(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication: 13.06.2012 Bulletin 2012/24

(21) Application number: 10817308.9

(22) Date of filing: 14.09.2010

(51) Int Cl.: *C10B 53/08* (2006.01)

C10B 57/04 (2006.01)

(86) International application number: **PCT/JP2010/066272**

(87) International publication number: WO 2011/034195 (24.03.2011 Gazette 2011/12)

(84) Designated Contracting States:

AL AT BE BG CH CY CZ DE D

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 SE SI SK SM TR

(30) Priority: **15.09.2009 JP 2009212822 09.09.2010 JP 2010201702**

(71) Applicant: JFE Steel Corporation Tokyo 100-0011 (JP)

(72) Inventors:

 FUJIMOTO, Hidekazu Tokyo 100-0011 (JP) ANYASHIKI, Takashi Tokyo 100-0011 (JP)

 SATO, Hideaki Tokyo 100-0011 (JP)

 SATO, Takeshi Tokyo 100-0011 (JP)

 SUMI, Hiroyuki Tokyo 100-0011 (JP)

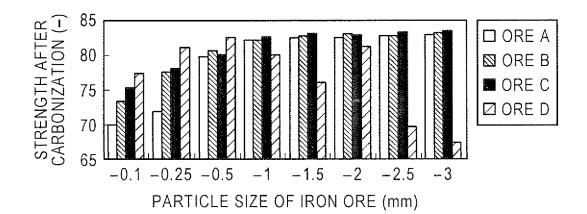
81925 München (DE)

(74) Representative: HOFFMANN EITLE Patent- und Rechtsanwälte Arabellastraße 4

(54) PROCESS FOR PRODUCING FERRO COKE

(57) To provide a method for manufacturing metallurgical formed carbon iron composite, in which the particle size of a raw material iron ore is optimized in the manufacture of carbon iron composite having a relatively small particle size so as to manufacture high-strength carbon iron composite while maintaining a target reduction ratio. The method for manufacturing carbon iron composite includes mixing coal and iron ore having a maximum particle size of 1 to 2 mm to produce a briquetted material, and carbonizing the briquetted material. Preferably, the iron content of the iron ore is 63% by mass or less, the blending ratio of the iron ore is 40% by mass or less relative to the total amount of coal and iron ore, and the iron ore is undersize of a 1-to 2-mm mesh screen.

FIG. 3



Description

Field of the Invention

⁵ **[0001]** The present invention relates to a method for briquetting and carbonizing a mixture of coal and iron ore to manufacture carbon iron composite (ferrocoke).

Description of the Related Arts

[0002] For efficient operation of a blast furnace, coke manufactured by carbonization of coal in a chamber coke oven is charged into a blast furnace. The coke in the blast furnace plays a role of a spacer for improving permeability within the blast furnace, a role as a reducing material, and a role as a heat source. In recent years, from the viewpoint of improving the reactivity of coke, there has been known a technique for mixing coal with iron ore and briquetting and carbonizing the mixture to manufacture metallurgical carbon iron composite.

[0003] A continuous process for manufacturing formed coke using a vertical carbonization furnace has recently been developed (see, for example, Non Patent Document 1). The manufacture of carbon iron composite using a similar vertical carbonization furnace is also being studied. In the continuous process for manufacturing formed coke, a vertical shaft furnace constructed of chamotte bricks in place of silica stone bricks is used as a carbonization furnace. Coal is briquetted into a predetermined size, is charged into the vertical shaft furnace, and is heated with a circulating heating medium gas to carbonize the formed coal, thus manufacturing formed coke. The formed coal is gradually converted into formed coke while falling through the vertical shaft furnace, is cooled with a coolant gas sent from the bottom of the vertical shaft furnace, and is discharged from the furnace. Since the formed coal is worn down, high abrasion resistance is required. The development of carbon iron composite is similar to this and emphasizes the I type strength (30 revolutions, 16 mm index), which indicates the abrasion resistance. When carbon iron composite manufactured by carbonization in the vertical carbonization furnace is used as a raw material in a blast furnace, it is desirable that the carbon iron composite have high strength because carbon iron composite generally has a higher reaction load in the blast furnace than coke. Common metallurgical coke manufactured in a chamber coke oven is hereinafter referred to as "conventional coke".

[0004] One factor responsible for the strength of carbon iron composite is the particle size of iron ore. Patent Document 1 describes the manufacture of formed carbon iron composite having a size of 92 cc that contains up to 75% iron ore based on the total amount. The iron ore has a particle size of 10 mm or less. Patent Document 1 states that the strength of the formed carbon iron composite containing iron ore can be maintained when the amount of iron ore having a particle size of 2 mm or more and 10 mm or less is in the range from 6% to 65% by weight of the total amount. In accordance with Patent Document 2, a mixture of carbon iron composite and sintered ore (iron ore) is charged into a blast furnace, because carbon iron composite improves the reducibility of sintered ore.

Prior Art Documents

Patent Document

40 [0005]

20

30

35

55

Patent Document 1: Japanese Unexamined Patent Application Publication No. 08-012975 Patent Document 2: Japanese Unexamined Patent Application Publication No. 2006-28594

45 Non Patent Document

[0006] Non Patent Document 1: The Iron and Steel Institute of Japan, "Renzokusiki Seikei Kokusu Seize Gijutsu no Kenkyu Seika Hokokusyo", 1978-1986

50 Summery or the Invention

Technical Problem

[0007] Charging of carbon iron composite in a blast furnace results in a decrease in the amount of conventional coke. Thus, it is important to ensure the air permeability of the blast furnace. It is therefore desirable that the size of the carbon iron composite in the upper portion of the blast furnace be substantially the same as the size of the sintered ore (approximately 6 cc). Thus, 92 cc described in Patent Document 1 is too large. In the manufacture of carbon iron composite having a smaller size, the upper limit of the size of iron ore to be added should be decreased. A decrease in the particle

size of iron ore facilitates the reduction of the iron ore. The particle size of iron ore used as a raw material for carbon iron composite is very important.

[0008] In general, lumps of iron ore brought in an ironworks are passed through an approximately 10-mm mesh screen. Large iron ore on the screen is sent to a blast furnace, and small iron ore under the screen is sent to a sintering plant. Thus, iron ore under the screen as a raw material for carbon iron composite is used to blend iron ore having a particle size of 10 mm or less with coal. Whether iron ore under the screen is directly used or crushed into a raw material having an appropriate size affects the structure of the manufacturing facilities of carbon iron composite, the cost of equipment, and the operating costs. Thus, the effects of iron ore size on the qualities (strength and reduction ratio) of carbon iron composite must be investigated.

Carbon iron composite (having a size of 6 cc and an average particle size of 22 mm) containing iron ore having a particle size of 10 mm will have large structural defects therein and may therefore have reduced strength. In addition, iron ore having a large particle size possibly has a lower reduction ratio than iron ore having a small particle size under the same carbonization conditions.

[0009] It is an object of the present invention to provide a method for manufacturing metallurgical carbon iron composite, in which the particle size of a raw material iron ore is optimized in the manufacture of carbon iron composite having a relatively small particle size so as to manufacture high-strength carbon iron composite while maintaining a target reduction ratio.

Solution to Problem

20

30

35

40

50

55

[0010] In order to achieve this object, the present invention provides a method for manufacturing carbon iron composite, comprising mixing coal and iron ore having a maximum particle size of 1 to 2 mm to produce a briquetted material, and carbonizing the briquetted material.

[0011] In the method for manufacturing carbon iron composite, the iron ore preferably has an iron content of 63% by mass or less. When the iron content is 63% by mass or less, cracking that originates from metallic iron produced by the reduction of iron ore can be prevented even in iron ore having a large particle size. More preferably, the iron ore has iron content of 55% to 63% by mass.

Preferably, the iron ore has a blending ratio of 40% by mass or less relative to the total amount of coal and iron ore. The blending ratio of the iron ore of 40% by mass or less allows the coking component of coal to be retained in the formed product, preventing reduction in strength. The blending ratio of the iron ore preferably ranges from 1% to 40% by mass, most preferably 10% to 40% by mass.

Preferably, the iron ore is iron ore that passes through a 1- to 2-mm mesh screen. It is desirable that the coal have a particle size of 3 mm or less. In order to increase the strength of the carbon iron composite, the particle size is more preferably 2 mm or less.

[0012] In the method for manufacturing carbon iron composite, it is desirable that the producing of the briquetted material comprises mixing coal, iron ore having a maximum particle size in the range of 1 to 2 mm, and a binder to produce the briquetted material. It is desirable that the amount of the binder range from 4% to 6% by mass of the total amount of coal and iron ore.

[0013] Preferably, the carbon iron composite has a size in the range of 0.5 to 25 cc, more preferably 5 to 8 cc. This is because the size of the carbon iron composite is desirably substantially the same as sintered ore, that is, 6 cc so as to ensure the air permeability of the blast furnace. Advantageous Effects of Invention

[0014] In accordance with the present invention, high-strength carbon iron composite can be manufactured while maintaining a target reduction ratio.

45 Brief Description of the Drawings

[0015]

Fig. 1 is a graph showing the relationship between the green strength of a formed product and the particle size of iron ore.

Fig. 2 is a graph showing the relationship between the reduction ratio of a formed product after carbonization and the particle size of iron ore.

Fig. 3 is a graph showing the relationship between the strength of a formed product after carbonization and the particle size of iron ore.

Fig. 4 is a graph showing the relationship between the blending ratio of iron ore and the strength after carbonization.

Embodiments for carrying out the Invention

[0016] In the present embodiment, when a briquetted material of coal and iron ore is carbonized to manufacture carbon iron composite having a small particle size in the range of approximately 5 to 8 cc, iron ore having a maximum particle size in the range of 1 to 2 mm is mixed with coal to manufacture the briquetted material. Iron ore, for example, having a maximum particle size of 1 mm refers to crushed iron ore that passes through a 1-mm mesh screen and hereinafter referred to as a particle size of 1 mm or less (-1 mm. Thus, as iron ore to be used in the present embodiment, a raw material iron ore is passed through a 1-to 2-mm mesh screen directly or after crushing, and iron ore under the screen is preferably used.

[0017] When iron ore to be used as a raw material for a briquetted material is crushed to a particle size of 0.25 mm or less, the briquetted material has low strength unless a large amount of binder is added. Thus, crushing of the iron ore to a particle size of 0.25 mm or less is unfavorable. On the other hand, when the particle size of the iron ore is 2 mm or less, the reduction ratio of the carbon iron composite after the carbonization of a briquetted material can be 80% or more. When the particle size of the iron ore ranges from 1 mm or less to 3 mm or less, carbon iron composite after the carbonization of a briquetted material can have sufficiently high drum strength. Thus, use of iron ore having a particle size in the range of 1 mm or less to 2 mm or less as a raw material can provide carbon iron composite having a high reduction ratio and high drum strength.

[0018] Use of iron ore having an iron content of more than 63% by mass and a large particle size tends to cause cracking that originates from metallic iron produced by the reduction of the iron ore. Thus, iron ore having an iron content of 63% by mass or less is preferably used. At an iron content of 63% by mass or less, cracking that originates from metallic iron produced by the reduction of iron ore can be prevented even in iron ore having a large particle size. More preferably, the iron ore has an iron content in the range of 55% to 63% by mass. When iron ore having an iron content of more than 63% by mass is used, the particle size of the iron ore is preferably 1 mm or less.

[0019] Coal to be used as a raw material for a briquetted material is preferably crushed to a particle size of 3 mm or less before use. A particle size of more than 3 mm tends to result in fusion of a briquetted material during carbonization and may result in low strength of carbon iron composite after the carbonization of briquetted material.

In order to increase the strength of carbon iron composite, the particle size of coal is more preferably 2 mm or less. The coal is preferably a mixture of slightly caking coal and non-caking coal.

[0020] The blending ratio of iron ore is preferably 40% by mass or less of the total amount of raw materials (the total amount of coal and iron ore). The blending ratio of iron ore more preferably ranges from 1% to 40% by mass, most preferably 10% to 40% by mass. At a blending ratio of iron ore of more than 40% by mass, a coking component of coal in a briquetted material is relatively decreased, and carbon in carbon iron composite is consumed with the reduction of the iron ore. This makes the interior of the carbon iron composite more porous and markedly decreases the strength of the carbon iron composite.

[0021] In the manufacture of a briquetted material, it is preferable to add a binder to coal and iron ore. Preferably, the amount of binder ranges from 4% to 6% by mass of the total amount of coal and iron ore.

[0022] For example, a briquetted material of coal and iron ore is manufactured by kneading coal, iron ore, and a binder in a high-speed mixer and using a briquetting machine. The briquetted material is carbonized in a carbonization furnace or the like to manufacture carbon iron composite.

EXAMPLE 1

[0024]

[0023] A manufacturing test of carbon iron composite was performed using coal and iron ore as raw materials. Table 1 shows the briquetting conditions for forming a briquette of carbon iron composite raw materials.

Table 1

Briquetting conditions				
Briquetting pressure	4-5 t/cm			
Roll size	650 mmφ x 104 mm			
Roll peripheral speed	0.2 m/s			
Cup volume	30 mm x 25 mm x 18 mm, 6 cc			
Mixer Temperature	140°C-160°C			

55

50

20

30

35

40

45

[0025] In the formation of a formed product, 6% by mass of a binder based on the tonal mass of the raw materials coal and iron ore was added to the raw materials, which were then kneaded in a high-speed mixer at a temperature in the range of 140° C to 160° C for approximately two minutes. The kneaded raw materials were formed into briquettes with a double roll briquetting machine. The briquetting machine had a roll size of 650 mm ϕ x 104 mm. The peripheral speed was 0.2 m/s, and the briquetting pressure ranged from 4 to 5 t/cm. The briquetted material had a size of 30 mm x 25 mm x 18 mm (6 cc) and was egg-shaped.

[0026] Table 2 shows the conditions for the raw materials of a formed product.

Table 2

Conditions for raw materials		
Binder	6% by mass	
Briquetting raw materials	Coal/iron ore = 7/3	
Particle size of coal	All particles, -3 mm	
Particle size of iron ore	-0.1, -0.25, -0.5, -1.0, -1.5, -2.0, -2.5, -3.0 mm	

[0027] Coal was crushed such that all the particles had a size of 3 mm or less. The coal was a mixture of slightly caking coal and non-caking coal. The particle sizes of iron ore were adjusted to 0.1 mm or less (-0.1 mm), 0.25 mm or less (-0.25 mm), 0.5 mm or less (-0.5 mm), 1.0 mm or less (-1.0 mm), 1.5 mm or less (-1.5 mm), 2.0 mm or less (-2.0 mm), 2.5 mm or less (-2.5 mm), and 3.0 mm or less (-3.0 mm) by screening after crushing. 30% by mass of iron ore based on the total amount of raw materials was mixed with coal. Four types of iron ores having different iron contents were prepared and tested. Table 3 shows the iron content of each of the iron ores used.

[0028]

10

15

20

25

30

35

40

45

50

55

Table 3

Type of iron ore	Iron content (% by mass)
Ore A	57.6
Ore B	61.5
Ore C	62.8
Ore D	65.5

[0029] Table 4 shows the particle size distribution of iron ore A as an example.

Table 4

Tubio 4				
	-1 mm	-1.5 mm	-2 mm	
-0.075	15.1 (%)	11.2	6.5	
0.075-0.15	10.7	8.7	5.1	
0.15-0.25	11.2	9.4	5.4	
0.25-0.5	26.7	21.2	14	
0.5-1	35.9	33.9	22.4	
1-2	0.4	15.6	44.6	

[0030] 3 kg of a briquetted material was charged into a carbonization vessel 300 mm in length, 300 mm in width, and 400 mm in height and was carbonized at a furnace wall temperature of 1000°C for six hours to manufacture carbon iron composite.

[0031] Fig. 1 shows the relationship between the strength of the briquetted material (green strength) and the particle size of the iron ore. The strength of a briquetted material was determined with a I type drum test apparatus (cylindrical with an inner diameter of 130 mm x 700 mm) by the residual rate of 16 mm or more after 30 revolutions at a rotation speed of 20 revolutions per minute. For any of ores A to D, crushing of the whole iron ore to 0.25 mm or less resulted in reduced strength of the formed product. Crushing of iron ore results in an increase in the outer surface area of particles

and an increase in the amount of binder required. In the present experiment, however, the constant amount of binder was responsible for the results described above. At a particle size of iron ore in the range of 0.5 mm or less to 3 mm or less, the strength of the briquetted material did not change significantly for the same type of ore.

[0032] Fig. 2 shows the relationship between the reduction ratio of a briquetted material after carbonization and the particle size of iron ore. When the particle size of the iron ore was 0.5 mm or less, the reduction ratio was substantially constant. However, the reduction ratio gradually decreased at a particle size of 0.5 mm or more. When the particle size of the iron ore was 3 mm or less, the reduction ratio decreased by approximately 10%. This is probably because the reduction of the central portion of the iron ore was decreased. For a target reduction ratio of 80% or more, it is desirable that the particle size of the iron ore be 2 mm or less for any type of ore.

[0033] Fig. 3 shows the relationship between the strength of a briquetted material after carbonization and the particle size of iron ore. The strength after carbonization was determined with a drum test apparatus by the residual rate of 6 mm or more after 150 revolutions. The strength of the ore A, B, or C having an iron content of 63% by mass or less decreased when the particle size of iron ore was 0.5 mm or less. This is partly because a decrease in the particle size of iron ore made a coke portion more porous (an increase in porosity) as the reduction of the iron ore proceeded. For a target strength after carbonization (drum strength) of 82 or more, it is shown that the target drum strength could be achieved when all the particle sizes of iron ore ranged from 1 mm or less to 3 mm or less. On the other hand, the ore D having an iron content of 65.5% by mass exhibited strength reduction when the particle size of iron ore was more than 1 mm. Observation of the appearance of the iron ore D after crushing showed the presence of flat pointed particles. This is probably because a large particle size of iron ore resulted in cracking that originates from metallic iron produced by the reduction of the iron ore caused by an impact in the strength test. For ore having an iron content of 63% by mass or less, it is shown that the target reduction ratio and the target strength were achieved at a particle size of iron ore in the range of 1 mm or less to 2 mm or less.

[0034] Fig. 4 shows the relationship between the blending ratio of iron ore and the strength after carbonization for the ores A and C. At a blending ratio of iron ore up to 40% by mass, the strength after carbonization gradually decreased with an increase in the blending ratio of the iron ore. On the other hand, a significant reduction in strength was observed at a blending ratio of iron ore of more than 40% by mass. This is probably because an increase in the blending ratio of iron ore resulted in a decrease in the coking component of coal and because carbon in carbon iron composite was consumed with the reduction of the iron ore, making the interior of the carbon iron composite more porous.

Claims

15

20

30

35

40

55

1. A method for manufacturing carbon iron composite, comprising:

mixing coal and iron ore having a maximum particle size of 1 to 2 mm to produce a briquetted material; and carbonizing the briquetted material.

- 2. The method for manufacturing carbon iron composite according to claim 1, wherein the iron ore has an iron content of 63% by mass or less.
- 3. The method for manufacturing carbon iron composite according to claim 1, wherein the iron ore has an iron content of 55% to 63% by mass.
- 4. The method for manufacturing carbon iron composite according to claim 1, wherein the iron ore has a blending ratio of 40% by mass or less relative to an total amount of the coal and the iron ore.
 - **5.** The method for manufacturing carbon iron composite according to claim 4, wherein the blending ratio of the iron ore is 1% to 40% by mass.
- 50 **6.** The method for manufacturing carbon iron composite according to claim 5, wherein the blending ratio of the iron ore is 10% to 40% by mass.
 - 7. The method for manufacturing carbon iron composite according to claim 1, wherein the iron ore is an iron ore that passes through a 1- to 2-mm, mesh screen.
 - **8.** The method for manufacturing carbon iron composite according to claim 1, wherein the coal has a particle size of 3 mm or less.

9. The method for manufacturing carbon iron composite according to claim 1, wherein the producing of the briquetted material comprises mixing coal, iron ore having a maximum particle size in the range of 1 to 2 mm, and a binder to produce the briquetted material.
10. The method for manufacturing carbon iron composite according to claim 9, wherein the binder has an addition amount of 4% to 6% by mass relative to the total amount of the coal and the iron ore.

- **11.** The method for manufacturing carbon iron composite according to claim 1, wherein the carbon iron composite has a size of 0.5 to 25 cc.
- **12.** The method for manufacturing carbon iron composite according to claim 1, wherein the size of the carbon iron composite is 5 to 8 cc.

FIG. 1

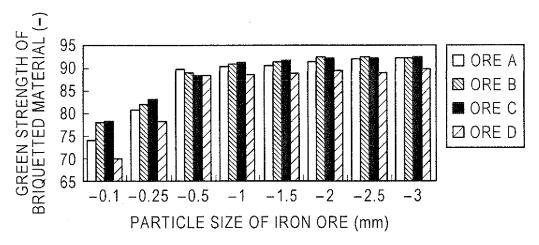


FIG. 2

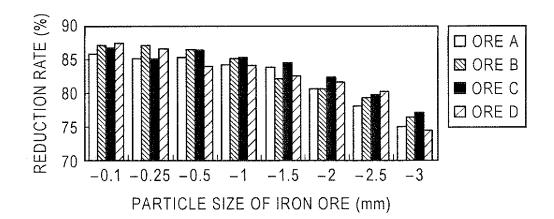


FIG. 3

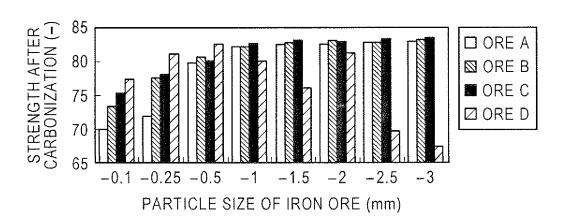
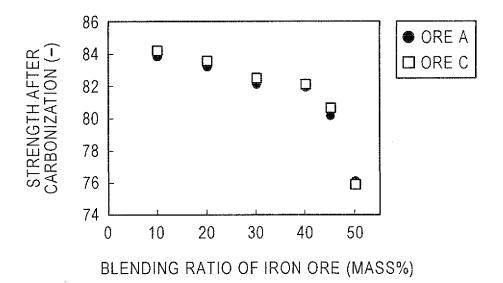


FIG. 4



International application No. INTERNATIONAL SEARCH REPORT PCT/JP2010/066272 A. CLASSIFICATION OF SUBJECT MATTER C10B53/08(2006.01)i, C10B57/04(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) C10B53/08, C10B57/04 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 1996-2010 Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010 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. JP 2007-246786 A (JFE Steel Corp.), 1,4-8,11,12 Χ 27 September 2007 (27.09.2007), entire text (Family: none) Χ JP 2007-169603 A (JFE Steel Corp.), 1,4-8,11,12 05 July 2007 (05.07.2007), entire text (Family: none) Χ JP 6-65579 A (Nippon Steel Corp.), 1-6,8,9 08 March 1994 (08.03.1994), entire text (Family: none) X Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: 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 "A" document defining the general state of the art which is not considered to be of particular relevance earlier application or patent but published on or after the international "E" "X" document of particular relevance; the claimed invention cannot be filing date considered novel or cannot be considered to involve an inventive step when the document is taken alone 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) "T." "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 referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 25 October, 2010 (25.10.10) 02 November, 2010 (02.11.10) Name and mailing address of the ISA/ Authorized officer

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

Japanese Patent Office

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/066272

		PCT/JP2	010/066272
C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
Х	JP 2004-217914 A (JFE Steel Corp.), 05 August 2004 (05.08.2004), examples (Family: none)		1,4-6,8-10
X	examples		1,4-6

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

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

• JP 8012975 A [0005]

• JP 2006028594 A **[0005]**

Non-patent literature cited in the description

 Renzokusiki Seikei Kokusu Seize Gijutsu no Kenkyu Seika Hokokusyo. The Iron and Steel Institute of Japan, 1978 [0006]