 A1      | 18/03/2004          |
|                                           |                     | US 6641780 B2           | 04/11/2003          |
|                                           |                     | WO 03-048402 A1         | 12/06/2003          |
|                                           |                     | ZA 200403628 B          | 22/02/2006          |

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