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(71) Applicant: **Hitachi Metals, Ltd.**
Tokyo 105-8614 (JP)

(72) Inventors:
• **SATOH Naoya**
Yasugi-shi
Shimane 692-8601 (JP)
• **INTOH Yuuki**
Yasugi-shi
Shimane 692-8601 (JP)
• **FUKUSHIMA Hideko**
Yasugi-shi
Shimane 692-8601 (JP)

- **KATAOKA Kouta**
Yasugi-shi
Shimane 692-8601 (JP)
- **AYABE Yousuke**
Yasugi-shi
Shimane 692-8601 (JP)
- **TANIGUCHI Toru**
Yasugi-shi
Shimane 692-8601 (JP)
- **MIKI Takahiro**
Sendai-shi
Miyagi 982-0031 (JP)

(74) Representative: **Beetz & Partner**
Patentanwälte
Steinsdorfstraße 10
80538 München (DE)

(54) **METHOD FOR ADDING ZINC TO MOLTEN STEEL AND PROCESS FOR PRODUCING ZINC-CONTAINING STEEL**

(57) A method is provided by which it is possible to easily add zinc to a molten steel in high yield. The method for adding zinc to a molten steel comprises supplying a composite oxide of Zn with Al and/or Si to a molten steel. The method for adding zinc to a molten steel may further include supplying the oxide of Ca to the molten steel. The molten steel preferably is a molten steel for a hot

work tool steel. A process for producing a zinc-containing steel is also provided in which the molten steel to which zinc has been added by the method for adding zinc to a molten steel is cast. The cast zinc-containing steel preferably has a Zn content of 0.001 mass% or higher.

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Description

[Technical Field]

5 **[0001]** The present invention relates to a method for adding zinc to a molten steel in a process of melting the steel, and to a process for producing a zinc-containing steel using the method.

[Background Art]

10 **[0002]** It has been desirable to reduce zinc in a steel as low as possible since zinc, which is mixed from scraps or the like, has been conventionally considered as impurities of the steel, that deteriorates mechanical properties of the steel products. On the other hand, we found that a certain amount of zinc improves, for example, toughness of hot work tool steels, and has proposed the method in Patent Literature 1. The method of Patent Literature 1 make it possible to improves the toughness of hot work tool steels by adding zinc as an alloying element.

15 **[0003]** Zinc is a volatile element having a melting point and a boiling point much lower than those of a steel (iron). Therefore, when zinc is added in a form of a metal in a molten steel in a process of melting the steel, most of zinc evaporate and is lost from the steel immediately after the addition. Thus, yield percentage relative to an intended addition is poor. Therefore, a method of adding zinc to a steel has been proposed, in which zinc metal is previously coated with a material having the same composition as the molten steel with an insulating material such as paper or plastics there-
20 between, and the resultant is supplied to the molten steel, thereby preventing the decrease in the yield due to the zinc evaporation (see Patent Literature 2).

[Citation List]

25 [Patent Literature]

[0004]

Patent Literature 1: JP-A-2007-224418

30 Patent Literature 2: JP-A-2-61006

[Summary of Invention]

[Technical Problem]

35 **[0005]** The method of Patent Literature 2 allows the zinc metal to penetrate deep into the molten steel and has an effect of improving the yield of zinc to a certain degree. However, since a form of a zinc metal is added, still a large amount of zinc evaporates although some zinc melts into the molten steel. Further, a cost increase may be caused since the coating of the zinc metal needs a complex step. Therefore, a method that can further improve the yield of zinc in a simpler way is required.

40 **[0006]** An object of the present invention is to provide a method for adding zinc to a molten steel in a higher yield and in a simple way, and a process for producing a zinc-containing steel using the method.

[Solution to Problem]

45 **[0007]** A main reason why added zinc evaporates immediately in the molten steel is because zinc is added in a form of a single metal. The present inventors have studied a method for adding zinc in a form of a compound. As a result, the present inventors have found that a certain form of a zinc compound is suitable for achieving both a high yield of addition and a low cost, and have reached the present invention.

50 **[0008]** Thus, a method is provided for adding zinc to a molten steel, including supplying a composite oxide of:

zinc; and
aluminum and/or silicon

55 to the molten steel. The method may further comprise supplying an oxide of calcium to the molten steel. The molten steel is preferably for a hot work tool steel.

[0009] The present invention also provides a process for producing a zinc-containing steel, including casting a molten steel added with zinc by the above method. The cast zinc-containing steel preferably includes not lower than 0.001

mass% zinc.

[Advantageous Effects of Invention]

[0010] According to the method of the present invention, for example, not lower than 0.001 mass%, or as high as 0.01 mass% of zinc can be mixed in the steel with a good yield and at a low cost, and a steel including the above amount of zinc can be produced. Thus, the present invention is useful for producing a high zinc steel, such as the hot work tool steel as disclosed in Patent Literature 1.

[Description of Embodiments]

[0011] Compounds, etc., used for the addition of zinc according to the method of the present invention will be described in detail below. Please note that the method of the present invention is not limited to the following description or the methods described in Examples.

[0012]

(1) The compound supplied to the molten steel is a composite oxide of: zinc; and aluminum and/or silicon:

A temperature of a molten steel reaches as high as 1600°C. Since a zinc metal has a low boiling point of about 900°C (and high vapor pressure), zinc rapidly evaporates after it is supplied to a molten steel and before the steel is casted. If the zinc metal is made into a zinc compound which is difficult to be decomposed (in other words, a vapor pressure of the zinc component is low) even at e.g. 1600°C in an open air environment and the zinc compound is supplied to a molten steel, the zinc component in the compound will not evaporate immediately and remains in the molten steel.

[0013] The present inventors have studied on the zinc compounds which meet the above requirement. As a result, it has been found that a composite oxide of zinc and aluminum and a composite oxide of zinc and silicon are not easily decomposed at such a high temperature, while a simple oxide of zinc is more likely to be decomposed at a high temperature of 1600°C. These zinc compounds can be reduced by silicon, manganese, aluminum, magnesium or calcium that are usually present in a molten steel. Therefore, when the zinc component is added to a molten steel in the form of the composite oxide where zinc is combined with aluminum and/or silicon, the zinc component will not evaporate immediately and the reduction reaction is facilitated in the molten steel. As a result, more zinc metal is added to the molten steel.

[0014] The zinc compound in the present invention may include zinc aluminate that is a composite oxide of ZnO and Al₂O₃, or zinc silicate that is a composite oxide of ZnO and SiO₂. Zinc silicate has a lower melting point than zinc aluminate and is decomposed (or reduced) relatively faster. Therefore, a predetermined amount of zinc can be added to a molten steel in a short time. However, as the decomposition proceeds faster, zinc generated by the decomposition evaporates and escapes from the molten steel earlier than in the case of zinc aluminate. In an actual operation, a molten steel is usually cast less than one hour after a composition of the steel is adjusted. When zinc silicate is supplied to the molten steel at the end of the adjustment of the composition, casting can be completed before a large amount of zinc escapes from the molten steel to which zinc silicate has been supplied. Thus, zinc silicate is suitable for the improvement of the yield of zinc. On the other hand, the reduction reaction of zinc aluminate progresses relatively slowly and therefore zinc aluminate can suppress strong fuming caused by the evaporation of zinc due to rapid decomposition of the zinc compound immediately after the supply to a molten steel. The use of zinc aluminate is preferred in that smoke extraction facility can be simplified in an actual operation.

[0015] When both of a composite oxide of zinc and aluminum and a composite oxide of zinc and silicon are used as the zinc compounds for supplying to the molten steel, both of the composite oxides may be supplied to the molten steel, or alternatively a composite oxide in which zinc, aluminum and silicon are combined may be supplied. The zinc compound according to the present invention may be directly supplied to the molten steel, or it may be wrapped by e.g. a metal and inserted in the molten metal as far as properties of the steel are not affected. When the zinc compound is supplied in the molten steel directly, a surface of the molten steel is coated with the zinc compound. The zinc compound may also be inserted in a deep portion of the molten steel by using a charging guide or the like. Also, an upper surface of the molten steel may be coated with slag before or after the supply of the zinc compound. This prevents the upper surface of the molten steel from coming into contact with an ambient air and can retard the evaporation of zinc after the decomposition. Usual methods for preparing the slag and usual composition of the slag may be used, but a suitable method described later may be also used.

[0016]

(2) Preferably, an oxide of calcium is supplied to the molten steel:

Even if a large amount of zinc metal is successfully added to the molten steel by the above method, zinc in the molten steel evaporates from the upper surface of the molten steel over a long time after the addition. Thus, it is preferable to supply an oxide of calcium also to the molten steel. Generally, the oxide of calcium is used for forming a slag in a steel smelting process. In the present invention, the upper surface of the molten steel is covered with the slag of the calcium oxide, and is prevented from contact with an ambient air. This retards the evaporation of zinc in the molten steel even if a long time is passed after the addition of zinc. The oxide of calcium may be supplied to the molten steel in a period when sufficient added zinc remains in the molten steel, and before or after the supply of the zinc compound. The calcium oxide may be supplied at the same time of supplying of the zinc compound by mixing and/or combining with the zinc compound. It is preferable that the calcium oxide is in an amount of 10 to 50 mass% of the total of the calcium oxide and the zinc compound, when the calcium oxide is mixed and/or combined with the zinc compound. When the amount of the calcium oxide is too large, a melting point of the zinc compound at the time of the supply is lowered to facilitate the decomposition of the zinc compound. As a result, zinc generated by the decomposition evaporates faster. Since calcium fluoride (CaF_2) increases a fluidity of a slag, a part of the calcium oxide may be placed with the calcium fluoride to be supplied to the molten steel.

(3) Preferably the molten steel is for a hot work tool steel:

Toughness of a hot work tool steel can be improved by adding zinc during a melting step of the hot work tool steel with use of the method of the present invention (see Patent Literature 1). Therefore, the method of the present invention is suitable for adding zinc to molten steel for a hot work tool steel. It is more preferable that a cast steel for the hot work tool steel includes not lower than 0.001 mass% of zinc. As the components of a hot work tool steel, the elements defined in Standard steel grades in JIS etc., those elements described in Patent Literature 1, or those elements which have been proposed so far may be included according to necessary.

[Example 1]

[0017] JIS standard hot work tool steel SKD61 was prepared and the method for adding zinc according to the present invention was applied thereto. A chemical composition of the prepared SKD61 steel is shown in Table 1. (Ni, W, Zn, Nb and Co were not added.)

[Table 1]

(mass%)						
C	Si	Mn	P	S	Ni	Cr
0.38	0.98	0.41	0.010	0.0007	0.05	5.11
Mo	W	V	Zn	Nb	Co	Fe*
1.21	<0.01	0.83	<0.001	<0.01	<0.01	Balance
*Including impurities						

[0018] The steel of Table 1 having a weight of 50 g of was melted in a MgO dense crucible in an electric furnace. A zinc compound (or a zinc metal) was directly supplied from the surface of the molten steel maintained at 1600°C in the following manner. The amount of zinc in the molten steel was calculated to be 1.0 mass% if the yield of zinc was 100% (hereinafter simply referred to as "calculated amount"). Then, the molten steel was maintained in an Ar atmosphere for a predetermined time. The molten steel was then water-cooled with the crucible to a room temperature. The zinc content in the solidified steel was analyzed to evaluate the yield of zinc. The analysis of the zinc content was conducted by the emission spectrometric analysis using spark discharge.

[Example 1 according to the invention]

[0019] Zinc aluminate powder (represented by $\text{ZnO} \cdot \text{Al}_2\text{O}_3$, having a stoichiometric composition of ZnO: 44.4 mass% and Al_2O_3 : 55.6 mass%) was supplied to the molten steel.

[Example 2 according to the invention]

[0020] A mixture of the zinc aluminate powder described in Example 1 and a CaO powder ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$ 90 mass% and CaO: 10 mass%) was supplied to the molten steel.

[Comparative Example 1]

[0021] A zinc metal was supplied to the molten steel.

[Comparative Example 2]

[0022] A ZnO powder was supplied to the molten steel.

[0023] Table 2 shows the zinc contents in the steel. In Comparative Example 1 where a zinc metal was directly supplied to the molten steel, zinc started to evaporate immediately after the supply, and almost all of them evaporated after 30 minutes from the supply. Thus, the yield was poor. In Comparative Example 2 where ZnO was used for the addition of zinc, the yield of zinc was improved compared to Comparative Example 1. However, ZnO was decomposed rapidly after the supply, and almost all of the zinc components generated from the decomposition evaporated after 30 minutes. Thus, the yield was poor. In Examples 1 and 2 where the method for adding zinc of the present invention was used, the yield of zinc was greatly improved. When the molten steel was cast after a predetermined time, it was found that a steel including not lower than .001 mass% of zinc could be produced.

[0024] Comparing between Examples 1 and 2, an upper surface of the molten steel was covered with slag after the supply in Example 2 where CaO was mixed to the zinc compound, and the zinc content in the molten steel after 10 minutes and 30 minutes were smaller than those in Example 1. In Example 2, since CaO was mixed to the zinc compound, the melting point of the zinc compound was more or less lowered at the time of the supply, and therefore the zinc compound after the supply was decomposed faster than in Example 1. It is considered that the decomposition of the zinc compound progressed within a few minutes after the supply under the condition of Example 1 where the total amount of the molten steel was as low as 50 g. Thus, it is assumed that more zinc was present in the molten steel of Example 2 than in Example 1 in a few minutes after the supply. It is considered that zinc in the molten steel already evaporated after 10 minutes and started to escape from the molten steel even in the presence of slag, since the amount of the molten steel was small.

[Table 2]

	Zn content in steel (mass%)		
	Before supply	After 10 minutes	After 30 minutes
Example1 ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$)	<0.001	0.048	0.040
Example2 ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$ -CaO)	<0.001	0.042	0.016
Comparative Example1 (Zn)	<0.001	0.002	0.001
Comparative Example2 (ZnO)	<0.001	0.003	0.002

[Example 2]

[0025] Fe - 15 mass% Ni alloy steel was prepared and the method according to the present invention was applied thereto. The chemical composition of the above alloy steel is shown in Table 3. (Cr, Mo, W, V, Zn, Nb and Co were not added.)

[Table 3]

(mass%)						
C	Si	Mn	P	S	Ni	Cr
1.21	0.08	0.22	0.007	0.0029	15.6	0.10
Mo	W	V	Zn	Nb	Co	Fe*
<0.01	<0.01	<0.01	<0.001	<0.01	<0.01	Balance
*Including impurities						

[Example 3 according to the invention]

[0026] The alloy steel of Table 1 having a weight of 25 tons was melted in an electric furnace and tapped into a ladle. Subsequently, the ladle with the molten steel was moved to the secondary refining equipment. A zinc compound was supplied to the molten steel maintained at 1600°C in the ladle, in a calculation amount such that the zinc content in the molten steel was 0.036 mass%. The molten steel was maintained for a predetermined time in an Ar atmosphere. The supplied zinc compound was mixed powder composed of 90 mass% of zinc aluminate powder and 10 mass% of CaO powder which is used in Example 2. The zinc compound was directly supplied to the molten steel.

[0027] Samples of the molten steel were taken from the top of the ladle after every given time period using an iron mold and a final sample was taken from a runner after casting by a bottom pouring method. The zinc content of the samples was measured. Based on the analysis, a change of the zinc content over time in the molten steel after the supply of the zinc compound was determined. The zinc contents were analyzed by emission spectrometric analysis using spark discharge. Table 4 shows the zinc contents in the steel. In Example 3 where the method according to the present invention was employed, the yield of zinc was good and a high zinc content was maintained even 80 minutes after the supply of the zinc compound. Little fuming was visually observed after the supply of the zinc compound. A steel containing a specific amount of not lower than 0.001 mass% was produced after casting.

[Table 4]

	Zn content in steel (mass%)			
	Before supply	After 10 minutes	After 30 minutes	After 80 minutes (after casting)
Example 3 (ZnO·Al ₂ O ₃)-CaO	<0.001	0.027	0.027	0.025

[Example 3]

[0028] JIS standard hot work tool steel SKD61 was prepared and the method according to the present invention was applied thereto. The chemical composition of SKD61 is shown in Table 5. (Ni, W, Zn, Nb or Co was not added.)

[Table 5]

(mass%)						
C	Si	Mn	P	S	Ni	Cr
0.40	1.15	0.47	0.009	0.0030	0.03	5.14
Mo	W	V	Zn	Nb	Co	Fe*
1.28	<0.01	0.85	<0.001	<0.01	<0.01	Balance
*Including impurities						

[0029] The steel of Table 5 having a weight of 25kg was melted in a high frequency induction furnace. A zinc compound was directly supplied to the molten steel maintained at 1600°C in the following manner, in a calculation amount such that the zinc content in the molten steel was 0.5 mass%. The molten steel was maintained for a predetermined time in an Ar atmosphere. Samples were taken from the top of the ladle using an iron mold at every given time period. Zinc contents of the samples were analyzed to evaluate the yield of zinc. The zinc contents were analyzed by emission

spectrometric analysis using inductively coupled plasma.

[Example 4 according to invention]

[0030] The zinc aluminate powder ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$) which was used in Example 1 was supplied to the molten steel.

[Example 5 according to invention]

[0031] A mixture of the zinc aluminate powder of Example 1 and a CaO powder ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$ 70 mass%, CaO: 30 mass%) was supplied to the molten steel.

[Example 6 according to invention]

[0032] A zinc silicate powder (represented by $2\text{ZnO} \cdot \text{SiO}_2$, having a stoichiometric composition of ZnO: 71.6 mass% and SiO_2 : 28.4 mass%) was supplied to the molten steel.

[Comparative Example 3]

[0033] A ZnO powder was supplied to the molten steel.

[0034] Table 6 shows the zinc contents in the steel. Table 6 also shows the state of fuming visually observed after the supply of the zinc compound. In Comparative Example 3 where ZnO was supplied to the molten steel, the decomposition of ZnO progressed rapidly immediately after the supply, and the zinc component generated by the decomposition evaporated at an early stage. Thus, the yield of zinc was poor. Due to strong fuming, the test was abandoned after 10 minutes. On the other hand, in Examples 4 to 6 where the method according to the present invention was used, the zinc compound continued to decompose even after 10 minutes from the supply of the zinc compound. The amount of zinc in the molten steel further increased after 30 minutes, showing a remarkable improvement in the yield of zinc. It has been found that a steel containing not lower than 0.001 mass% of zinc can be produced when the molten steel is subjected to casting after a predetermined time.

[0035] Examples 4 to 6 are compared. In Examples 4 and 5 where zinc aluminate was supplied to the molten steel, the reduction reaction immediately after the supply was further suppressed, and fuming was hardly observed throughout the retention time. In Example 5 where CaO was mixed to zinc aluminate, the upper surface of the molten steel was covered with slag after the supply, and the amounts of zinc in the molten steel after 10 minutes and 30 minutes were greater than those in Example 4. In Example 6 where zinc silicate was supplied to the molten steel, the zinc compound decomposed faster than in Examples 4 and 5, and the zinc content after a predetermined time is higher than those in Examples 4 and 5.

[Table 6]

	Zn content in steel (mass%)			Fuming
	Before supply	After 10 minutes	After 30 minutes	
Example4 ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$)	<0.001	0.048	0.054	Little fuming
Example5 ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$ -CaO)	<0.001	0.073	0.106	Little fuming
Example6 ($2\text{ZnO} \cdot \text{SiO}_2$)	<0.001	0.185	0.215	Fumed immediately after supply
Comparative Example3 (ZnO)	<0.001	0.007	-	Fumed strongly immediately after supply

[Example 4]

[0036] A Fe - 6 mass% Cr alloy steel was prepared and the method according to the present invention was applied thereto. The chemical composition of the above alloy steel is shown in Table 7. (Ni, W, Zn, Nb and Co were not added.)

[Table 7]

(mass%)						
C	Si	Mn	P	S	Ni	Cr
0.67	0.34	0.65	0.026	0.0011	0.33	5.77
Mo	W	V	Zn	Nb	Co	Fe*
0.98	0.17	0.18	<0.001	<0.01	0.05	Balance
*Including impurities						

[Example 7]

[0037] The alloy steel of Table 7 having a weight of 25 tons was melted in an electric furnace and tapped into a ladle. Subsequently, the ladle with the molten steel was moved to a secondary refining equipment. A zinc compound was supplied to the molten steel maintained at 1600°C in the ladle, in a calculation amount such that the zinc content in the molten steel was 0.036 mass%. The molten steel was maintained for a predetermined time in an Ar atmosphere. The supplied zinc compound was the mixed powder composed of 90 mass% of zinc aluminate powder and 10 mass% of CaO powder used in Example 2. The zinc compound was directly supplied to the molten steel.

[0038] Samples of the molten steel were taken from the top of the ladle at every given time periods using an iron mold, and a final sample was taken from a runner after casting by a bottom pouring method. The zinc content of the samples was measured. Based on the analysis, a change of the zinc content in the molten steel after the supply of the zinc compound was determined. The zinc contents were analyzed by emission spectrometric analysis using inductively coupled plasma. Table 8 shows the zinc contents in the steel. In Example 7 where the method of the present invention was employed, the yield of zinc was good and a high zinc content was maintained even 80 minutes after the supply of the zinc compound. Little fuming was visually observed after the supply of the zinc compound. After casting, a steel containing a specific amount of not lower than 0.001 mass% was produced.

[Table 8]

	Zn content in steel (mass%)			
	Before supply	After 10 minutes	After 30 minutes	After 80 minutes (after casting)
Example7 (ZnO·Al ₂ O ₃)-CaO	<0.001	0.027	0.025	0.024

[Industrial Applicability]

[0039] The present invention can be applied to the manufacture of various steel materials including zinc, and can also be used for adding zinc to Ni or Cr metal, an alloy including such metal as a main component or the like.

Claims

1. A method for adding zinc to a molten steel, comprising supplying a composite oxide of:

zinc; and
aluminum and/or silicon

to the molten steel.

2. The method according to claim 1, further comprising supplying an oxide of calcium to the molten steel.

3. The method according to claim 1 or 2, wherein the molten steel is for a hot work tool steel.

4. A process for producing a zinc-containing steel, comprising casting a molten steel added with zinc by the method according to any one of claims 1 to 3.

5. The process according to claim 4, wherein the zinc-containing steel after casting comprises not lower than 0.001 mass% of zinc.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/079350

A. CLASSIFICATION OF SUBJECT MATTER

C21C7/04(2006.01)i, C22C38/00(2006.01)n, C22C38/52(2006.01)n

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)

C21C7/04, C22C38/00, C22C38/52

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-224418 A (Hitachi Metals, Ltd.), 06 September 2007 (06.09.2007), entire text (Family: none)	1-5
A	JP 2-61006 A (Hitachi Cable, Ltd.), 01 March 1990 (01.03.1990), entire text (Family: none)	1-5
A	WO 2005/035798 A1 (Hitachi Metals, Ltd.), 21 April 2005 (21.04.2005), claim 1; page 4, line 10 to page 5, line 6 & EP 1679384 A1 claim 1; paragraphs [0028] to [0034]	1-5

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

* Special categories of cited documents:

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Date of the actual completion of the international search
12 March, 2012 (12.03.12)Date of mailing of the international search report
27 March, 2012 (27.03.12)Name and mailing address of the ISA/
Japanese Patent Office

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2011/079350

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-171714 A (Nippon Steel Corp.), 20 June 2003 (20.06.2003), paragraphs [0005], [0011] (Family: none)	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007224418 A [0004]
- JP 2061006 A [0004]