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(54) **METHOD FOR PRODUCING MOLTEN PIG IRON**

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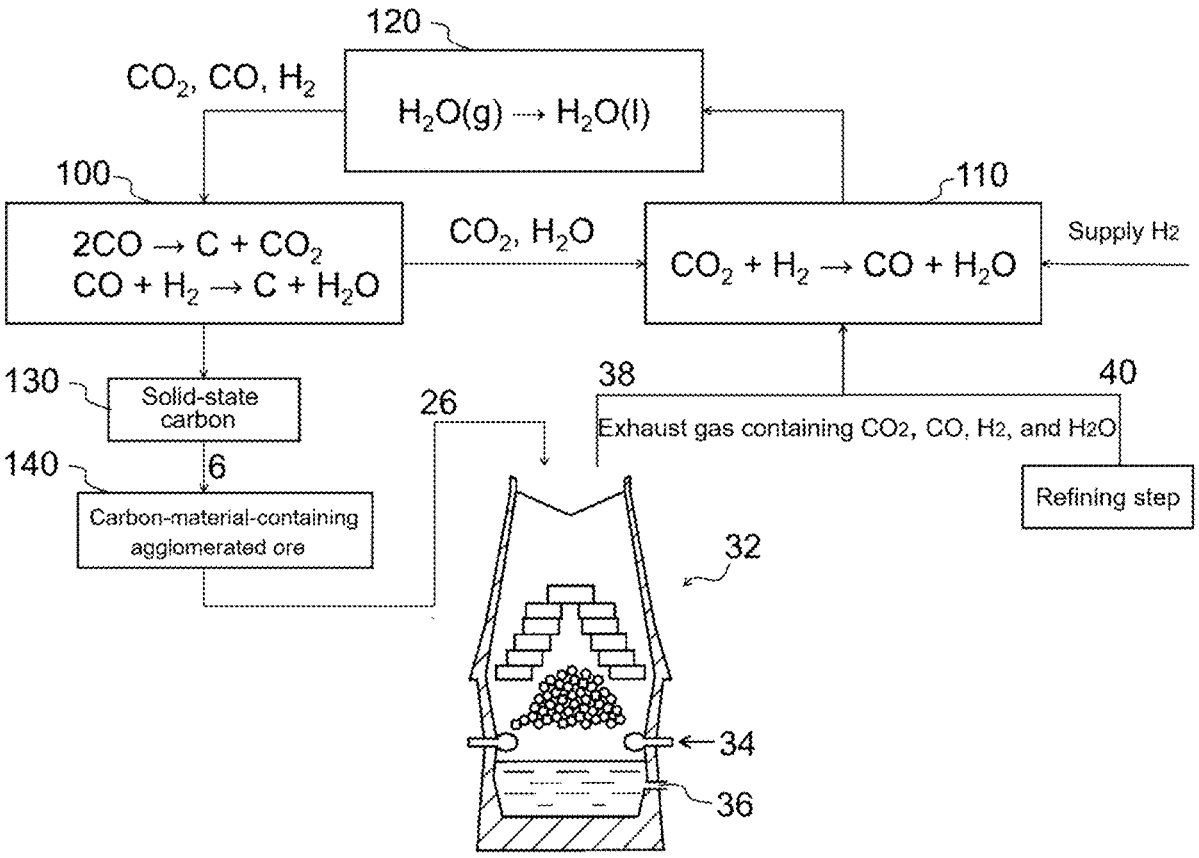
(57) **ABSTRACT**

A method for producing molten pig iron includes a first step of producing carbon-material-containing agglomerated ore from an iron-containing and carbon-containing raw materials, a second step of blowing an oxygen-containing gas into the carbon-material-containing agglomerated ore to reduce and melt it, thereby producing molten pig iron, and a third step of bringing a carbon-containing gas containing carbon monoxide and carbon dioxide produced as a by-product of the reduction into contact with a porous material, thereby recovering carbon, in which in the first step, the carbon recovered in the third step is used for a part of or an entirety of the carbon-containing raw material. The method may include, instead of the second step, a reduction step of heating the carbon-material-containing agglomerated ore to 1160 to 1450° C., and then cooling the carbon-material-containing agglomerated ore to obtain reduced iron, and a step of melting the reduced iron to produce molten pig iron.



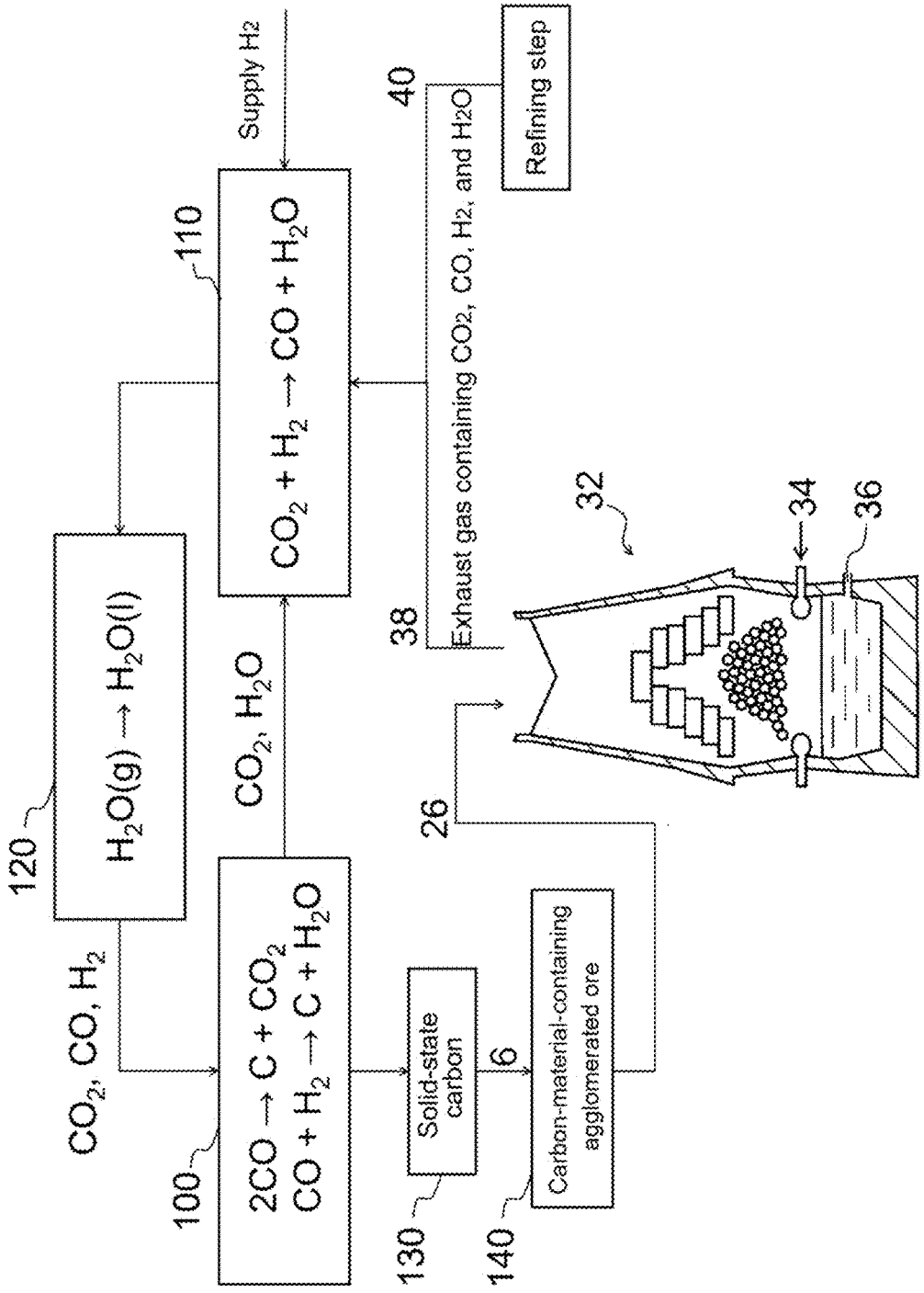

Supply H2
110
$CO_2 + H_2 \rightarrow CO + H_2O$
40
Refining step
Exhaust gas containing CO_2, CO, H_2, and H_2O
38
32
34
36
26
120
$H_2O(g) \rightarrow H_2O(l)$
CO_2, H_2O
CO_2, CO, H_2
100
$2CO \rightarrow C + CO_2$
$CO + H_2 \rightarrow C + H_2O$
Solid-state carbon
130
6
Carbon-material-containing agglomerated ore
140

Fig. 1

Fig. 2

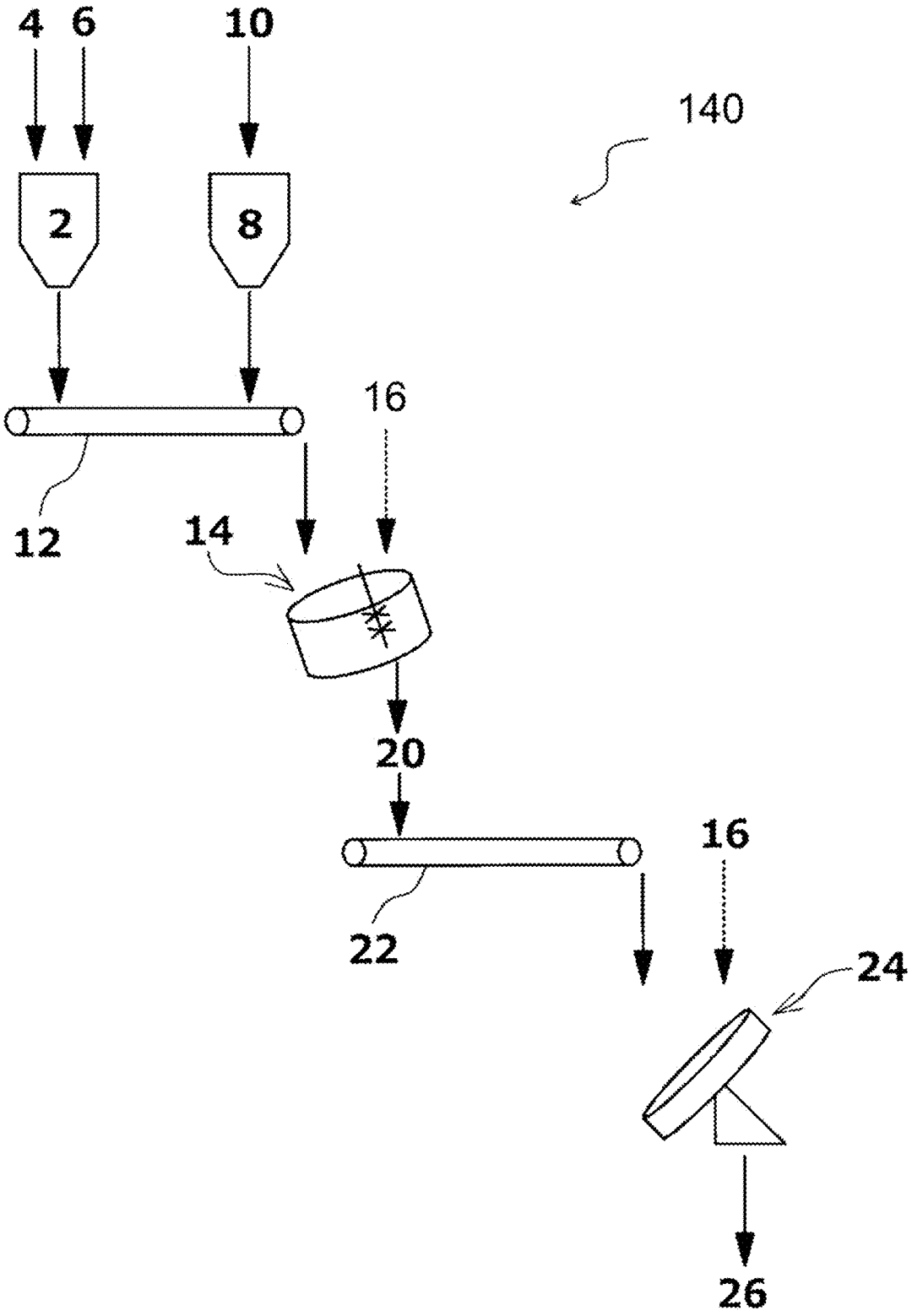


Fig. 3

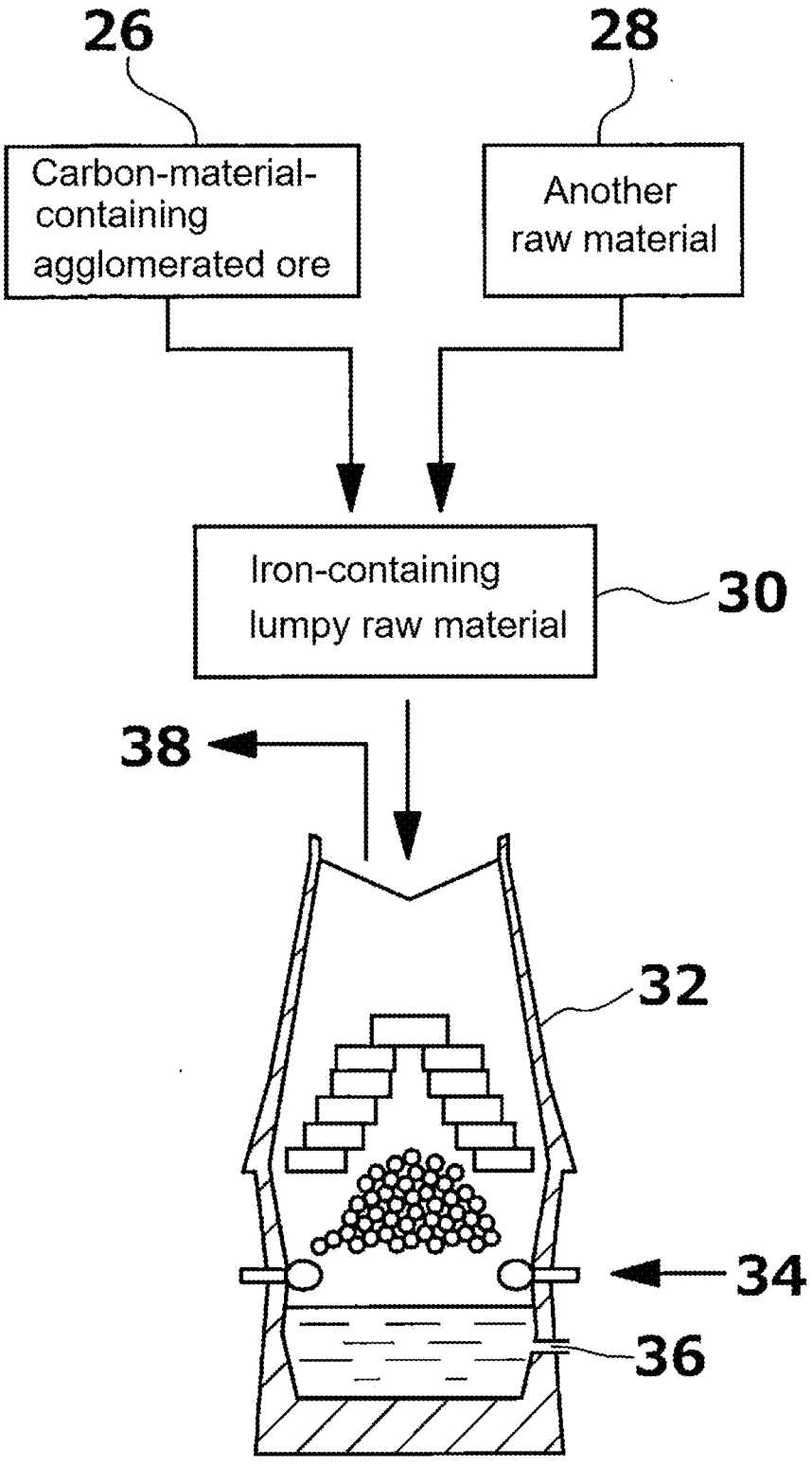

26
28
Carbon-material-containing agglomerated ore
Another raw material
Iron-containing lumpy raw material
30
38
32
34
36

Fig. 4

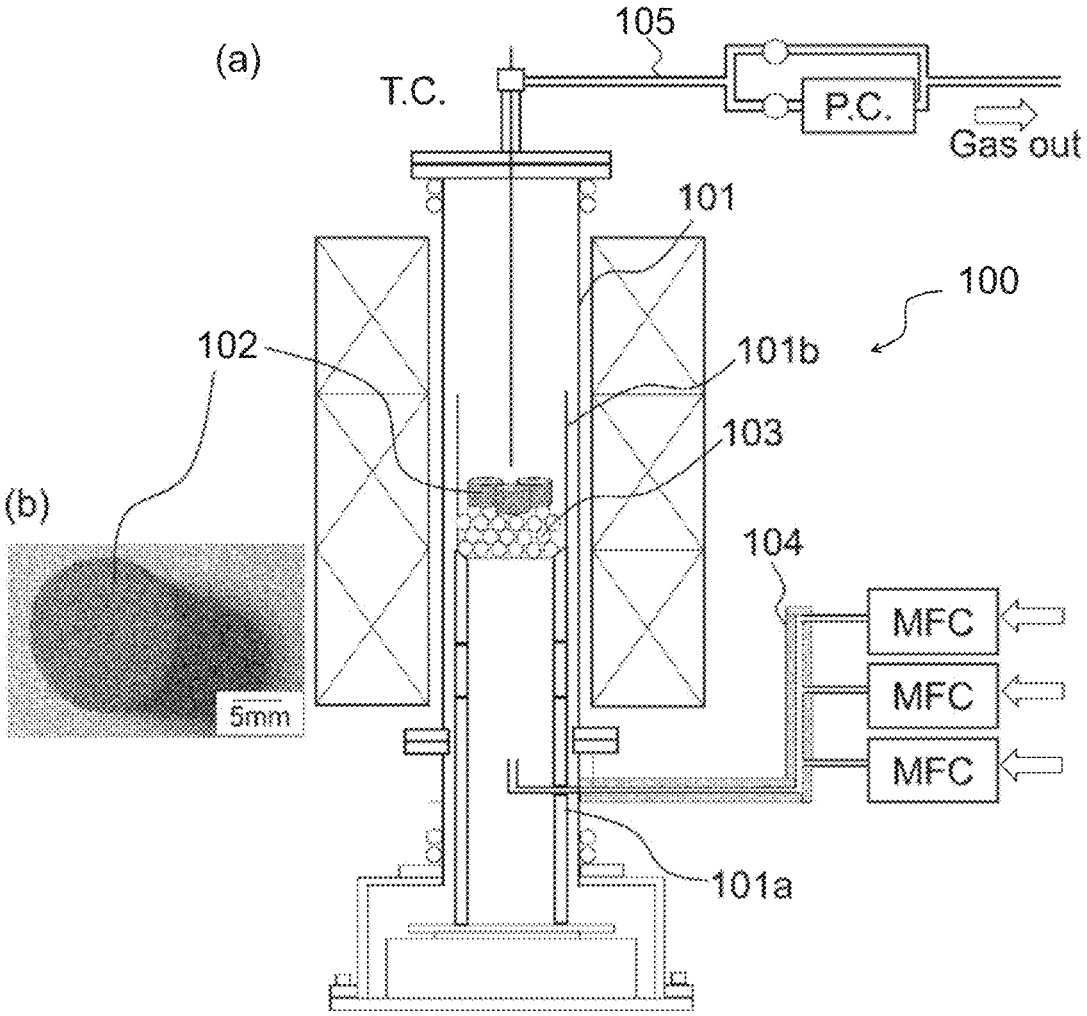

(a)
T.C.
105
P.C.
Gas out
101
100
102
101b
103
(b)
104
MFC
MFC
MFC
5mm
101a

Fig. 5

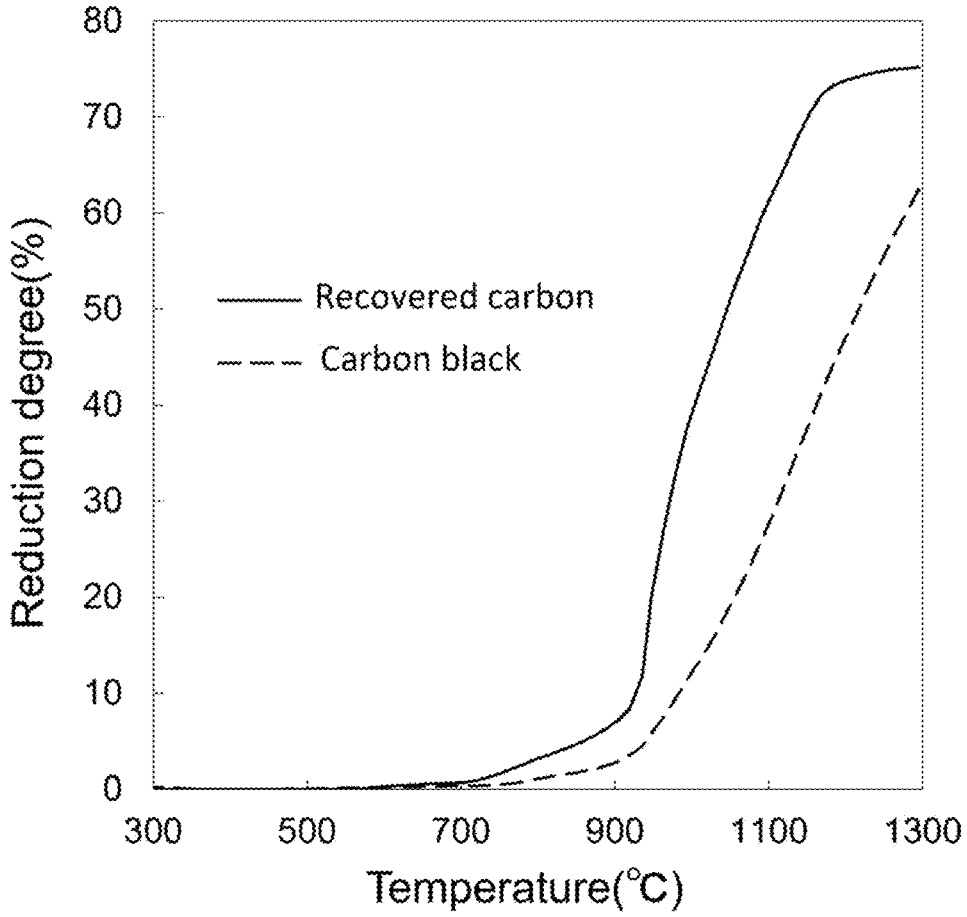
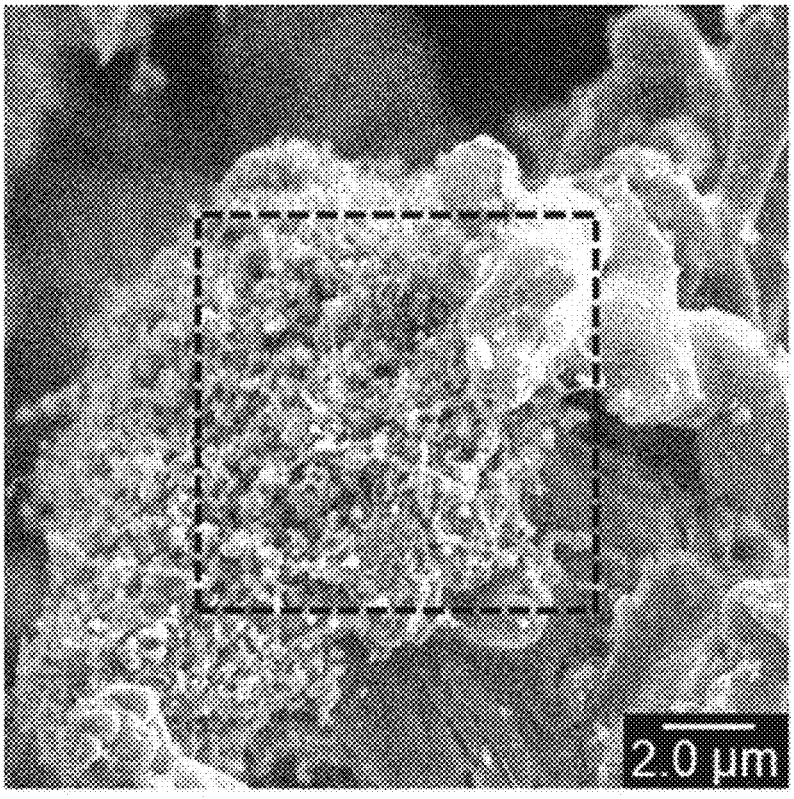

80
70
60
50
40
30
20
10
0
Reduction degree(%)
Recovered carbon
Carbon black
300
500
700
900
1100
1300
Temperature(°C)

Fig. 6

(a)



(b)

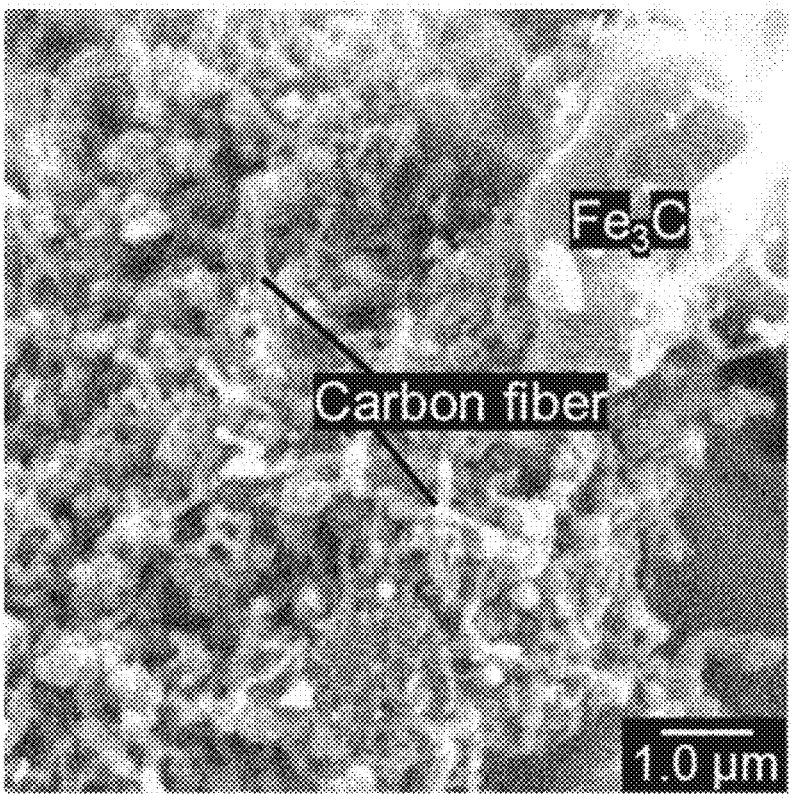
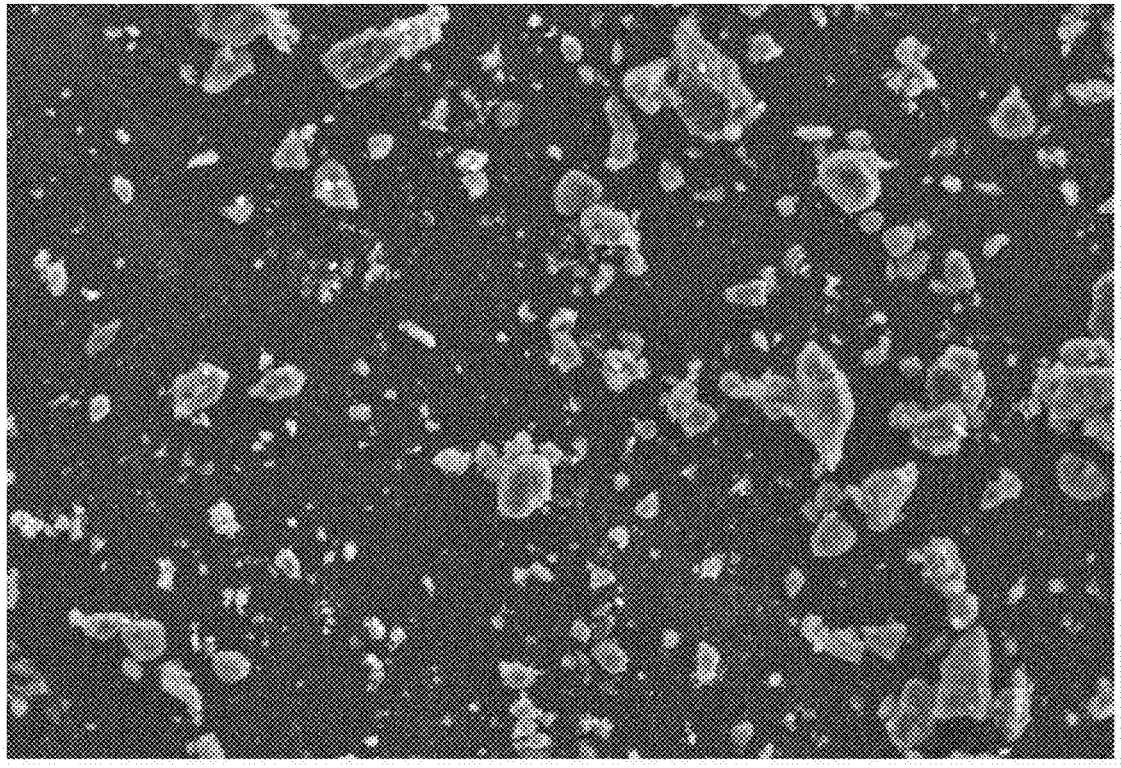


Fig. 7



METHOD FOR PRODUCING MOLTEN PIG IRON

TECHNICAL FIELD

[0001] The present invention relates to a method for producing molten pig iron in the steel industry.

BACKGROUND ART

[0002] Reducing carbon dioxide emissions is required across all industries, as mandated by the SDGs and the Paris Agreement, for example. Among all manufacturing industries, the steel industry emitting large amounts of CO_2 is particularly required to reduce CO_2 emissions. In the steel industry, the molten pig iron production process accounts for 60% or more of the CO_2 emissions of all processes. The molten pig iron production process involves reducing and melting iron ores using a carbon source to produce molten pig iron. The reason that the molten pig iron production process involves very high CO_2 emissions is considered to be the use of coke or coal for the reduction and melting. There has been demand for the development of a molten pig iron production process that does not discharge CO_2 to the outside of the system.

[0003] An iron-making process intended for net-zero carbon emissions has been devised.

[0004] Non Patent Literature 1 describes a review of the technological prospects for achieving the long-term goal of carbon dioxide reduction in the steel industry. For example, Non Patent Literature 1 introduces a method (CCS: Caron dioxide Capture and Storage) of separating CO_2 from an exhaust gas generated through a reduction reaction, and storing CO_2 in an isolated manner so as to reduce CO_2 emissions to the outside. Another known method is a technology (CCU: Carbon dioxide Capture and Utilization) for separating CO_2 from an exhaust gas to reuse it. The technology involves synthesizing CH_4 using CO_2 in an exhaust gas and blowing the synthesized CH_4 into a blast furnace through its tuyere so as to use the synthesized CH_4 for a reduction reaction again.

CITATION LIST

Non Patent Literature

[0005] Non Patent Literature 1: "Perspective toward Long-term Global Goal for Carbon Dioxide Mitigation in Steel Industry," Tetsu-to-Hagane, Tatsuro ARIYAMA, Vol. 105, 2019, No. 6, pp. 567-586

[0006] Non Patent Literature 2: Materials Transactions, Vol. 58, No. 12 (2017), pp. 1742 to 1748, "Development of Manufacturing Principle of Porous Iron by Carbothermic Reduction of Composite of Hematite and Biomass Char"

SUMMARY OF INVENTION

Technical Problem

[0007] However, the existing technologies have the following problems. That is, although applying the CCS method can contribute to the reduction of CO_2 emissions, the process would consume lots of energy. The method also has problems in that the C source should be moved to the outside of the system and the storage capacity is limited. Meanwhile, when CH_4 is synthesized from CO_2 to blow the synthesized CH_4 into a blast furnace through its tuyere, a line for blowing CH_4 into the tuyere would be needed, which is problematic.

[0008] The present invention has been made in view of the above circumstances and aims to provide a method for producing molten pig iron by circulating a C source through a process and feeding the recovered C source into a shaft furnace through its throat as a carbon-material-containing agglomerated ore to produce molten pig iron.

Solution to Problem

[0009] A method for producing molten pig iron according to the present invention that advantageously solves the above problems includes a first step of producing a carbon-material-containing agglomerated ore from an iron-containing raw material and a carbon-containing raw material; a second step of blowing an oxygen-containing gas into the carbon-material-containing agglomerated ore to reduce and melt the carbon-material-containing agglomerated ore, thereby producing molten pig iron; and a third step of bringing a carbon-containing gas containing carbon monoxide and carbon dioxide produced as a by-product of the reduction into contact with a porous material, thereby recovering carbon, in which in the first step, the carbon recovered in the third step is used for a part of or an entirety of the carbon-containing raw material.

[0010] The method for producing molten pig iron according to the present invention may have more preferable solutions as follows.

[0011] (a) The method includes, instead of the second step, a reduction step of obtaining reduced iron in which the carbon-material-containing agglomerated ore is heated to 1160 to 1450° C., reduced, melted, and then cooled, and a melting step of producing molten pig iron in which the reduced iron is melted.

[0012] (b) In the third step, the carbon-containing gas further contains a gas containing carbon monoxide and carbon dioxide produced as a by-product of a refining step of molten iron.

[0013] (c) The method further includes, before bringing the carbon-containing gas into contact with the porous material in the third step, supplying hydrogen to the carbon-containing gas and heating the carbon-containing gas to 800 to 1200° C. to convert the carbon dioxide contained in the carbon-containing gas to carbon monoxide.

[0014] (d) The method further includes, after heating the carbon-containing gas but before bringing the carbon-containing gas into contact with the porous material in the third step, removing water contained in the carbon-containing gas.

[0015] (e) Water contained in the carbon-containing gas and water generated by a reforming reaction of the carbon-containing gas are removed so as to satisfy the following expression (1):

[Math. 1]

$$[H_2O]/([H_2O]+[H_2]) < 0.1, \quad (1)$$

[0016] where $[H_2O]$ represents a water concentration (volume %) in a reformed mixed gas, and $[H_2]$ represents a hydrogen concentration (volume %) in the reformed mixed gas.

[0017] (f) In the third step, the porous material is iron, and a part of the recovered carbon is iron carbide.

[0018] (g) The particle size of the carbon-containing raw material is 100 μm or less.

[0019] (h) In the first step, the carbon-containing raw material further contains biomass.

[0020] (i) The iron-containing raw material is iron ores, and the method further includes a pretreatment step of subjecting the iron ores to heat treatment in a temperature range of 300° C. to 1000° C. before the first step.

Advantageous Effects of Invention

[0021] According to the present invention, molten pig iron can be produced by charging a carbon-material-containing agglomerated ore using the recovered carbon into a shaft furnace through its throat. Thus, the recovered carbon can be circulated through a process without the need to modify the shaft furnace.

BRIEF DESCRIPTION OF DRAWINGS

[0022] FIG. **1** is a schematic view showing an example of a method for producing molten pig iron according to the present invention.

[0023] FIG. **2** is a schematic view showing an example of a process for producing a carbon-material-containing agglomerated ore according to a first step of the present invention.

[0024] FIG. **3** is a schematic view showing an example of a facility in which a countercurrent reduction layer is used according to a second step of the present invention.

[0025] FIG. **4**(*a*) is a schematic view showing an example of a carbonization apparatus according to a third step of the present invention, and FIG. **4**(*b*) is an enlarged photograph of a porous material used in the carbonization apparatus.

[0026] FIG. **5** is a graph showing the influence of carbon species on the reducibility of iron ores.

[0027] FIG. **6**(*a*) is an SEM photograph of recovered carbon to be used in the present invention, and FIG. **6**(*b*) is an enlarged photograph of a portion indicated by a broken line in FIG. **6**(*a*).

[0028] FIG. **7** is a SEM photograph of carbon black used in a comparative example.

DESCRIPTION OF EMBODIMENTS

[0029] Hereinafter, a method for producing molten pig iron according to the present embodiment will be described with reference to the drawings. The following embodiment only illustrates examples of an apparatus and a method for embodying the technical idea of the present invention. Thus, the configuration of the present invention is not limited thereto. That is, the technical idea of the present invention can be modified in various ways within the technical scope recited in the claims.

[0030] FIG. **1** is a schematic view showing an example of a method for producing molten pig iron according to the present embodiment. FIG. **2** is a schematic view showing an example of a process for producing a carbon-material-containing agglomerated ore. FIG. **3** is a schematic view showing an example of a facility in which a countercurrent reduction layer is used. In the present embodiment, molten pig iron **36** is produced by reducing an iron-containing raw material **4** contained in a carbon-material-containing agglomerated ore **26** in a countercurrent reduction layer. To produce the molten pig iron **36**, a vertical shaft furnace is preferably used, for example. The following embodiment will describe a method for producing molten pig iron according to the present invention with reference to an example in which a blast furnace **32** is used as the vertical shaft furnace. Note that there has been no vertical shaft furnace for producing molten pig iron without using coke.

[0031] In a first step, an iron-containing raw material **4** and a carbon-containing raw material **6** are mixed to produce the carbon-material-containing agglomerated ore **26**. The iron-containing raw material **4** is composed mainly of crushed iron ores, and may also contain dust generated in a steel mill, for example. In a second step, the obtained carbon-material-containing agglomerated ore **26** is charged into the blast furnace **32**, and a blow gas **34** is blown into the furnace to allow a reduction reaction to proceed and thus produce the molten pig iron **36**. In the third step, an exhaust gas **38**, which has been produced as a by-product of the reduction reaction in the second step, is recovered, and the carbon monoxide contained in the exhaust gas **38** is brought into contact with a porous material so that a process of precipitating solid-state carbon and thus recovering it is performed. The exhaust gas **38** treated herein preferably contains an exhaust gas **40** produced as a by-product of a refining process of molten iron.

[0032] A part of or all of the carbon-containing raw material **6** used in the first step is the solid-state carbon recovered in the third step. If the carbon content of the recovered solid-state carbon alone is insufficient, a carbon source such as biomass may be used to supplement the deficiency. In such a case, the carbon-containing raw material **6** contains a carbon source such as biomass. Further, the particle size of the carbon-containing raw material **6** is preferably 100 μm or less. If the iron-containing raw material **4** used in the first step is crushed iron ores and contains a large amount of crystal water, it is preferable to apply a heat treatment step of subjecting the iron-containing raw material **4** to heat treatment in the temperature range of 300° C. to 1000° C. before the first step. Hereinafter, each step will be described in detail.

[First Step]

[0033] The first step is a step of mixing an iron-containing raw material and a carbon-containing raw material to produce a carbon-material-containing agglomerated ore. In the example shown in FIG. **2**, first, the iron-containing raw material **4** and the carbon-containing raw material **6**, which contains solid-state carbon recovered from the carbon monoxide contained in the exhaust gas **38**, stored in a storage tank **2**, and cement powder **10** stored in a storage tank **8** are respectively cut in predetermined amounts out of the storage tanks **2** and **8** to be delivered to a conveyor **12**. The iron-containing raw material **4**, the carbon-containing raw material **6**, and the cement powder **10** are conveyed to a kneader **14** by the conveyor **12**. The thus conveyed iron-containing raw material **4**, carbon-containing raw material **6**, and cement powder **10** are mixed in the kneader **14** together with an appropriate amount of water **16** to form mixed powder **20**. Then, the mixed powder **20** is conveyed to a granulator **24** by a conveyor **22** and granulated in the

granulator **24** together with an appropriate amount of water **16** to produce the carbon-material-containing agglomerated ore **26**.

[0034] In the first step, if the carbon content of the obtained carbon-material-containing agglomerated ore **26** is less than a target carbon mass percent, it is preferable to include biomass, for example, in the carbon-containing raw material **6** to achieve the target carbon mass percent. In addition, the carbon-material-containing agglomerated ore **26** is preferably obtained by cold forming because it is necessary to avoid combustion and gasification of carbon. Examples of the cold forming method include a method of adding a cement-based solidification agent, for example, and then granulating the mixture with a pelletizer or a drum mixer, and a method of performing compression forming using a briquette machine, for example. In addition, it is preferable to set the carbon mass percent of each particle of the carbon-material-containing agglomerated ore to 15 mass % or less to maintain the strength after a reduction process. Herein, if the carbon mass percent of each particle of the carbon-material-containing agglomerated ore exceeds 15 mass %, the crushing strength of the agglomerated material as measured with an autograph (1 mm/min) will be less than the threshold (2.5 MPa), which is not preferable.

[Second Step]

[0035] The second step is a process of producing molten pig iron by reducing and melting the iron-containing raw material **4** contained in the carbon-material-containing agglomerated ore **26**, which has been produced in the first step, using a countercurrent reduction layer. In the example shown in FIG. **3**, an iron-containing lumpy raw material **30** containing the carbon-material-containing agglomerated ore **26** produced by the above method for producing a carbon-material-containing agglomerated ore and another raw material **28** is fed into the blast furnace **32** through its throat, and a reducing gas is flowed upward from below. Accordingly, it is possible to reduce and melt the iron-containing lumpy raw material **30** as a countercurrent moving layer with respect to the reducing gas, and thus produce the molten pig iron **36**. An oxygen-containing gas is blown into the blast furnace **32** as the blow gas **34**, so that indirect reduction proceeds with a carbon monoxide gas generated through a reaction between the carbon source and oxygen in the furnace, and also, direct reduction proceeds with a solid-state carbon source arranged in proximity to the iron-containing raw material **4**. Note that the blow gas **34** may contain hydrogen, and when hydrogen is contained, direct reduction of the iron-containing raw material **4** with hydrogen proceeds. When hydrogen is blown in, the hydrogen is preferably derived from renewable energy. Thus, with the method for producing molten pig iron according to the present embodiment, it is possible to produce molten pig iron by feeding the carbon-material-containing agglomerated ore, which has been obtained with carbon recovered from the exhaust gas **38**, into the blast furnace **32** through its throat. Therefore, the existing blast furnace **32** can be used as is without the need to modify the blast furnace **32**.

[Third Step]

[0036] The third step is a step of precipitating solid-state carbon from an exhaust gas or the like, which has been produced as a by-product of the reduction reaction in the second step, for recovery purposes. The exhaust gas **38** produced as a by-product of the reduction reaction and the exhaust gas **40** produced as a by-product of a refining step of molten iron contain carbon monoxide, carbon dioxide, hydrogen, and water. In the method for producing molten pig iron according to the present embodiment, it is acceptable as long as each of the exhaust gases **38** and **40** contains at least carbon monoxide and carbon dioxide. In the third step of the present embodiment, as shown in FIG. **1**, the exhaust gases **38** and **40** are treated in a carbonization apparatus **100**, a gas reforming furnace **110**, and a water removal device **120**. As the exhaust gas, it is also possible to use an exhaust gas discharged from an automobile, a gas turbine, an incinerator, a thermal power station, or a plant other than the foregoing gas. The volume percent of each gas component in the exhaust gas can be adjusted in accordance with the combustion conditions for a fuel that is the raw material of the exhaust gas. For example, when the exhaust gas is a blast furnace gas, the blast furnace gas contains 21 to 23 volume % of carbon monoxide gas, 19 to 22 volume % of carbon dioxide gas, 2 to 3 volume % of hydrogen, and 53 to 56 volume % of nitrogen gas, and thus is preferable. Note that such blast furnace gas is generated as coke, heavy oil, and pulverized coal fed into the blast furnace are partially combusted with air to produce a reducing gas that is composed mainly of carbon monoxide and nitrogen, and then iron ores are reduced with the reducing gas

<Gas Reforming Step>

[0037] Each of the exhaust gases **38** and **40** used in the present embodiment contains carbon monoxide, carbon dioxide, hydrogen, and water. The exhaust gases **38** and **40** are caused to fill the gas reforming furnace **110**. Next, a hydrogen gas supplied from a hydrogen supply unit is added to the gas reforming furnace **110** to form a mixed gas. An internal space of the gas reforming furnace **110** filled with the mixed gas is then heated to 800 to 1200° C. When the internal space of the gas reforming furnace is heated to a temperature in such a range, carbon dioxide in the mixed gas that is present within the gas reforming furnace undergoes a water-gas shift reaction with hydrogen in accordance with the following chemical equation (I), thereby generating carbon monoxide and water.

[Formula 1]

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (I)$$

[0038] A water-gas shift reaction between carbon dioxide and hydrogen is reversible. In a region where the reaction temperature is above 500° C., the chemical equilibrium of the water gas shift reaction shifts in the direction in which carbon monoxide is generated. Thus, in the method for producing molten pig iron of the present embodiment, setting the temperature in the gas reforming furnace **110** to 800 to 1200° C. can efficiently convert carbon dioxide into carbon monoxide, and thus generate carbon monoxide as a raw material of solid-state carbon. That is, in the gas reforming step, setting the temperature in the gas reforming furnace **110** to 800 to 1200° C. can efficiently reform the mixed gas.

[0039] The water-gas shift reaction that proceeds in the gas reforming furnace **110** is a reaction between carbon

dioxide contained in the mixed gas, hydrogen contained in the mixed gas, and hydrogen in the hydrogen gas supplied from the hydrogen supply unit. Herein, it is preferable to supply hydrogen from the hydrogen supply unit so that the hydrogen concentration in the mixed gas (with reference to the gas composition excluding a nitrogen gas and an inert gas) becomes 58 volume % or more. If the hydrogen concentration in the mixed gas is 58 volume % or more, it is possible to increase the proportion of carbon monoxide in a water-gas shift reaction, and also recover solid-state carbon in the following carbon separation step, which is preferable. A hydrogen concentration of 58 volume % or more in the mixed gas has been determined by taking into consideration the conditions under which a carbon monoxide gas would increase through a water-gas shift reaction in the temperature range of 800 to 1200° C. The conditions under which a carbon monoxide gas would increase can be determined based on the relationship between the temperature of the water-gas shift reaction and an equilibrium constant. Note that the upper limit of the hydrogen concentration in the mixed gas may be less than 100 volume %, and the upper limit of the hydrogen concentration in the mixed gas may be determined in accordance with the carbon dioxide concentration.

[0040] As the hydrogen gas supplied from the hydrogen supply unit disposed outside of the gas reforming furnace **110**, a hydrogen gas derived from renewable energy is preferably used. This can further reduce carbon dioxide emissions, which is preferable. Note that the amount of the hydrogen gas supplied from the hydrogen supply unit can be set by taking into consideration the amount of hydrogen contained in the exhaust gases **38** and **40**.

<Step of Removing Water from Carbon-Containing Gas>

[0041] The reformed gas after the water-gas shift reaction of the mixed gas is supplied to the water removal device **120**. The reformed gas contains water (water vapor) generated through the water-gas shift reaction. The water contained in the reformed gas is removed while passing through the water removal device **120**. The removal of the water herein can be effected by a method of passing the reformed gas containing the water through a layer filled with an adsorbent in the water removal device **120**, or a method of passing the reformed gas through a separating film, for example. The reformed gas preferably has the water removed therefrom so as to satisfy the relationship of the following expression (1). By removing water from the reformed gas so as to satisfy the relationship of the expression (1), carbon recovery efficiency in the carbon recovery step is increased. In the expression (1) below, $[H_2O]$ represents the water concentration (volume %) in the reformed gas, and $[H_2]$ represents the hydrogen concentration (volume %) in the reformed gas.

[Math. 2]

$$[H_2O]/([H_2O]+[H_2])<0.1 \quad (1)$$

[0042] An adsorbent or a separating film can be used to remove the water from the reformed gas, as described above. As the adsorbent, oxide, such as silica, zeolite, or alumina; calcium chloride; magnesium sulfate; and so on can be used. Examples of the separating film for water in the gas include a carbon film, a resin film, and an inorganic film. Such films have pores with a diameter on the order of subnanometers. The water in the gas is recovered as liquid water at room temperature by the water removal device **120**.

[0043] The dehumidified gas with the water removed therefrom becomes a raw material of solid-state carbon. The solid-state carbon is separated from the carbon monoxide in the carbonization apparatus **100** by a bimolecular decomposition reaction (II) that occurs when two carbon monoxide molecules are decomposed as represented by the following chemical equation (II), or by a monomolecular decomposition reaction (III) that occurs when one carbon monoxide molecule reacts with hydrogen, as represented by the following chemical equation (III).

[Formula 2]

$$2CO \rightarrow C+CO \quad (II)$$

[Formula 3]

$$CO+H_2 \rightarrow C+H_2O \quad (III)$$

[0044] The carbon monoxide contained in the dehumidified gas preferably satisfies $CO/(CO+CO_2)$ of 0.5 or more, more preferably 0.7 or more. Thus, solid-state carbon can be efficiently recovered from the carbon monoxide.

[0045] The dehumidified gas is supplied to a carbon separating unit in the carbonization apparatus **100**, which includes a porous material, at a predetermined supply rate.

<Step of Bringing Carbon-Containing Gas into Contact with Porous Material to Separate Solid-State Carbon>

[0046] A method for recovering carbon from the dehumidified gas includes a step of bringing the dehumidified gas into contact with the porous material to separate solid-state carbon. Bringing the dehumidified gas into contact with the porous material and separating carbon from the dehumidified gas are performed within the carbon separating unit in the carbonization apparatus **100**. A filled layer filled with a porous material **102** is provided in the carbon separating unit in the carbonization apparatus **100** as shown in an example of FIG. **4**.

[0047] As shown in FIG. **1**, the carbon that constitutes the carbon monoxide contained in the dehumidified gas is separated from the carbon monoxide gas in the carbonization apparatus **100**. The carbon monoxide contained in the dehumidified gas is separated as a solid-state carbon by the bimolecular decomposition reaction (II) of the carbon monoxide as represented by the above chemical equation (II), or through the monomolecular decomposition reaction (III) of the carbon monoxide as represented by the above chemical equation (III). The solid-state carbon separated from the carbon monoxide is adsorbed on the surface of the porous material **102** to be precipitated. An off-gas, which results from the contact between the dehumidified gas and the porous material **102** and thus has carbon separated therefrom, is discharged from the carbonization apparatus **100**. The off-gas contains carbon dioxide, and it is therefore preferable to mix all or part of the off-gas with the mixed gas.

[0048] In the step of bringing the dehumidified gas into contact with the porous material **102** to separate solid-state carbon, the contact between the dehumidified gas and the porous material **102** is preferably effected under an atmosphere in the temperature range of 500 to 800° C. The temperature at which the reformed gas is brought into

contact with the porous material **102** is preferably 500° C. or higher because the decomposition reaction of the carbon monoxide is promoted, while the temperature is preferably 800° C. or lower because thermal energy generated by the decomposition reaction of the carbon monoxide can be effectively utilized. The temperature at which the reformed gas is brought into contact with the porous material **102** is within the range of 500 to 800° C. which corresponds to the temperature condition adopted for a direct-reduction iron-making reaction. Note that the contact between the dehumidified gas and the porous material may be effected by passing the dehumidified gas through the layer filled with the porous material **102** provided within the carbon separating unit. Accordingly, a decomposition reaction of carbon monoxide represented by the above chemical equation proceeds. As the decomposition reaction of carbon monoxide proceeds, the solid-state carbon that constitutes the carbon monoxide is precipitated on the surface of the porous material **102**. When a porous iron material is used, solid-state carbon precipitated on its surface partially or entirely causes carburizing to form iron carbide.

[0049] In the step of bringing the dehumidified gas into contact with the porous material **102** and separating solid-state carbon, the contact between the dehumidified gas and the porous material **102** is preferably effected under an atmosphere where the pressure of the dehumidified gas is 1.0 to 10 atm. The pressure of 1.0 atm or more at which the dehumidified gas is brought into contact with the porous material **102** corresponds to the pressurization condition, and allows the equilibrium of a decomposition reaction of the carbon monoxide to shift rightward, thus promoting the decomposition reaction of the carbon monoxide, which is preferable. The pressure of 10 atm or less can ensure the safety of the carbon separating unit of the carbonization apparatus **100** with respect to the legal restraints, which is preferable.

[0050] The open porosity, as measured by the Archimedes' method, of the porous material **102** with which the dehumidified gas is brought into contact is preferably 50 to 99%, more preferably 80 to 95%. When the open porosity of the porous material is 50% or more, the dehumidified gas passes through the pores of the porous material to promote the decomposition reaction of the carbon monoxide and also absorb the decomposed carbon, which is preferable. Meanwhile, when the open porosity of the porous material **102** is 99% or less, the thermal shock resistance to the dehumidified gas supplied to the porous material **102** can be maintained, which is preferable. The pore diameter of the porous material **102** is preferably 10 μm or more. Note that the open porosity of the porous material **102** is measured by the Archimedes' method. Specifically, a value measured by a measurement method defined by the Japanese Industrial Standards (JIS R2205; 1992) can be used as the open porosity of the porous material.

[0051] The porous material **102** with which the dehumidified gas is brought into contact preferably contains at least one element selected from the group consisting of iron, platinum, nickel, cobalt, rhodium, and palladium. That is, the porous material may contain one metal element selected from the group consisting of iron, platinum, nickel, cobalt, rhodium, and palladium, or a combination of two or more of such metal elements. Further, the porous material may be a metal compound containing one metal element selected from the group consisting of iron, platinum, nickel, cobalt, rhodium, and palladium as carbide, oxide, carbonate, sulfate, or the like.

[0052] Among such metals adopted as the porous material **102** with which the dehumidified gas is brought into contact, iron, platinum, and nickel are preferable. When platinum or nickel is used as the porous material, each element functions as a decomposition reaction catalyst for the carbon monoxide, and the catalyst would undergo little deterioration, which is preferable. In addition, when platinum or nickel is used as the porous material **102**, solid-state carbon generated by a decomposition reaction of the carbon monoxide is precipitated as graphite alone, which is preferable.

[0053] The porous material **102** with which the dehumidified gas is brought into contact is more preferably iron. The use of iron as the porous material **102** causes the porous material **102** to be carburized by carbon generated by the decomposition reaction of the carbon monoxide to thus obtain austenite (i.e., Y iron) with the carbon being dissolved as a solid-solution. The use of iron as the porous material **102** also causes the porous material **102** to be carburized by carbon generated by the decomposition reaction of the carbon monoxide to obtain cementite (i.e., iron carbide (Fe_3C)) through a reaction between the carbon and the iron, which is preferable. Austenite and cementite resulting from the carburizing of the porous material **102** by carbon generated by a decomposition reaction of carbon monoxide have almost the same hardness as quenching steel and thus can be directly used as iron-making raw materials. Further, the porous material **102** with which the dehumidified gas is brought into contact is preferably one or more types of iron selected from iron oxide and reduced iron.

[0054] The porous material **102** with which the dehumidified gas is brought into contact is particularly preferably an iron whisker. An iron whisker is a crystal that grows on the surface of a crystal in an outward direction like a beard and is formed such that, when compression stress is generated around the surface of the crystal, a new crystal grows on the original crystal in an outward direction in an attempt to relax the stress. Since such an iron whisker has a small start point of crystal growth and tends to keep growing continuously, it is formed as a single crystal in the shape of an extremely long and thin beard and has a length of 1 mm or more relative to a diameter of about 1 μm. When an iron whisker is adopted as the porous material with which the dehumidified gas is brought into contact, it is possible to allow the iron whisker to be carburized by the carbon generated by a decomposition reaction of carbon monoxide, thereby obtaining a whisker formed of austenite or formed of cementite.

[0055] The iron whisker as the porous material **102** with which the dehumidified gas is brought into contact can be produced by a method of producing an iron whisker described in Non Patent Literature 2, for example. According to the method of producing an iron whisker, it is possible to obtain an iron whisker as a porous material with an open porosity of 90% or more and a pore diameter of 10 μm or more. The iron whisker obtained by the method of producing an iron whisker also has a high open porosity and thus can be preferably used as the porous material **102** used for a carbon recovery method. It should be noted that even when a metal other than iron is used as the metal for forming the porous material **102** with which the dehumidified gas is brought into contact, the porous material **102** can be produced in the same manner.

<Step of Recovering Carbon Adsorbed on Porous Material>

[0056] The carbon adsorbed on the porous material **102** is recovered within a carbon recovery unit **130**. Herein, "recovering the carbon adsorbed on the porous material" includes recovering the solid-state carbon precipitated on the surface of the porous material **102** or recovering the carbon causing carburizing inside of the porous material as a solid solution or a metal carbide compound of the carbon and the metal element contained in the porous material.

[0057] The carbon obtained by the decomposition reaction of the carbon monoxide contained in the dehumidified gas is precipitated on the surface of the porous material **102**. The carbon obtained by the decomposition reaction of the carbon monoxide contained in the dehumidified gas also causes carburizing inside of the porous material **102** and reacts with the metal element forming the porous material, thereby forming a carbon solid solution or a metal carbide compound. Further, the carbon obtained by a decomposition reaction of the carbon monoxide contained in the dehumidified gas is precipitated on the surface of the carbon solid solution or the metal carbide compound.

[0058] The carbon precipitated on the surface of the porous material **102** can be recovered by subjecting the porous material **102** containing the carbon to an operation of separating powder and granular materials using a sieve mesh, for example. In addition, to recover the carbon that has become a carbon solid solution or a metal carbide compound by reacting with the metal element forming the porous material after carburizing the inside of the porous material **102**, it is possible to directly recover the carbon solid solution or the metal carbide compound. It should be noted that when the recovered carbon is to be used as an iron-making raw material, using iron as the porous material **102** can collectively use them as the iron-making raw material, which is preferable, without performing an operation of separating the recovered carbon from the porous material **102**.

[0059] As described above, in the third step according to the present embodiment, bringing the carbon monoxide contained in the dehumidified gas into contact with the porous material **102** can promote the decomposition reaction of the carbon monoxide and separate solid-state carbon, recovering the carbon as the solid-state carbon, or as a carbon solid solution or a carbon metal compound containing the carbon. In addition, since molten pig iron can be produced by using, as a raw material, the carbon-material-containing agglomerated ore obtained with the recovered carbon, the recovered carbon can be circulated through a process, reducing CO_2 emissions to the outside of the system. The exhaust gases **38** and **40**, the mixed gas, and the dehumidified gas of the present embodiment are examples of a carbon-containing gas containing carbon monoxide and carbon dioxide.

[0060] Although the present embodiment describes an example in which the second step is performed with the blast furnace **32**, the present invention is not limited thereto. For example, molten pig iron may be produced by performing a reduction step of heating the carbon-material-containing agglomerated ore to 1160 to 1450° C. using a rotary hearth furnace, instead of the blast furnace **32**, to reduce and melt them, and then cooling them to obtain reduced iron, and a melting step of melting the reduced iron using an electric furnace, for example. Even when a rotary hearth furnace is used, it is possible to use the existing rotary hearth furnace as is as long as the carbon-material-containing agglomerated ore obtained with the recovered carbon is used.

[0061] FIG. **4**(*a*) shows an example of a carbonization apparatus according to the present embodiment. As shown in the example of FIG. **4**(*a*), the carbonization apparatus **100** includes a tubular reaction tower **101** in which a carbon separation reaction from carbon monoxide contained in a carbon-containing gas occurs, a supply pipe **104** for supplying a carbon-containing gas from a lower portion of the reaction tower **101**, a layer of the porous material **102** provided in the reaction tower, and an exhaust gas pipe **105** for discharging an off-gas generated after the carbon separation reaction. The reaction tower **101** contains a silica tube **101***a* and a sample holder **101***b*. As the porous material **102** equipped in the carbonization apparatus **100**, it is preferable to use a plurality of materials as shown in FIG. **4**(*b*) each made by forming iron whiskers having an open porosity of 97.7% into a tablet shape. The porous material **102** is disposed on a layer of granular alumina balls **103** (with a particle size of 10 mm). Note that the porous material **102** is produced in accordance with the method of producing an iron whisker described in Non Patent Literature 2.

EXAMPLE

[0062] The influence of the carbon recovered by the device shown in FIG. **4**(*a*) on the reducibility of iron ores was investigated. Table I shows the ingredient compositions of the iron ores used. "T·Fe" in Table I represents the total iron content. "LOI" represents the loss on ignition when the iron ores are heated to 1000° C. for 60 minutes, most of which is crystal water in the case of iron ores. The recovered carbon was found to contain C: 38.35 mass % as cementite and solid-state carbon, with the balance being Fe. Of the entire portion of carbon, the content of C existing as the cementite was found to be 18.7 mol %, and the content of C existing as the solid-state carbon was found to be 81.3 mol %.

TABLE 1

	Ingredient composition [mass %]			LOI
	T. Fe	SiO_2	Al_2O_3	mass %
Iron ore A	57.16	5.51	2.54	10.13

[0063] The particle size of iron ore A and the particle size of the recovered carbon were each set to −105 μm. "−105 μm" herein represents the particle size of the iron ore A that has passed through a sieve with a mesh size of 105 μm. A sample was obtained by mixing the iron ore A and the weighed powder of the recovered carbon in a mortar without pressing a pestle against each other for 3 minutes. Thus, uniform mixed powder was formed without changing the particle size during mixing. To the sample, carbon was added in an amount of 0.8 times the oxygen molar content in the iron oxide, and further added in an amount of 0.2 times the iron molar content in the iron oxide or the iron carbide, and then, the sample was mixed. By adding carbon in an amount of 0.8 times the oxygen molar content in the iron oxide, the carbon was used as a reducing material, and by adding carbon in an amount of 0.2 times the iron molar content in the iron oxide or the iron carbide, the effect of carburizing the metallic iron was attempted to be achieved.

That is, carbon was provided with two functions that are a reducing material and a carburizing material.

[0064] The uniformly mixed sample was press-formed with an applied pressure of 98 MPa for 30 seconds into a cylindrical shape with a diameter of 10 mm and a height of 10 mm. The formed sample was heated to 1300° C. at a heating rate of 10° C./min in an atmosphere where 5 volume % of N_2—Ar mixed gas was supplied at a flow rate of 0.5 NL/min. The generated gas was analyzed with an infrared spectrophotometer to calculate the reduction rate of the iron ores. FIG. **5** shows the results. FIG. **5** also shows the results of a similar test conducted using carbon black instead of the recovered carbon as a comparative example. As is obvious from FIG. **5**, the recovered carbon (indicated by a solid line) increases the reducibility of the iron ore A more than the carbon black (indicated by a broken line).

[0065] Although the reason for the above is not clear, the inventors consider it due to the difference in the particle size of the carbon-containing materials. Specifically, the recovered carbon is in the form of fibers of about several nm as shown in FIGS. **6**(*a*) and **6**(*b*), while the carbon black contains particles with a particle size of about several ten μm as shown in FIG. **7**. As described above, since solid-state carbon recovered from carbon monoxide is extremely small, it is considered that using such carbon for the carbon-material-containing agglomerated ore can increase the contact area with an iron-containing raw material and a gas, and thus obtain the carbon-material-containing agglomerated ore with high reducibility.

INDUSTRIAL APPLICABILITY

[0066] The method for producing molten pig iron according to the present invention has the effect of reducing CO_2 emissions to the outside of the system. In addition, the method can, by recovering CO_2 from an exhaust gas as solid-state carbon, and producing a carbon-material-containing agglomerated ore by combining the recovered solid-state carbon with an iron-containing raw material, increase the reducibility of the agglomerated ores. This can reduce the unit consumption of carbon required for reduction and contribute to reducing environmental burdens in the steel industry. Thus, the present invention is industrially quite advantageous.

REFERENCE SIGNS LIST

[0067] **2**, **8** storage tank
[0068] **4** iron-containing raw material
[0069] **6** carbon-containing raw material (i.e., solid-state carbon and/or iron carbide)
[0070] **10** cement powder
[0071] **12**, **22** conveyor
[0072] **14** kneader
[0073] **16** water
[0074] **20** mixed powder
[0075] **24** granulator
[0076] **26** carbon-material-containing agglomerated ore
[0077] **28** another raw material
[0078] **30** iron-containing lumpy raw material
[0079] **32** blast furnace
[0080] **34** blow gas
[0081] **36** molten pig iron
[0082] **38** blast furnace exhaust gas
[0083] **40** exhaust gas of refining process
[0084] **100** carbonization apparatus (i.e., carbon separating unit)
[0085] **101** reaction tower
[0086] **101***a* silica tube
[0087] **101***b* sample holder
[0088] **102** porous material (i.e., iron whisker)
[0089] **103** alumina ball
[0090] **104** supply pipe (for carbon-containing gas)
[0091] **105** exhaust gas pipe
[0092] **110** gas reforming furnace (i.e., gas reforming unit)
[0093] **120** water removal device (i.e., water removal unit)
[0094] **130** carbon recovery unit
[0095] **140** facility for producing carbon-material-containing agglomerated ore

1. A method for producing molten pig iron, comprising:
a first step of producing a carbon-material-containing agglomerated ore from an iron-containing raw material and a carbon-containing raw material;
a second step of blowing an oxygen-containing gas into the carbon-material-containing agglomerated ore to reduce and melt the carbon-material-containing agglomerated ore, thereby producing molten pig iron; and
a third step of bringing a carbon-containing gas containing carbon monoxide and carbon dioxide produced as a by-product of the reduction into contact with a porous material, thereby recovering carbon,
characterized in that:
in the first step, the carbon recovered in the third step is used for a part of or an entirety of the carbon-containing raw material.

2. The method for producing molten pig iron according to claim **1**, comprising, instead of the second step:
a reduction step of obtaining reduced iron in which the carbon-material-containing agglomerated ore is heated to 1160 to 1450° C., reduced, melted, and then cooled, and
a melting step of producing molten pig iron in which the reduced iron is melted.

3. The method for producing molten pig iron according to claim **1**, wherein in the third step, the carbon-containing gas further contains a gas containing carbon monoxide and carbon dioxide produced as a by-product of a refining step of molten iron.

4. The method for producing molten pig iron according to claim **1**, further comprising, before bringing the carbon-containing gas into contact with the porous material in the third step, supplying hydrogen to the carbon-containing gas and heating the carbon-containing gas to 800 to 1200° C. to convert the carbon dioxide contained in the carbon-containing gas to carbon monoxide.

5. The method for producing molten pig iron according to claim **4**, further comprising, after heating the carbon-containing gas but before bringing the carbon-containing gas into contact with the porous material in the third step, removing water contained in the carbon-containing gas.

6. The method for producing molten pig iron according to claim **5**, comprising removing water contained in the carbon-containing gas and water generated through a reforming reaction of the carbon-containing gas so as to satisfy the following expression (1):

[Math. 1]

$$[H_2O]/([H_2O]+[H_2])<0.1 \quad (1)$$

where $[H_2O]$ represents a water concentration (volume %) in a reformed mixed gas, and $[H_2]$ represents a hydrogen concentration (volume %) in the reformed mixed gas.

7. The method for producing molten pig iron according to claim **1**, wherein in the third step, the porous material is iron, and a part of the recovered carbon is iron carbide.

8. The method for producing molten pig iron according to claim **1**, wherein a particle size of the carbon-containing raw material is 100 μm or less.

9. The method for producing molten pig iron according to claim **1**, wherein in the first step, the carbon-containing raw material further contains biomass.

10. The method for producing molten pig iron according to claim **1**,

wherein:

the iron-containing raw material is iron ores, and

the method further comprises a pretreatment step of subjecting the iron ores to heat treatment in a temperature range of 300° C. to 1000° C. before the first step.

11. The method for producing molten pig iron according to claim **2**, wherein in the third step, the carbon-containing gas further contains a gas containing carbon monoxide and carbon dioxide produced as a by-product of a refining step of molten iron.

12. The method for producing molten pig iron according to claim **2**, further comprising, before bringing the carbon-containing gas into contact with the porous material in the third step, supplying hydrogen to the carbon-containing gas and heating the carbon-containing gas to 800 to 1200° C. to convert the carbon dioxide contained in the carbon-containing gas to carbon monoxide.

13. The method for producing molten pig iron according to claim **3**, further comprising, before bringing the carbon-containing gas into contact with the porous material in the third step, supplying hydrogen to the carbon-containing gas and heating the carbon-containing gas to 800 to 1200° C. to convert the carbon dioxide contained in the carbon-containing gas to carbon monoxide.

14. The method for producing molten pig iron according to claim **11**, further comprising, before bringing the carbon-containing gas into contact with the porous material in the third step, supplying hydrogen to the carbon-containing gas and heating the carbon-containing gas to 800 to 1200° C. to convert the carbon dioxide contained in the carbon-containing gas to carbon monoxide.

15. The method for producing molten pig iron according to claim **12**, further comprising, after heating the carbon-containing gas but before bringing the carbon-containing gas into contact with the porous material in the third step, removing water contained in the carbon-containing gas.

16. The method for producing molten pig iron according to claim **13**, further comprising, after heating the carbon-containing gas but before bringing the carbon-containing gas into contact with the porous material in the third step, removing water contained in the carbon-containing gas.

17. The method for producing molten pig iron according to claim **14**, further comprising, after heating the carbon-containing gas but before bringing the carbon-containing gas into contact with the porous material in the third step, removing water contained in the carbon-containing gas.

18. A method for producing molten pig iron according to claim **15**, comprising removing water contained in the carbon-containing gas and water generated through a reforming reaction of the carbon-containing gas so as to satisfy the following Expression (1):

[Math. 1]

$$[H_2O]/([H_2O]+[H_2])<0.1 \quad (1)$$

where $[H_2O]$ represents a water concentration (volume %) in a reformed mixed gas, and $[H_2]$ represents a hydrogen concentration (volume %) in the reformed mixed gas.

19. A method for producing molten pig iron according to claim **16**, comprising removing water contained in the carbon-containing gas and water generated through a reforming reaction of the carbon-containing gas so as to satisfy the following Expression (1):

[Math. 1]

$$[H_2O]/([H_2O]+[H_2])<0.1 \quad (1)$$

where $[H_2O]$ represents a water concentration (volume %) in a reformed mixed gas, and $[H_2]$ represents a hydrogen concentration (volume %) in the reformed mixed gas.

20. A method for producing molten pig iron according to claim **17**, comprising removing water contained in the carbon-containing gas and water generated through a reforming reaction of the carbon-containing gas so as to satisfy the following Expression (1):

[Math. 1]

$$[H_2O]/([H_2O]+[H_2])<0.1 \quad (1)$$

where $[H_2O]$ represents a water concentration (volume %) in a reformed mixed gas, and $[H_2]$ represents a hydrogen concentration (volume %) in the reformed mixed gas.

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