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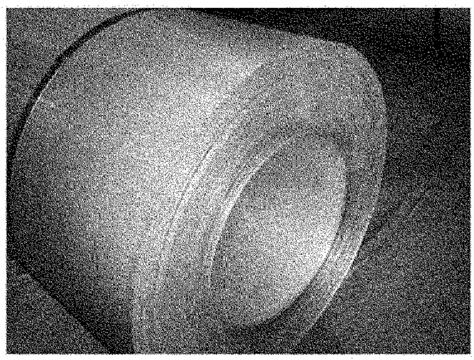
(54) **SUPER HIGH STRENGTH PLATED STEEL SHEET HAVING TENSILE STRENGTH OF 1300 MPA OR MORE, AND MANUFACTURING METHOD THEREFOR**

(57) The present invention relates to a super high strength plated steel sheet used in a vehicle, etc. and, more specifically, to a super high strength plated steel sheet having a tensile strength of 1300 MPa or more, and a manufacturing method therefor. According to the present invention, it is possible to provide a super high strength plated steel sheet in which cracks on an edge portion do not occur after slitting and coiling processes.

【Fig.1】

(C)



EP 3 243 923 A1

Description

[Technical Field]

[0001] The present disclosure relates to a plated steel sheet having ultra-high strength and used in vehicles and the like, and more particularly, to a plated steel sheet having ultra-high strength and a tensile strength of 1300 MPa or more, and a method of manufacturing the same.

[Background Art]

[0002] In recent years, in order to increase the stability and to lighten the weight of vehicles, the ultra-high strengthening of steel sheets for vehicles has been continuously increased. In addition, plated steel sheets having been subjected to plating on surfaces of ultra-high strength steel sheets have been mainly used to improve the corrosion resistance of steel sheets.

[0003] At present, martensite steel having a tensile strength of 1300 MPa or more has been developed and used as an ultra-high strength plated steel sheet, and plating products having enhanced corrosion resistance have also been being developed.

[0004] Since such ultra-high strength steel sheets usually have an elongation of 10% or less, steel sheet coils commonly produced in steel mills are slit and coiled to be formed as coils having a relatively narrow width, and then, are formed as components by applying a roll forming method or a simple forming method thereto.

[0005] However, in the case in which ultra-high strength plated steel sheets are slit and then coiled, a problem in which cracking may occur in edge portions of the produced steel plate coils in a width direction, and may propagate to center portions of the steel sheets, may occur.

[0006] Thus, the development of a technology, in which cracking of edge portions of ultra-high strength plated steel sheets which will subsequently be subjected to slitting and coiling processes may be reduced, is required.

[Technical Problem]

[0007] An aspect of the present disclosure is to provide a plated steel sheet having ultra-high strength, in which the occurrence and propagation of cracking in edges thereof in a width direction may be prevented, even when a slitting and coiling process is performed on a plated steel sheet having ultra-high strength, and a method of manufacturing the same.

[Technical Solution]

[0008] According to an aspect of the present disclosure, a plated steel sheet having ultra-high strength and a tensile strength of 1300 MPa or more is characterized in that an amount of hydrogen in the plated steel sheet is 0.000015 wt% or less.

[0009] According to an aspect of the present disclosure, a method of manufacturing a plated steel sheet having ultra-high strength includes preparing a steel sheet having a tensile strength of 1300 MPa or more, plating the steel sheet to produce a plated steel sheet, and performing a heat treatment on the plated steel sheet. The heat treatment is performed such that an amount of hydrogen in the plated steel sheet is 0.000015 wt% or less.

[Advantageous Effects]

[0010] According to an exemplary embodiment in the present disclosure, a plated steel sheet having ultra-high strength, in which the occurrence of cracking in an edge portion in a width direction, after a slitting and coiling process, may be prevented, may be provided.

[Description of Drawing]

[0011] FIG. 1 illustrates a result of observing whether or not cracking occurs after slitting heat-treated and untreated plated sheets having ultra-high strength.

[Best Mode]

[0012] As a result of research to prevent the occurrence and propagation of cracking in edges of a manufactured coil in a width direction in the case of slitting and coiling a plated steel sheet having ultra-high strength and a tensile strength of 1300 MPa or more, it has been confirmed that the aforementioned problems may be solved by performing a heat treatment before slitting and coiling processes are performed on a plated steel sheet having ultra-high strength to reduce a hydrogen concentration in the plated steel sheet, from which an exemplary embodiment in the present disclosure is provided as below.

[0013] In detail, the present inventors have found that cracking in a width direction edge portion after slitting and coiling a plated steel sheet having ultra-high strength is related to an amount of hydrogen, and thus, a plated steel sheet having ultra-high strength and a reduced amount of hydrogen, and a method for effectively reducing an amount of hydrogen, may be provided.

[0014] According to an exemplary embodiment in the present disclosure, a plated steel sheet having ultra-high strength, and having an amount of hydrogen of 0.000015 wt% or less and a tensile strength of 1300 MPa or more, may be provided.

[0015] The plated steel sheet having ultra-high strength according to an exemplary embodiment may include 0.12 wt% to 0.2 wt% of carbon (C), 0.5 wt% or less of silicon (Si) (excluding 0wt%), 2.6 wt% to 4.0 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P) (excluding 0 wt%), 0.015 wt% or less of sulfur (S) (excluding 0 wt%), 0.1 wt% or less of aluminum (Al) (excluding 0 w%), 1 wt% or less of chromium (Cr) (excluding 0 wt%), 48/14*[N] to 0.1 wt% of titanium (Ti), 0.1 wt% or less of niobium (Nb) (excluding 0 wt%), 0.005 wt% or less of boron (B) (excluding 0 wt%), 0.01 wt% or less of nitrogen (N) (excluding 0wt%), iron (Fe) as a remainder thereof, and other inevitably contained impurities. The plated steel sheet may have a microstructure obtained by plating and heat-treating a steel sheet comprised of 90% or more of tempered martensite and 10% or less of ferrite and bainite in a volume fraction.

[0016] Hereinafter, the reason for limiting the components of the steel sheet will be described in detail. The content unit of each component will refer to weight% unless otherwise specified.

C: 0.12% to 0.20%

[0017] Carbon (C) is an element essentially added to secure strength of a steel. In order to obtain the above-mentioned effect, carbon (C) may be added in an amount of 0.12% or more. However, if the content thereof is relatively high, exceeding 0.20%, a problem in which weldability is deteriorated may occur, which may be problematic.

[0018] Thus, the content of C may be limited to 0.12% to 0.20%.

Si: 0.5% or less (Excluding 0%)

[0019] Silicon (Si) is a ferrite stabilizing element and may have a disadvantage in that strength may be reduced by accelerating generation of ferrite at the time of slow cooling after annealing in a continuous annealing type hop-dip heat treatment furnace of the related art in which a slow cooling section is present. In addition, in the case in which a relatively large amount of Mn is added to suppress phase transformation as in the present disclosure, since a risk of deterioration of molten plating characteristics due to formation of a surface oxide by Si during annealing and the occurrence of dent defects due to surface thickening and oxidation by Si may be present, an upper limit of Si may be determined. In detail, the content of Si may be limited to 0.5% or less.

Mn: 2.6% to 4.0%

[0020] Manganese (Mn) is well known as an element inhibiting the formation of ferrite and facilitating the formation of austenite. In the case of slow cooling after annealing in a continuous annealing type hop-dip heat treatment furnace, if a content of Mn is less than 2.6%, ferrite may be easily formed during slow cooling, while if the content of Mn exceeds 4.0%, band formation due to slabs, and segregation caused in a hot rolling process, may be excessive, and a problem in which a cost of alloy iron is increased due to an excessive amount of alloying input when a convertor is operated.

[0021] Thus, the content of Mn may be limited to 2.6% to 4.0%.

P: 0.03% or less (Excluding 0%)

[0022] Phosphorus (P) may be an impurity element in steel. If the content thereof exceeds 0.03%, weldability may be decreased, a risk of brittleness of steel may be increased, and a possibility of the occurrence of dent defects may increase. Thus, the content of P may be limited to 0.03% or less.

S: 0.015% or less (Excluding 0%)

[0023] Sulfur (S) may be an impurity element in steel as well as P, and if the content thereof exceeds 0.015%, a possibility of deterioration of ductility and weldability of steel may increase. Thus, the content of S may be limited to 0.015% or less.

Al: 0.1% or less (Excluding 0%)

[0024] Aluminum (Al) is an element for expanding a ferrite region. In the case in which a general continuous annealing type hop-dip heat treatment furnace having a slow cooling section is used, there may be a disadvantage in that ferrite formation is promoted, and the possibility of causing deteriorations in high temperature heat hot-rolling characteristics due to the formation of AlN may increase. Thus, the content of Al may be limited to 0.1% or less.

Cr: 1% or less (Excluding 0%)

[0025] Chromium (Cr) is an element suppressing ferrite transformation and facilitating low-temperature transformation. In the case in which a general continuous annealing type hop-dip heat treatment furnace having a slow cooling section is used, there may be an advantage in that ferrite formation is suppressed. However, if the content thereof exceeds 1%, a problem in which a cost of alloying iron is increased due to an excessive amount of alloying may occur. Thus, the content thereof may be limited to 1% or less.

Ti: 48/14 * [N] to 0.1%

[0026] Titanium (Ti) is an element for forming a nitride, and may serve to precipitate N in steel as TiN to scavenge N therein. To this end, Ti may be required to be added at a chemical equivalent of 48/14 * [N] or more. On the other hand, if Ti is not added, a problem in which cracks may occur during continuous casting by AlN formation may be caused. However, if the content thereof exceeds 0.1%, a problem in which the strength of martensite is reduced due to precipitation of additional carbides in addition to the removal of solid solution N, may be caused.

Nb: 0.1% or less (Excluding 0%)

[0027] Niobium (Nb) is an element segregated at an austenite grain boundary to suppress coarsening of austenite grains during an annealing heat treatment, and thus, may be added. However, if the content thereof exceeds 0.1%, a problem in which a cost of alloy iron is increased due to an excessive amount of added alloy may occur. Thus, the content of Nb may be limited 0.1% or less.

B: 0.005% or less (Excluding 0%)

[0028] Boron (B) is an element inhibiting ferrite formation. In detail, B has an advantage of inhibiting the formation of ferrite at the time of cooling after annealing, and thus, may be added. However, if the content thereof exceeds 0.005%, since a problem in which ferrite formation is promoted by precipitation of $Fe_{23}(C,B)_6$ may occur, the content thereof may be limited to 0.005% or less.

N: 0.01% or less (Excluding 0%)

[0029] Nitrogen (N) is an element reacting with Al to be precipitated into AlN nitride, and the formed AlN may have a problem in that it is a cause of occurrence of cracking during continuous casting. Thus, the content of Al may be limited to 0.01% or less, and thus, the formation of AlN may be suppressed.

[0030] Fe and unavoidable impurities may be included as a remainder. In this case, examples of the impurities may include molybdenum (Mo), vanadium (V), nickel (Ni), rare earth metals (REM), and the like.

[0031] A steel sheet used to obtain a plated steel sheet having ultra-high strength according to an exemplary embodiment may have a microstructure comprised of 90% or more of martensite and 10% or less of ferrite and bainite in a volume fraction, while satisfying the above-mentioned compositional composition. As effective characteristics according to the configuration of the microstructure, as martensite of a hard phase has a microstructure, a main phase, securing ultra-high strength may be facilitated.

[0032] The plated steel sheet having ultra-high strength, ultimately obtained by heat-treating the steel sheet as described above, according to an exemplary embodiment may also have the same microstructure as above, and when an additional tempering heat treatment thereto is performed, martensite may be converted into tempered martensite.

[0033] On the other hand, it may not be easy to actually measure a volume fraction, a three-dimensional concept, and thus, measurement of the volume fraction may be replaced with area fraction measurement through a cross-sectional observation normally used in observation of a microstructure.

[0034] In addition, the steel sheet having the component system and the microstructure as described above may be plated and heat-treated, and an amount of hydrogen after heat treatment may be 0.000015 wt% or less, as compared with the case before the heat treatment. Thus, the target ratio of a yield strength and a tensile strength of the plated steel sheet having ultra-high strength according to an exemplary embodiment may be 0.75 or more.

[0035] In order to produce the plated steel sheet having ultra-high strength and the composition and microstructure as described above, a process as below may be performed.

[0036] First, a steel sheet including 0.12 wt% to 0.2 wt% of carbon (C), 0.5 wt% or less of silicon (Si) (excluding 0wt%), 2.6 wt% to 4.0 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P) (excluding 0 wt%), 0.015 wt% or less of sulfur (S) (excluding 0 wt%), 0.1 wt% or less of aluminum (Al) (excluding 0 wt%), 1 wt% or less of chromium (Cr) (excluding 0 wt%), 48/14*[N] to 0.1 wt% of titanium (Ti), 0.1 wt% or less of niobium (Nb) (excluding 0 wt%), 0.005 wt% or less of boron (B) (excluding 0 wt%), 0.01 wt% or less of nitrogen (N) (excluding 0 wt%), iron (Fe) as a remainder thereof, and other inevitably contained impurities; and having a microstructure comprised of 90% or more of tempered martensite and 10% or less of ferrite and bainite in a volume fraction, may be prepared.

[0037] Subsequently, the steel sheet may be plated to produce a plated steel sheet, and the plated steel sheet may be subjected to a heat treatment.

[0038] In this case, a plating process is not particularly limited, and for example, a process such as hot-dip galvanizing, hot-dip aluminum plating, electro-galvanizing, or the like may be performed.

[0039] In addition, a heat treatment after plating may be performed such that an amount of hydrogen in the plated steel sheet may be 0.000015 wt% or less. In this case, by performing the heat treatment for a relatively short time at a high temperature or at a relatively low temperature for a relatively long time, the amount of hydrogen may be reduced to a required level. Thus, a heat treatment time and temperature conditions according to an exemplary embodiment are not particularly limited.

[0040] However, as a normal heat treatment temperature increases, a reduction in tensile strength may be increased. Thus, the heat treatment temperature and time may be set in consideration of a tensile strength level required by a customer.

[0041] A plated steel sheet having ultra-high strength is generally manufactured as a coil having a constant width through a slitting and coiling process, and the slitting process is a process of adding relatively high stress to an edge portion of a steel sheet. In the case of a plated steel sheet having ultra-high strength, a disadvantage in that the quality of a cut surface of an edge portion may be deteriorated due to a plating layer may be present. Hydrogen in steel tends to segregate under a relatively high stress state. Thus, for example, when a slitting process is performed on the plated steel sheet having ultra-high strength, hydrogen in steel may segregate on a relatively highly stressed portion of an edge portion of the plated steel sheet after the slitting, whereby cracks may start to occur in the edge portion of the plated steel sheet having ultra-high strength and the propagation of cracks may occur in a width direction.

[0042] Thus, by performing the heat treatment according to an exemplary embodiment, an amount of hydrogen of the plated steel sheet having ultra-high strength may be reduced to 0.000015 wt% or less, and thus, cracking of an edge portion over time during coiling, after slitting, may be effectively suppressed.

[0043] Hereinafter, a plated steel sheet having ultra-high strength according to an exemplary embodiment will be described in detail with reference to Embodiment. It should be noted, however, that the following embodiments are intended to illustrate the present disclosure in more detail and not to limit the scope of the invention. In other words, the scope of the invention is determined by the matters described in the claims and the matters reasonably deduced therefrom.

[Mode for Invention]

(Embodiment)

[0044] A plated steel sheet having ultra-high strength, an initial yield strength of 1149 MPa, and an initial tensile strength of 1556 MPa was evaluated for changes in an amount of hydrogen before a heat treatment and after a heat treatment under conditions provided in Table 1 below. Evaluation results are provided as illustrated in Table 1.

[0045] In this case, a steel material having a component system consisting of 0.18% of C, 0.1% of Si, 3.6% of Mn, 0.011% of P, 0.11% of Cr, 0.021% of Ti, 0.038% of Nb, 0.0017% of B, 0.003% of S, 0.025% of Al, and 0.004% of N was prepared as a specimen having a size of thickness*12mm*100mm, and was heated to a temperature from 25°C to 250°C at a heating rate of 100°C per hour. An amount of hydrogen was measured using gas chromatography, simultaneously with performing a heat treatment.

[0046] First, as a result of measuring amounts of hydrogen of a cold rolled steel sheet, not subjected to plating, and in a plated steel sheet, the cold rolled steel sheet had no hydrogen, 0 wt% of hydrogen, while the plated steel sheet had a relatively high content, 0.000022 wt% of hydrogen.

[0047] These results show that in the case of a relatively small amount of bainite having a BCC structure and martensite having a BCT structure (in the case of martensite having a relatively low carbon content, the martensite has substantially the same crystal structure as that of BCC), since solubility of hydrogen is relatively low and diffusion of hydrogen is relatively fast, hydrogen may have disappeared within a few minutes to several hours after the production of a cold-rolled steel sheet, and thus, the amount of hydrogen was measured as 0 wt% in the cold-rolled steel sheet formed of martensite as a main phase.

[Table 1]

Heat Treatment Conditions		150°C					200°C			
	Temperature	150°C					200°C			
	Hydrogen Atmosphere	100%	7%		0%		7%		0%	
	Time	24h	24h	72h	24h	72h	24h	48h	24h	48h
Amount of Hydrogen (Weight%)		0.000017	0.000016	0.000010	0.000010	0.000007	0.000008	0.000006	0.000007	0.000004

[0048] As illustrated in Table 1, when the heat treatment temperature was 150°C, in a case in which an amount of hydrogen in atmospheric gas was 0%, a reduction of hydrogen proceeded relatively fast as compared to the case in which an amount of hydrogen in atmospheric gas was 7%. In addition, it can be seen that when an amount of hydrogen in atmospheric gas was 0%, in the case in which the heat treatment temperature was 200°C, a reduction of hydrogen progressed relatively fast as compared to 150°C.

[0049] For example, as the content of hydrogen in atmospheric gas during a heat treatment is reduced, and as the heat treatment temperature is increased, the amount of hydrogen may be further reduced.

[0050] Further, after a plated steel sheet (A) not subjected to heat treatment, a plated steel sheet (B) having been subjected to heat treatment at 150°C for 24 hours in a 100% of hydrogen atmosphere, and a plated steel sheet (C) having been subjected to heat treatment at 200°C for 24 hours in a 7% of hydrogen atmosphere were slit, whether or not cracks occurred as time passed was observed, and the results thereof are provided in FIG. 1.

[0051] As illustrated in FIG. 1, it can be confirmed that cracking has occurred in the case of the plated steel sheet (A) not subjected to the heat treatment and in the case of the plated steel sheet (B) in which an amount of hydrogen exceeded 0.000015 wt% even after heat treatment. Meanwhile, in the case of the plated steel sheet (C) having been subjected to a heat treatment at a relatively low rate in a hydrogen atmosphere and at a relatively high temperature, no cracking occurred.

[0052] These results may indicate that a plated steel sheet having ultra-high strength and having a yield strength ratio of 0.75 or more with respect to a tensile strength, by tempering heat treatment of an ultra-high strength plated steel sheet having martensite as a main phase, may be provided. However, as the heat treatment temperature increases, a decrease in tensile strength may increase. Thus, setting heat treatment temperature and time according to a tensile strength level required by a customer may be required.

Claims

1. A plated steel sheet having ultra-high strength and a tensile strength of 1300 MPa or more, being **characterized in that** an amount of hydrogen in the plated steel sheet is 0.000015 wt% or less.

2. The plated steel sheet of claim 1, wherein the plated steel sheet comprises 0.12 wt% to 0.2 wt% of carbon (C), 0.5 wt% or less of silicon (Si) (excluding 0 wt%), 2.6 wt% to 4.0 wt% of manganese (Mn), 0.03 wt% or less of phosphorus (P) (excluding 0 wt%), 0.015 wt% or less of sulfur (S) (excluding 0 wt%), 0.1 wt% or less of aluminum (Al) (excluding 0 wt%), 1 wt% or less of chromium (Cr) (excluding 0 wt%), 48/14*[N] to 0.1 wt% of titanium (Ti), 0.1 wt% or less of niobium (Nb) (excluding 0 wt%), 0.005 wt% or less of boron (B) (excluding 0 wt%), 0.01 wt% or less of nitrogen (N) (excluding 0wt%), iron (Fe) as a remainder thereof, and other inevitably contained impurities; and has a microstructure obtained by plating and heat-treating a steel sheet comprised of 90% or more of tempered martensite and 10% or less of ferrite and bainite in a volume fraction.

3. The plated steel sheet of claim 1, wherein the plated steel sheet has a yield strength ratio of 0.75 or more.

4. A method of manufacturing a plated steel sheet having ultra-high strength, the method comprising:

   preparing a steel sheet having a tensile strength of 1300 MPa or more;
   plating the steel sheet to produce a plated steel sheet; and
   performing a heat treatment on the plated steel sheet,
   wherein the heat treatment is performed such that an amount of hydrogen in the plated steel sheet is 0.000015 wt% or less.

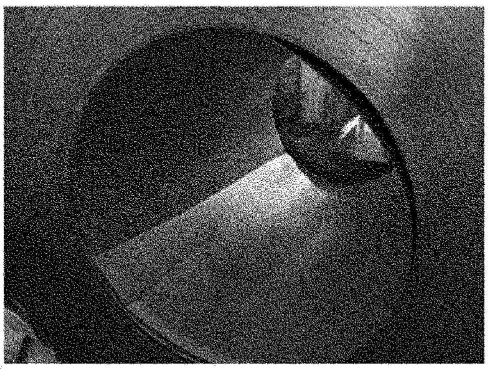
5. The method of claim 4, wherein the steel sheet comprises 0.12 wt% to 0.2 wt% of carbon (C), 0.5 wt% or less of silicon (Si) (excluding 0wt%), 2.6 wt% to 4.0 wt% of manganese (Mn), 0. 03 wt% or less of phosphorus (P) (excluding 0 wt%), 0.015 wt% or less of sulfur (S) (excluding 0 wt%), 0.1 wt% or less of aluminum (Al) (excluding 0 wt%), 1 wt% or less of chromium (Cr) (excluding 0 wt%), 48/14*[N] to 0.1 wt% of titanium (Ti), 0.1 wt% or less of niobium (Nb) (excluding 0 wt%), 0. 005 wt% or less of boron (B) (excluding 0 wt%), 0.01 wt% or less of nitrogen (N) (excluding 0 wt%), iron (Fe) as a remainder thereof, and other inevitably contained impurities; and has a microstructure comprised of 90% or more of tempered martensite and 10% or less of ferrite and bainite in a volume fraction.

6. The method of claim 4, wherein a yield strength ratio of the plated steel sheet having been subjected to the heat treatment is 0.75 or more.

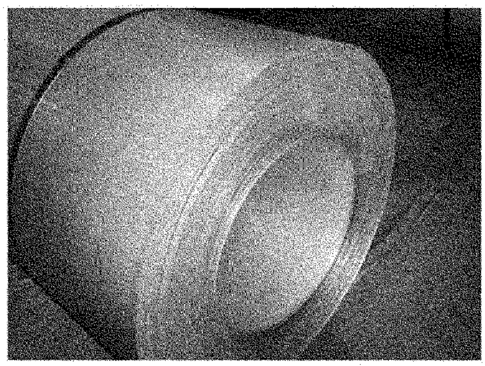
【Fig.1】

(A)

(B)



(C)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2015/000136

A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/26(2006.01)i, C22C 38/28(2006.01)i, C23C 2/00(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 38/26; C21D 9/46; C22C 38/06; C21D 8/02; C22C 38/00; C23C 2/06; C22C 38/28; C23C 2/00

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: metal coated steel sheet, high strength, hydro, martensite, ferrite, bainite, heat treatment, slitting, winding

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A		2,5
A	KR 10-2013-0056052 A (POSCO) 29 May 2013 See abstract; paragraphs [0058]-[0067]; and claims 1-12.	1-6
A	KR 10-2014-0061457 A (NIPPON STEEL & SUMITOMO METAL CORPORATION) 21 May 2014 See abstract; paragraphs [0119]-[0136]; and claim 1.	1-6
A	KR 10-2013-0056051 A (POSCO) 29 May 2013 See abstract; paragraphs [0059]-[0073]; and claims 1-11.	1-6
A	JP 2013-227614 A (NIPPON STEEL & SUMITOMO METAL CORP.) 07 November 2013 See abstract; paragraphs [0034]-[0047]; and claims 1-6.	1-6

☐ 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)
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"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	Date of mailing of the international search report
13 AUGUST 2015 (13.08.2015)	**13 AUGUST 2015 (13.08.2015)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2015/000136

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