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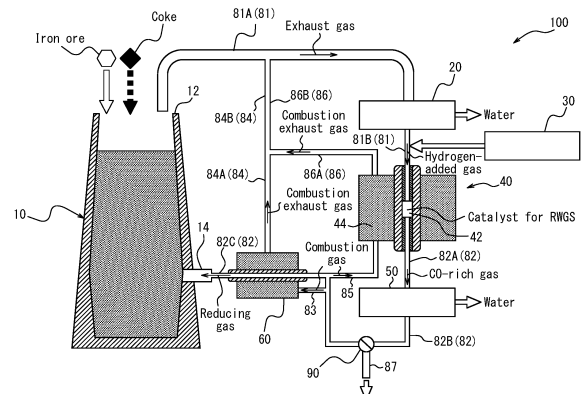
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(54) **CIRCULATING REDUCTION SYSTEM, IRON ORE REDUCTION METHOD, AND BLAST FURNACE OPERATION METHOD**

(57) Provided is a circulating reduction system capable of efficiently recycling, as reducing gas, CO-rich gas obtained by reforming exhaust gas containing CO₂ generated in a reduction furnace. In the circulating reduction system 100, exhaust gas containing CO₂ generated in the reduction furnace 10 is recovered via first piping 81, and hydrogen gas is added to the exhaust gas from a hydrogen gas supply apparatus 30 to obtain hydrogen-added gas. CO₂ in the hydrogen-added gas is converted to CO by the reverse water-gas shift reaction in a catalytic apparatus 40, resulting in a CO-rich gas. The CO-rich gas is supplied to the inside of the reduction furnace 10 as reducing gas via second piping 82. No separation apparatus is disposed at any point along the first piping 81 nor the second piping 82 to separate and either recover or remove a specific gas component other than water vapor from gas passing through the first piping or gas passing through the second piping.

FIG. 1



Description

TECHNICAL FIELD

- 5 **[0001]** The present disclosure relates to a circulating reduction system, an iron ore reduction method, and a smelting furnace operation method that can drastically reduce CO₂ emissions, which contribute to global warming.

BACKGROUND

- 10 **[0002]** Amid global calls to reduce CO₂ emissions, which contribute to global warming, the iron and steel industry in Japan, which accounts for around 15 % of the country's CO₂ emissions, has declared that it will be carbon neutral by 2050 in response to government policy. To achieve this, it is necessary to develop an iron ore reduction process and reduction furnace that will enable crude steel production similar to current levels at a low cost, but at present there is little prospect of this being technologically feasible.

- 15 **[0003]** Here, the hydrogen reduction process, in which hydrogen is used as a reductant for iron ore, has attracted worldwide attention as an ideal crude steel production technology that does not generate CO₂. However, to maintain domestic production of approximately 75 million tonnes of hot metal per year using this method would require approximately 75 billion Nm³ of hydrogen. To cover this amount with the water electrolysis method, a typical green hydrogen production method, some estimate that as much as 0.34 trillion kWh of electricity would be required annually, even when all
20 electricity required for hydrogen transportation, liquefaction, storage, and the like is ignored. Even if the issue of high power costs could be overcome, it would be extremely unrealistic to procure this much power for domestic blast furnace manufacturers in Japan, where annual power consumption is on the order of 1 trillion kWh.

- [0004]** Meanwhile, various attempts are underway to procure large quantities of hydrogen produced from inexpensive renewable energy sources from overseas. However, even if the issue of high transportation costs could be overcome,
25 there is no clear technical prospect for safely storing large quantities of hydrogen, which has a wide explosive concentration range, in the vicinity of steelworks.

- [0005]** The domestic iron and steel industry emitting around 15 % of the country's CO₂ emissions is because it produces high-grade steel material mainly using the blast furnace-converter steelmaking process, which uses coke to reduce iron ore. Crude steel production methods are mainly classified into the blast furnace-converter steelmaking process and the
30 electric furnace steelmaking process, with the blast furnace-converter steelmaking process generating approximately 2 t of CO₂ per 1 t of steel material and the electric furnace steelmaking process generating approximately 0.5 t of CO₂ per 1 t of steel material. The electric furnace steelmaking process is superior in terms of suppressing the amount of CO₂ generated. However, high-grade steel material used for automobiles and other applications is not mass-produced in the electric furnace steelmaking process, which uses scrap as raw material, because impurities such as copper tend to adversely
35 affect quality. As a result, about 75 % of crude steel in Japan is produced by the blast furnace-converter steelmaking process.

- [0006]** For blast furnaces, where CO₂ emissions are particularly high, attempts have been made to decrease the amount of coke used. For example, Patent Literature (PTL) 1 describes substituting the hot air blown in through the tuyere with a reducing gas such as hydrogen, methane, or the like. However, in addition to its role as a reductant, coke has two other
40 roles: as a heating material that heats the furnace interior via reaction with oxygen blown in from the hot air oven, and as a gas permeable material that secures gas permeability in the furnace. Therefore, it is extremely difficult to drastically curb the use of coke until new means (other than coke) are found to maintain furnace temperatures and to secure gas permeability without adversely affecting hot metal quality.

- [0007]** Against this background, Japanese steelmakers have no choice but to get by for the time being by decreasing the
45 number of blast furnaces in operation and increasing the ratio of electric furnaces. As a result, demand for scrap for use in electric furnaces is already strong, and the fierce competition for procurement of such scrap is expected to become even more intense in the future.

- [0008]** Under these circumstances, the direct reduction process, which emits less CO₂ than the blast furnace-converter steelmaking process, is attracting worldwide attention. In the so-called Midrex process, a representative direct reduction
50 process, iron ore is reduced in solid phase by modified natural gas to obtain direct reduced iron (DRI) (see PTL 2). The early Midrex process could only produce sponge-like DRI, and therefore from the viewpoint of oxidation and ignition, handling and transportation had been difficult. However, since the development and industrialization of hot briquetting apparatus, those problems have been largely eliminated, and there is a growing global trend toward mixing DRI with scrap and feeding the mix into electric furnaces to decrease the amount of scrap fed and improve steel material quality. Further, attempts
55 have been made to substitute natural gas with methane synthesized from CO₂ and hydrogen using the methanation reaction ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$), or with hydrogen itself.

- [0009]** On the other hand, in the direct reduction process, which is a solid-phase reduction process, in order to maintain the grade of DRI produced, it is necessary to use high-grade iron ore as raw material, which has cost and procurement

constraints. This is a major disadvantage compared to a conventional blast furnace method, which allows approximately 85 % of the iron ore material to be pellets or sintered ore produced from low-grade powdered ore or fine ore.

[0010] Further, crude steel cannot be extracted in the form of hot metal in the direct reduction process, and therefore refining facilities such as pretreatment furnaces and converters used for conventional integrated steelmaking processes cannot be used. This is another factor contributing to Japanese blast furnace manufacturer attachment to the blast furnace process. The reason why the direct reduction process remains limited to solid-phase reduction is presumably because, as mentioned above, the problems of gas permeability and maintaining the furnace temperature required to obtain hot metal have not been fundamentally resolved.

[0011] That is, there is no clear prospect of drastically reducing coke used in the blast furnace-converter steelmaking process, mainly because of the stumbling blocks of a lack of a reductant and heating material that can replace coke and a lack of a new means to secure gas permeability without adversely affecting hot metal quality. Further, the direct reduction process, which emits less CO₂ than the blast furnace-converter steelmaking process, has the disadvantage of not being able to use low-grade powdered ore or fine ore that are low cost, easy to procure, and can be used in blast furnaces, and the disadvantage that conventional refining facilities for integrated iron and steelmaking processes cannot be used, because crude steel cannot be extracted as hot metal.

[0012] Against this background, PTL 3 proposes technology to utilize CO₂ contained in the exhaust gas from a blast furnace. That is, a proposal to separate CO₂ from blast furnace exhaust gas, reform the recovered CO₂ into CO, and reuse the CO as a reductant for the blast furnace.

CITATION LIST

Patent Literature

[0013]

PTL 1: WO 2021/220555 A1

PTL 2: JP 2017-088912 A

PTL 3: JP 2011-225968 A

SUMMARY

(Technical Problem)

[0014] In the technology described in PTL 3, the CO₂ separated and recovered from the exhaust gas generated in the blast furnace is reformed into CO and reused, resulting in a decrease in the amount of CO₂ generated. However, this technology involves multiple processes, where CO₂ is separated and recovered from the exhaust gas and CO₂ is reformed, and is therefore not free from the burden of lowered circulation efficiency of reduction components in the exhaust gas and the cost of equipment, operation, and maintenance for each process. Therefore, there has been a demand for a more efficient method to recycle the reduction components in the exhaust gas from blast furnaces and other reduction furnaces.

[0015] In view of the above issues, it would be helpful to provide a circulating reduction system capable of efficiently recycling, as reducing gas, CO-rich gas obtained by reforming exhaust gas containing CO₂ generated in a reduction furnace.

[0016] Further, it would be helpful to provide an iron ore reduction method of reducing iron ore by efficiently recycling, as reducing gas, CO-rich gas obtained by reforming exhaust gas containing CO₂ generated in a reduction furnace.

[0017] Further, it would be helpful to provide a method of operating a smelting furnace capable of maintaining furnace temperature and securing gas permeability by a means other than coke by using the circulating reduction system.

(Solution to Problem)

[0018] The inventors conducted extensive research into ways of realizing an efficient reduction process in which exhaust gas from a reduction furnace can be circulated as a starting material of a reductant, and have found that the so-called reverse water-gas shift reaction can be used to efficiently recycle the exhaust gas.

[0019] That is, the exhaust gas generated in the iron ore reduction process typically contains excess reductants such as CO and H₂ in addition to CO₂ and air-derived nitrogen. For example, the exhaust gas from a blast furnace contains around 23 vol% of CO₂, the same percentage of CO, around 4 vol% of H₂, and around 50 vol% of air-derived nitrogen. The inventors added hydrogen to such exhaust gas and brought this gas into contact with a catalyst for the reverse water-gas shift reaction (RWGS: CO₂ + H₂ → CO + H₂O) to significantly convert the balance of CO₂ and CO in the exhaust gas to be

CO-rich, after which the gas is recycled as a reducing gas together with H₂ and nitrogen originally contained in the exhaust gas. The inventors found that when this recycling can be achieved, the input of conventionally-used reductants derived from fossil fuels, such as coke, may be minimized.

[0020] Here, CO is recycled as the main reductant because CO is the most efficient reductant that can maintain high temperatures in a reduction furnace, since the reduction of iron ore by CO is an exothermic reaction while the reduction of iron ore by H₂ is an endothermic reaction. Further, in reduction by CO, a solidification point depression of iron due to carbon that occurs when coke is used as a reductant can be used as is. This allows reduced iron, which does not melt until 1500 °C or greater in the case of reduction by H₂, to melt at around 1200 °C in the case of reduction by CO. This temperature difference of about 300 °C greatly reduces the heat load of the reducing gas heating furnace when the reduced iron is extracted as hot metal.

[0021] Further, although the CO-rich reducing gas synthesized from CO₂-rich exhaust gas is mainly fed to the reduction furnace, surplus can be discharged and recovered for various uses. In addition to use as a reductant and fuel gas, CO is the starting material for the Fischer-Tropsch reaction ($n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$), which is important for synthesizing various organic substances. Therefore, CO-rich reducing gas synthesized from CO₂-rich exhaust gas is not only a reductant, but also a synthesis gas that can be converted into fuel gas and raw material for various organic compounds. In particular, when the use of fossil fuels is drastically reduced to prevent global warming, the organic chemical industry, which has been using fossil fuels as raw materials, will have to find new sources of raw materials. These industries becoming recipients of the synthesis gas described above is of great significance.

[0022] As already mentioned, coke charged into a typical blast furnace serves as a heating and gas permeable material in addition to the role as a reductant. Therefore, when reduced iron is extracted as hot metal, even when the furnace temperature can be maintained by reduction heat of CO in the reducing gas, when coke input is suppressed to the limit, gas permeability cannot be maintained (that is, a stable reduction environment cannot be maintained).

[0023] The inventors also newly discovered that this problem can be solved by slowly cooling in a mold then crushing some of the molten slag that is generated with the hot metal and discharged from the furnace bottom, mixing the crushed slag with coke as a gas permeable material, and re-charging from the furnace top. The melting point of blast-furnace slag is about 1400 °C, and therefore the slag remains solid-state and serves as a gas permeable material even when the iron having a solidification point depression due to carbon begins to melt in the blast furnace. Further, the slag is a material originating in the smelting furnace, and therefore recycling does not change the material environment in the smelting furnace.

[0024] Starting up a smelting furnace operation using only slowly cooled and crushed slag as gas permeable material and only reducing gas as reductant is not easy. Therefore, the smelting furnace is first started up in "blast furnace mode", in which coke, a reductant and gas permeable material, and a source of iron are alternately layered in the blast furnace, and then hot air heated by a hot air oven is blown in, as in a typical blast furnace. Subsequently, the system is gradually switched to "coke-less mode", in which slag is gradually mixed into the coke and reducing gas is gradually added to the air blown into the smelting furnace. When the smelting furnace is to be shut down, it is easy to restart the blast furnace if the operation is finished in the blast furnace mode after the coke-less mode by the reverse procedure.

[0025] The present disclosure is based on these findings, and primary features of the present disclosure are as follows.

[1] A circulating reduction system comprising:

- a reduction furnace configured to reduce an oxide contained therein;
- first piping configured to recover from the reduction furnace exhaust gas generated in the reduction furnace that contains CO₂, wherein the exhaust gas is passed through the first piping;
- a hydrogen gas supply apparatus connected to a point along the first piping and configured to add hydrogen gas to the exhaust gas to produce hydrogen-added gas;
- a catalytic apparatus to which an end of the first piping is connected and which comprises a reaction chamber containing a catalyst for the reverse water-gas shift reaction, configured so that the hydrogen-added gas introduced into the reaction chamber from the first piping comes into contact with the catalyst to convert CO₂ in the hydrogen-added gas to CO by the reverse water-gas shift reaction to produce a CO-rich gas having an increased CO concentration; and
- second piping extending from the catalytic apparatus and connected to the reduction furnace, wherein the CO-rich gas is passed through the second piping and supplied to the inside of the reduction furnace as reducing gas, wherein no separation apparatus is disposed at any point along the first piping nor the second piping to separate and either recover or remove a specific gas component other than water vapor from gas passing through the first piping or gas passing through the second piping.

[2] The circulating reduction system according to [1], above, further comprising a gas heating apparatus disposed at a point along the second piping and configured to heat the CO-rich gas.

[3] The circulating reduction system according to [2], above, further comprising third piping that branches off from the second piping at a position upstream of the gas heating apparatus and is connected to the gas heating apparatus, wherein a portion of the CO-rich gas is supplied to the gas heating apparatus as combustion gas via the third piping.

[4] The circulating reduction system according to [2] or [3], above, further comprising fourth piping extending from the gas heating apparatus and connected to a point along the first piping, wherein combustion exhaust gas generated from the gas heating apparatus is merged with the exhaust gas in the first piping via the fourth piping.

[5] The circulating reduction system according to any one of [1] to [4], above, wherein

the catalytic apparatus further comprises a heating apparatus configured to heat the reaction chamber, and the circulating reduction system further comprises fifth piping that branches off from the second piping and is connected to the heating apparatus, wherein a portion of the CO-rich gas is supplied to the heating apparatus as combustion gas via the fifth piping.

[6] The circulating reduction system according to [5], above, further comprising sixth piping extending from the heating apparatus and connected to a point along the first piping, wherein combustion exhaust gas generated from the heating apparatus is merged with the exhaust gas in the first piping via the sixth piping.

[7] The circulating reduction system according to any one of [1] to [6], above, further comprising a first dehumidifier disposed at a point along the first piping, upstream from the site where the hydrogen gas supply apparatus is connected, and configured to remove water vapor from the exhaust gas.

[8] The circulating reduction system according to any one of [1] to [7], above, further comprising a second dehumidifier disposed at a point along the second piping and configured to remove water vapor from the CO-rich gas.

[9] The circulating reduction system according to any one of [1] to [8], above, further comprising:

a switching valve disposed at a point along the second piping; and seventh piping extending from the switching valve, wherein a portion of the CO-rich gas is recovered via the seventh piping.

[10] The circulating reduction system according to [9], above, further comprising a third dehumidifier disposed at a point along the seventh piping and configured to remove water vapor from the CO-rich gas passing through the seventh piping.

[11] The circulating reduction system according to any one of [1] to [10], above, wherein the reduction furnace is a smelting furnace and the oxide is iron ore.

[12] The circulating reduction system according to [11], above, wherein the smelting furnace is a blast furnace.

[13] An iron ore reduction method using the circulating reduction system according to any one of [1] to [12], above, wherein the CO-rich gas obtained by reforming the exhaust gas is recycled as the reducing gas to reduce iron ore as the oxide.

[14] A smelting furnace operation method using the circulating reduction system according to [11] or [12], above, the smelting furnace operation method comprising alternately charging, from the furnace top of the smelting furnace, (I) at least one of the iron ore selected from sintered ore, lump ore, iron ore pellets, and fine ore, and (II) gas permeable material consisting of crushed slag obtained by crushing solidified slag obtained by slow cooling molten slag discharged from the bottom of the smelting furnace, or a mixture of the crushed slag and coke, in layers to secure gas permeability in the furnace for the reducing gas.

[15] The smelting furnace operation method according to [14], above, further comprising:

supplying the reducing gas and air to the inside of the smelting furnace as blown gas from a tuyere disposed at a bottom portion of the smelting furnace; and gradually increasing a ratio of the crushed slag to the coke in the gas permeable material and a ratio of the reducing gas to the air in the blown gas to gradually decrease the amount of the coke.

(Advantageous Effect)

[0026] According to the circulating reduction system, CO-rich gas obtained by reforming exhaust gas containing CO₂ generated from a reduction furnace can be efficiently recycled as reducing gas.

[0027] According to the iron ore reduction method, CO-rich gas obtained by reforming exhaust gas containing CO₂ generated from a reduction furnace can be efficiently recycled as reducing gas for the reduction of iron ore.

[0028] According to the smelting furnace operation method, the circulating reduction system described above can be used to maintain furnace temperature and secure gas permeability by a means other than coke.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] In the accompanying drawings:

- 5 FIG. 1 is a schematic diagram illustrating a circulating reduction system 100 according to an embodiment of the present disclosure;
 FIG. 2 is a schematic diagram illustrating a circulating reduction system 200 according to another embodiment of the present disclosure;
 FIG. 3 is a schematic diagram illustrating an equilibrium calculation model of the circulating reduction system
 10 according to Inventive Example 1;
 FIG. 4 is a graph illustrating reduction in the model of FIG. 3 (Inventive Example 1);
 FIG. 5 is a schematic diagram illustrating an equilibrium calculation model of the circulating reduction system according to Inventive Example 2;
 FIG. 6 is a graph illustrating reduction in the model of FIG. 5 (Inventive Example 2);
 15 FIG. 7 is a schematic diagram illustrating an equilibrium calculation model of the circulating reduction system according to a comparative example;
 FIG. 8 is a graph illustrating reduction in the model of FIG. 7 (comparative example);
 FIG. 9 is a graph illustrating change in heat absorption in a reduction furnace versus the number of cycles in Inventive Examples 1 and 2 and the comparative example;
 20 FIG. 10 is a graph illustrating change in heat absorption in a reduction furnace in a FeO reduction zone versus the amount of hydrogen in hydrogen-added gas in Inventive Examples 1 and 2 and the comparative example;
 FIG. 11 is a schematic diagram of an experimental circulating reduction system according to Inventive Example 3; and
 FIG. 12 is a schematic diagram of an experimental circulating reduction system according to Inventive Example 4.

25 DETAILED DESCRIPTION

[Circulating reduction system]

[0030] A circulating reduction system 100 according to an embodiment of the present disclosure is described below, with
 30 reference to FIG. 1. The circulating reduction system 100 includes a reduction furnace 10, a first dehumidifier 20, a hydrogen gas supply apparatus 30, a catalytic apparatus 40, a second dehumidifier 50, a gas heating apparatus 60, and piping including first piping 81, second piping 82, third piping 83, fourth piping 84, fifth piping 85, sixth piping 86, seventh piping 87, and a switching valve 90.

[0031] The reduction furnace 10 may be a smelting furnace, for example a blast furnace. When the reduction furnace 10
 35 is a smelting furnace, iron ore and coke are charged into the reduction furnace 10 from a furnace top 12, and high-temperature reducing gas is blown into the reduction furnace 10 from a tuyere 14 disposed at a bottom portion of the reduction furnace 10.

[0032] The first piping 81 is piping that recovers exhaust gas generated in the reduction furnace 10 and containing CO₂
 40 from the reduction furnace 10, and passes the exhaust gas through the piping system. The first piping 81 is connected at a start end to the reduction furnace 10 (as an example, to the furnace top 12) and at a terminal end to the catalytic apparatus 40. The hydrogen gas supply apparatus 30 is connected to a point along the first piping 81. Further, the first dehumidifier 20 is disposed at a point along the first piping 81, upstream from the site where the hydrogen gas supply apparatus 30 is connected. The first piping 81 includes piping 81A extending from the reduction furnace 10 and connecting to the first dehumidifier 20, and piping 81B extending from the first dehumidifier 20 and connecting to the catalytic apparatus 40.
 45 Hereinafter, "upstream" or "downstream" with respect to piping refers to gas flow direction in the piping.

[0033] Exhaust gas discharged from the furnace top 12 of the reduction furnace 10 is dehumidified by the first
 dehumidifier 20 in the process of flowing through the first piping 81, and then hydrogen (H₂) gas is supplied from the
 hydrogen gas supply apparatus 30 to become hydrogen-added gas. Dehumidification is preferably carried out to suppress
 the water-gas shift reaction and promote the reverse water-gas shift reaction. The composition of the exhaust gas is not
 50 particularly limited, but typically has a composition consisting of CO₂: 13 vol% to 24 vol%, CO: 21 vol% to 31 vol%, and H₂: 3 vol% to 15 vol%, excluding water vapor, with the balance consisting of air-derived N₂. The composition of the hydrogen-added gas is not particularly limited, but typically has a composition consisting of CO₂: 13 vol% to 24 vol%, CO: 21 vol% to 31 vol%, and H₂: 10 vol% to 30 vol%, excluding water vapor, with the balance consisting of air-derived N₂. The hydrogen
 supplied from the hydrogen gas supply apparatus 30 is preferably green hydrogen obtained by water electrolysis using
 55 renewable energy, but until coke usage is decreased to zero by applying the circulating reduction system of the present disclosure to blast furnace operation, hydrogen purified from coke oven gas can be substituted.

[0034] A de-duster (not illustrated) is preferably provided at a point along the first piping 81, upstream of the first
 dehumidifier 20 or downstream of the first dehumidifier 20 and upstream of the site where the hydrogen gas supply

apparatus 30 is connected, to remove dust derived from raw material from the exhaust gas by applying dust removal treatment to the exhaust gas.

[0035] The catalytic apparatus (reverse shift reformer) 40 includes a reaction chamber 42 to which the terminal end of the first piping 81 is connected and which contains catalyst for the reverse water-gas shift reaction, and a heating apparatus 44 that heats the reaction chamber 42. In the catalytic apparatus 40, hydrogen-added gas introduced into the reaction chamber 42 from the first piping 81 comes into contact with the catalyst, and CO₂ in the hydrogen-added gas is converted to CO in a reverse water-gas shift reaction, resulting in CO-rich gas having increased CO concentration. The composition of the CO-rich gas after the reverse water-gas shift reaction is not particularly limited, but typically has a composition consisting of CO₂: 6 vol% to 20 vol%, CO: 24 vol% to 40 vol%, and H₂: 5 vol% to 24 vol% , excluding water vapor, with the balance consisting of air-derived N₂. There are many known catalysts that can be used for the reverse water-gas shift reaction, including nickel-based and precious metal-based catalysts, any of which may be used according to the present disclosure.

[0036] From the viewpoint of conversion efficiency of the reverse water-gas shift reaction, an endothermic reaction, when the hydrogen-added gas is brought into contact with the catalyst in the catalytic apparatus 40, the temperature of the introduced hydrogen-added gas is preferably as high as possible in a temperature range where the catalyst is not easily degraded. Specifically, the reaction chamber 42 is preferably heated by the heating apparatus 44 so that the temperature of the reaction gas (hydrogen-added gas) around the catalyst is 800 °C or more and 1200 °C or less.

[0037] The second piping 82 is piping that extends from the catalytic apparatus 40 and is connected to the reduction furnace 10 (in one example, to the tuyere 14). The CO-rich gas is passed through the second piping and supplied (in one example, via the tuyere 14) to the inside of the reduction furnace 10 as reducing gas. The second dehumidifier 50 that removes water vapor from the CO-rich gas and the gas heating apparatus 60 that heats the CO-rich gas are preferably disposed at points along the second piping 82. In this case, the gas heating apparatus 60 is preferably disposed downstream of the second dehumidifier 50. In this case, the second piping 82 includes piping 82A extending from the catalytic apparatus 40 and connecting to the second dehumidifier 50, piping 82B extending from the second dehumidifier 50 and connecting to the gas heating apparatus 60, and piping 82C extending from the gas heating apparatus 60 and connecting to the reduction furnace 10 (in one example, to the tuyere 14).

[0038] The CO-rich gas that has passed through the catalytic apparatus 40 is, in the process of flowing through the second piping 82, dehumidified by the second dehumidifier 50 then heated by the gas heating apparatus 60, and then blown into the reduction furnace 10 as reducing gas.

[0039] That is, the temperature of the CO-rich gas (reducing gas) blown into the reduction furnace 10 after the reaction with the catalyst is preferably adjusted by the gas heating apparatus 60. The higher the temperature of the reducing gas, the more efficient the reduction of iron ore in the reduction furnace 10. For solid phase reduction of iron ore, the temperature of the reducing gas blown into the reduction furnace 10 is preferably 900 °C or more. Further, when the reduced iron is extracted as hot metal at 1500 °C, the temperature of the molten source of iron and slag formed in the lower region of the reduction furnace 10 needs to be maintained at 1650 °C or more. Therefore, the reducing gas is preferably heated and blown in such that, when the coke input is up to about 50 % of that of a conventional blast furnace, the temperature of the reducing gas is 1200 °C or more, and when the coke input is less than 20 % than that of a conventional blast furnace, the temperature of the reducing gas is 1500 °C or more.

[0040] Suitable operation of the gas heating apparatus 60 is as follows. The circulating reduction system 100 according to the present embodiment preferably includes the third piping 83 that branches off from the second piping 82, at a position upstream of the gas heating apparatus 60 and downstream of the second dehumidifier 50, and is connected to the gas heating apparatus 60. A portion of the CO-rich gas flowing through the second piping 82 is preferably supplied to the gas heating apparatus 60 as combustion gas via the third piping 83. Thus, by burning a portion of the CO-rich gas as fuel gas in the gas heating apparatus 60, the temperature of the reducing gas can be raised to the desired temperature described above. Although omitted in FIG. 1, oxygen-containing gas supplied to the gas heating apparatus 60 to burn the combustion gas is preferably oxygen gas (not containing nitrogen that is not consumed).

[0041] The circulating reduction system 100 preferably includes the fourth piping 84 extending from the gas heating apparatus 60 and connected to a point along the first piping 81. The combustion exhaust gas generated from the gas heating apparatus 60 is preferably merged with the exhaust gas in the first piping 81 via the fourth piping 84, and reused. The fourth piping 84 is preferably connected at a point along the first piping 81, upstream of the first dehumidifier 20. When the combustion exhaust gas generated from the gas heating apparatus 60 is allowed to heat exchange with (1) the reducing gas piping between the catalytic apparatus 40 and the gas heating apparatus 60 and (2) the hydrogen-added gas piping between the hydrogen gas supply apparatus 30 and the catalytic apparatus 40, before merging with the exhaust gas in the first piping 81 upstream of the first dehumidifier 20, the reducing gas and the hydrogen-added gas can also be preheated.

[0042] When the gas heating apparatus 60 that is an indirect heating type, as illustrated in FIG. 1, cannot raise the reducing gas to the desired temperature, some of the CO and H₂ contained in the reducing gas may be burned directly by adding oxygen from near a leading end of the gas heating apparatus 60. Further, when oxygen-enriched air produced by

cryogenic separation or the like is used as hot blast blown into the reduction furnace 10 when starting up in the blast furnace mode, the heat load of the gas heating apparatus 60 that is lost to nitrogen heating is decreased, making raising the temperature of the reducing gas easier.

[0043] Next, regarding suitable operation of the catalytic apparatus 40, a portion of the CO-rich gas is preferably used as combustion gas in a similar way. That is, the circulating reduction system 100 according to the present embodiment preferably includes the fifth piping 85 branching off from the second piping 82 and connected to the heating apparatus 44 of the catalytic apparatus 40. The fifth piping 85 preferably branches off from a point along the second piping 82, at a position upstream from the gas heating apparatus 60 and downstream from the second dehumidifier 50. A portion of the CO-rich gas is preferably supplied as combustion gas to the heating apparatus 44 via the fifth piping 85. Although omitted in FIG. 1, oxygen-containing gas supplied to the heating apparatus 44 to burn the combustion gas is preferably oxygen gas (not containing nitrogen that is not consumed).

[0044] The circulating reduction system 100 preferably includes the sixth piping 86 extending from the heating apparatus 44 and connected to a point along the first piping 81. Combustion exhaust gas generated from the heating apparatus 44 is preferably merged with the exhaust gas in the first piping 81 via the sixth piping 86, and reused. According to the present embodiment, an upstream portion 86A of the sixth piping 86 is connected to a point along the fourth piping 84, which is a flow path of fuel exhaust gas from the gas heating apparatus 60, and therefore a downstream portion 86B of the sixth piping 86 also serves as a downstream portion 84B of the fourth piping 84. However, the present disclosure is not limited to this example, and the sixth piping 86 may of course be directly connected to the first piping 81 independently of the fourth piping 84. The combustion exhaust gas from the heating apparatus 44 can also preheat the hydrogen-added gas when heat exchanged with the hydrogen-added gas piping between the hydrogen gas supply apparatus 30 and the catalytic apparatus 40 and then merge with the exhaust gas in the first piping 81 upstream of the first dehumidifier 20.

[0045] According to the present embodiment described above, the processes of reducing iron ore by blowing in reducing gas, recovering exhaust gas from the reduction furnace, removing dust and dehumidifying exhaust gas (optional processes), adding hydrogen gas to the exhaust gas, generating CO-rich gas from the hydrogen-added gas by the reverse water-gas shift reaction, dehumidifying the CO-rich gas (optional process), heating the CO-rich gas (optional process), and blowing the CO-rich gas as reducing gas are repeated to realize a circulation process in which exhaust gas from the reduction furnace 10 is reused in a closed circulation system.

[0046] The unconverted CO₂ that remains in the CO-rich gas to be used as the reducing gas will eventually become a CO source during the circulation process, and therefore does not need to be separated from the reducing gas. That is, in the present embodiment, it is important that no separation apparatus is disposed at any point along the first piping 81 nor the second piping 82 to separate and either recover or remove a specific gas component other than water vapor from gas passing through the first piping 81 or gas passing through the second piping 82. According to the present embodiment, no new separation or concentration process is required other than dust removal and dehumidification, to which existing technology can be applied, and therefore reducing gas circulation efficiency is high.

[0047] According to the present embodiment, the reverse water-gas shift reaction is used that converts CO₂ to CO with an equimolar amount of hydrogen, and therefore the amount of hydrogen per CO₂ can be suppressed to about 1/4 of that of the conventional reduction method described above, which uses methane produced by a methanation reaction as the reductant, which requires four times as much hydrogen as CO₂ in moles.

[0048] According to the present embodiment, reducing gas mainly composed of CO converted from exhaust gas can be fed into the reduction furnace 10 at high temperature, and impurities in iron ore can be separated from hot metal as molten slag, and therefore low-grade powdered ore or fine ore, which are cost effective and easily procured, can be used as pellets or sintered ore, as in a typical blast furnace.

[0049] A surplus of CO-rich gas (according to the present embodiment, a remainder of the CO-rich gas used as reducing gas, combustion gas for the gas heating apparatus 60, and combustion gas for the heating apparatus 44) can be recovered. That is, the circulating reduction system 100 includes the switching valve 90 disposed at a point along the second piping 82, and the seventh piping 87 extending from the switching valve 90, through which a portion of the CO-rich gas can be recovered. The recovered CO-rich gas may be used as synthesis gas, for example, as a raw material for organic compounds. According to the present embodiment, the CO₂-rich exhaust gas discharged from the reduction furnace 10 is converted to CO-rich reducing gas and recycled, and therefore the surplus of CO-rich gas can be effectively utilized as synthesis gas in the organic chemical industry and the like, thereby reducing CO₂ emissions into air to a zero level.

[0050] Further, the molten slag separated from the hot metal is slowly cooled in a mold to solidified slag, which is then crushed into crushed slag, which can be reused as gas permeable material. When a portion of pig iron discharged from the reduction furnace (smelting furnace) adheres to the slag-derived gas permeable material, the pig iron can be returned to the reduction furnace as a source of iron via the gas permeable material.

[0051] The molten slag is automatically discharged onto the surface of the hot metal due to the difference in specific gravity, and therefore recycling has almost no adverse effect on the quality of the hot metal. The recycled molten slag has equivalent quality as regular blast-furnace slag, and can be used industrially as a raw material for blast-furnace cement and the like.

[0052] A circulating reduction system 200 according to another embodiment of the present disclosure is described below, with reference to FIG. 2. The circulating reduction system 200 has the same configuration as the circulating reduction system 100, except that the second dehumidifier 50 is not included and instead a third dehumidifier 70 is included, disposed at a point along the seventh piping 87. That is, according to the present disclosure, the second dehumidifier 50 is not an essential component. When the second dehumidifier 50 is not present, the third dehumidifier 70 is preferably used to remove water vapor from the CO-rich gas passing through the seventh piping 87.

[0053] The above mainly describes the case where the reduction furnace 10 is a smelting furnace such as a blast furnace and the material to be reduced is iron ore. The reduction furnace 10 may be a solid reduction furnace. Further, the material to be reduced is not limited to iron ore as long as it is an oxide. For example, the material to be reduced may be manganese ore, the raw material for ferromanganese and silicomanganese.

[Iron ore reduction method]

[0054] The iron ore reduction method according to an embodiment of the present disclosure uses the circulating reduction system 100, 200 described above to reduce iron ore as an oxide by recycling CO-rich gas obtained by reforming exhaust gas as reducing gas. This allows the CO-rich gas obtained by reforming the exhaust gas containing CO₂ generated from the reduction furnace 10 to be efficiently recycled as reducing gas for the reduction of iron ore.

[0055] Further, the reduction method according to the present embodiment realizes an efficient reduction process in which the exhaust gas from the reduction furnace 10 can be recycled as a starting material for reductant, and therefore can significantly decrease CO₂ generation. Further, the amount of fossil fuel-derived reductant such as coke conventionally used in the iron ore reduction process can be drastically decreased.

[Smelting furnace operation method]

[0056] The smelting furnace operation method according to an embodiment of the present disclosure is carried out using the circulating reduction system 100, 200 described above. It is essential that, from the furnace top of the reduction furnace (smelting furnace) 10, (I) at least one of iron ore selected from sintered ore, lump ore, iron ore pellets, and fine ore (source of iron), and (II) gas permeable material consisting of crushed slag obtained by crushing solidified slag obtained by slow cooling molten slag discharged from the bottom of the smelting furnace, or a mixture of the crushed slag and coke, are alternately charged in layers to secure gas permeability of the reducing gas in the furnace. This allows the circulating reduction system 100, 200 described above to maintain furnace temperature and secure gas permeability by a means other than coke.

[0057] In the operation according to the present embodiment, reducing gas and air are supplied to the inside of the smelting furnace as blowing gas from the tuyere 14. At this time, it is preferable to gradually increase a ratio of the crushed slag to the coke in the gas permeable material and a ratio of the reducing gas to the air in the blown gas to gradually decrease the amount of the coke.

[0058] According to the blast furnace operation method, reduced iron in the form of hot metal can be obtained using low-grade powdered ore or fine ore, which are low cost and easy to procure, and therefore a conventional integrated steelmaking process can be used directly for the next process and beyond.

[0059] The degree of gas permeability of the smelting furnace can be adjusted by the particle size of the crushed slag, and gas permeability is even easier to secure when, for example, the slow-cooled slag is cast in a way that adds ventilation holes. There is no particular problem in using typical blast-furnace slag as gas permeable material.

[0060] In the blast furnace operation method according to the present embodiment, the amount of molten slag generated in the circulation-type smelting furnace 100, 200 is greater than in a typical blast furnace because slag that is re-charged from the furnace top 12 is re-melted after the cohesive zone. Further, the more slag that is added, the more heat is lost as slag melting heat. Therefore, when starting up operation in the blast furnace mode, the layer thickness ratio of the source of iron layer and the gas permeable layer is preferably adjusted in advance so that the source of iron layer is richer than in a typical blast furnace.

EXAMPLES

[Examples 1]

[0061] As described below, equilibrium calculations were performed to confirm the effectiveness of the reduction method according to the present disclosure, as Inventive Examples 1 and 2 and a comparative example.

(Inventive Example 1)

[0062] An equilibrium calculation model of the circulating reduction system according to Inventive Example 1 is illustrated in FIG. 3. As an initial state, a state is assumed in which the reduction furnace 10 containing 25 mol of iron oxide (III) (Fe_2O_3) is connected to a reverse shift reformer serving as the catalytic apparatus 40 (hereinafter simply referred to as "reformer 40") containing a mixed gas equivalent to a total of 100 mol of blast furnace exhaust gas, consisting of CO: 22 mol, CO_2 : 22.8 mol, H_2 : 4.2 mol, and N_2 : 51 mol. The first dehumidifier 20 is disposed at the inlet of the reformer, the second dehumidifier 50 is disposed at the outlet of the reformer, and a hydrogen gas supply apparatus 30 is disposed between the first dehumidifier and the reformer to maintain the H_2 mole number in the reformer at 22.8 mol (corresponding to the CO_2 concentration in blast furnace exhaust gas). Assuming that no gases other than H_2 supplied from the hydrogen gas supply apparatus and H_2O removed by the first dehumidifier and the second dehumidifier enter or leave the reduction furnace and the reformer, all H_2O is generated from consumed H_2 and therefore the total number of moles of mixed gas circulating through the reformer and the reduction furnace does not change.

[0063] In Inventive Example 1, the temperature in the reduction furnace and the reformer are both maintained at 900 °C by externally supplied heat. Actual gas circulation between the reduction furnace and the reformer requires a gas transport system, but for the purpose of proof of principle, energy consumed by this is ignored. Likewise, energy consumed to drive the first dehumidifier, the second dehumidifier, and the hydrogen gas supply apparatus is also ignored. The reverse water-gas shift reaction in the reformer may not reach equilibrium and therefore may be dependent on the performance of the catalyst used, but is assumed to reach equilibrium.

[0064] Here, a repeated circulation process is considered in which the reducing gas generated when hydrogen-added gas reaches a steady state in the reformer is all sent to the reduction furnace, and the gas in the reduction furnace when the reduction reaction reaches a steady state is extracted as exhaust gas, to which hydrogen is added up to a certain level to produce hydrogen-added gas again, with this cycle being considered as one cycle. Equilibrium of gas components and a source of iron in the reformer and in the reduction furnace, which occur at each cycle of feeding the reducing gas from the reformer to the reduction furnace, were calculated using the thermodynamic equilibrium calculation software & thermodynamic database FactSage 8.1 from Research Center of Computational Mechanics, Inc. The results are illustrated in FIG. 4. Compounds formed in the reformer and the reduction furnace include methane and the like, but trace components of 0.005 mol or less were ignored.

[0065] In the reduction furnace described above, the reduction of the source of iron proceeds by CO supplied from the reformer and excess H_2 that was not consumed in the reverse water-gas shift reaction. The solid-phase Fe_2O_3 charged as a source of iron is converted into twice the molar amount of FeO (solid phase) in the first cycle, and from the second cycle onwards, the FeO is gradually reduced and converted to α -Fe (solid phase), with the reduction being completed in the seventh cycle. The main reduction reaction being from FeO to α -Fe is consistent with the findings known from blast furnaces. The amount of H_2 consumed in the reduction of this source of iron is 89 mol.

(Inventive Example 2)

[0066] An equilibrium calculation model of the circulating reduction system according to Inventive Example 2 is illustrated in FIG. 5. This is the same as the equilibrium calculation model of the circulating reduction system according to Inventive Example 1 illustrated in FIG. 3, except that there is no second dehumidifier on the outlet side of the reformer. The calculation conditions are the same as in Inventive Example 1, and equilibrium of gas components and source of iron in the reformer and in the reduction furnace were calculated. The results are illustrated in FIG. 6.

[0067] The solid-phase FeaOs charged as a source of iron is converted into twice the molar amount of FeO (solid phase) in the first cycle, and from the third cycle onwards, the FeO is gradually reduced and converted to α -Fe (solid phase), with the reduction being completed in the ninth cycle. The main reduction reaction being from FeO to α -Fe is consistent with the findings known from blast furnaces. The amount of H_2 consumed in the reduction of this source of iron is 85 mol.

(Comparative example)

[0068] An equilibrium calculation model of a circulating reduction system according to a comparative example is illustrated in FIG. 7. This is the same as the equilibrium calculation model of the circulating reduction system according to Inventive Example 1 illustrated in FIG. 3, except that there is no reformer or second dehumidifier on the outlet side of the reformer. The calculation conditions are the same as in Inventive Example 1, and equilibrium of gas components and source of iron in the reformer and in the reduction furnace were calculated. The results are illustrated in FIG. 8.

[0069] In the reduction furnace in the comparative example, the reduction of the source of iron proceeds only with H_2 , which is fed directly into the reduction furnace from the hydrogen gas supply apparatus. The 25 mol of Fe_2O_3 (solid phase) charged as the source of iron is converted to 8.2 mol of Fe_3O_4 (solid phase) and 22.5 mol of FeO (solid phase) in the first cycle, and from the second cycle onwards, the FeO is gradually reduced and converted to α -Fe (solid phase), with the

reduction being completed in the ninth cycle, as in Inventive Example 2. The main reduction reaction being from FeO to α -Fe is the same as in Inventive Examples 1 and 2. The amount of H₂ consumed in the reduction of this source of iron is 75 mol, 10 mol less than in Inventive Example 2.

(Heat absorption in reduction furnace)

[0070] The major difference between Inventive Examples 1 and 2 and the comparative example is the amount of heat absorbed in the reduction furnace. The total reaction heat (heat absorption) in the reduction furnace calculated from the reaction heat for each reaction by FactSage 8.1 is illustrated in FIG. 9 and FIG. 10.

[0071] The direct reduction of the source of iron by H₂ is an endothermic reaction, except for the reaction from Fe₂O₃ to Fe₃O₄, which is completed early in the process. Regarding this, in the reduction of the source of iron by CO and excess H₂ in Inventive Example 1, the amount of heat generated from CO reduction compensates for the heat absorption due to H₂ reduction, and therefore the total heat absorption can be greatly decreased (see FIG. 9). Further, in Inventive Example 2, the amount of heat generated by CO reduction exceeds the amount of heat absorbed by H₂ reduction in the FeO reduction range, and therefore the reduction temperature of FeO is spontaneously maintained at a high temperature (see FIG. 9). The FeO reduction phase becomes even longer as the amount of source of iron input increases. Normally, for a reduction furnace, which must maintain a high internal temperature, supplying heat from any source other than the tuyere and the furnace top is extremely difficult. Considering the need to compensate for absorbed heat with the heat of combustion of coke charged into the reduction furnace, the superiority of the present Inventive Examples is obvious.

[0072] From FIG. 10, the amount of H₂ supplied to the reformer to maximize the amount of heat generated in the reduction range of FeO is expected to be about the same as the molar amount of CO₂ in the exhaust gas. When the amount of H₂ supplied to the reformer is suppressed, the reduction rate is also expected to decrease. In practice, the amount of H₂ supplied is adjusted based on the balance between the temperature in the reduction furnace and the reduction rate.

[Examples 2]

[0073] The reduction of iron ore using experimental circulating reduction systems was performed as follows, as Inventive Examples 3 and 4.

(Inventive Example 3)

[0074] The configuration of the experimental circulating reduction system according to Inventive Example 3 is illustrated in FIG. 11. As illustrated in FIG. 11, 2.2 kg of coke pulverized to approximately 5 mm and 5.0 kg of lump ore pulverized to approximately 3 mm were alternately layered on a tungsten mesh partitioning the furnace bottom of a BF simulator (hereinafter also referred to as "reduction furnace 10"), which was an experimental reducing furnace installed on a weight scale, to form a raw material block A.

[0075] Further, a raw material block B was formed on top of the raw material block A, by alternately layering a uniform mixture of 1.1 kg of the coke described above and 2.8 kg of slow-cooled blast furnace slag pulverized to approximately 5 mm, and 5.0 kg of lump ore pulverized to approximately 3 mm.

[0076] Exhaust gas discharged from the furnace top, after passing through a de-duster, the dehumidifier 20, a first electric tube furnace 40, a dehumidifier, a second electric tube furnace 40, the dehumidifier 50, and a regenerative gas heating furnace 60, was connected via a switching valve 91 to an exhaust gas processor on one side and a nozzle 92 at a bottom portion of the reduction furnace on the other side. The two electric tube furnaces 40 were ceramic electric tube furnaces in which a quartz reaction tube holding 51 g of platinum catalyst is set in the center.

[0077] Two sampling tubes for gas composition analysis were installed, one just before the first electric tube furnace 40 and the other between the second electric tube furnace 40 and the dehumidifier 50, and connected to a micro gas chromatography analyzer (micro GC). Further, hydrogen piping 30 was connected between the dehumidifier 20 and the first electric tube furnace 40 via a switch valve 93 and a mass flow controller (MFC) 94.

[0078] On the opposite side of the nozzle 92 at the bottom portion of the reduction furnace 10 was a nozzle 96 that fed 2.3% oxygen-enriched air via a regenerative gas heating furnace 95. The flow rate of air introduced through the nozzle 96 was controlled by a mass flow controller (MFC) 97.

[0079] In order to completely exhaust the exhaust gas remaining in the reduction furnace 10 after the reduction experiment, purge nitrogen gas piping was connected between the dehumidifier 20 and the switching valve 93 via a switching valve 98.

[0080] First, the exhaust gas was separated from the reduction furnace 10 by setting the switching valve 91 to the exhaust gas processor side. Air heated to 1200 °C by MFC 97 was then introduced into the reduction furnace 10 at a flow rate of 17 L/min from the nozzle 96 of the reduction furnace 10. Both of the two electric tube furnaces 40 were set to reach an internal temperature of 800 °C using thermocouples (TC) located around the catalyst.

[0081] Representative compositions of the exhaust gas produced by the reduction of lump ore in the raw material block A and the mixed gas after passing through the second electric tube furnace 40 (without hydrogen replenishment at the inlet of the first electric tube furnace 40) are listed in Table 1. It can be seen that, after passing through the second electric tube furnace 40, CO increased by 2.7 % and CO₂ and H₂ decreased by 2.7 % each due to the reverse water-gas shift reaction caused by excess H₂ in the exhaust gas.

[0082] When all the 2.2 kg of coke in the raw material block A was consumed as exhaust gas, the air flow rate introduced through the nozzle 96 was changed to 8.5 L/min at the MFC 97. At the same time, the switching valve 93 was switched to the hydrogen piping 30 side to introduce hydrogen gas, and the MFC 94 was used to adjust the H₂ concentration in the mixed gas to 22.8 % (the same as the CO₂ concentration in the initial exhaust gas) before entering the first electric tube furnace 40. The switching valve 91 was then switched to the reduction furnace 10 side, and reducing gas was introduced through the nozzle 92. The total consumption of coke in the raw material block A was determined from the weight change of the reduction furnace 10.

[0083] In this state, waiting for all 1.1 kg of coke in the raw material block B to be consumed, the air introduced through the nozzle 96 was stopped, and the two electric tube furnaces and the two gas heating furnaces were shut down. Then, waiting for the water temperature in a water-cooling jacket to reach 30 °C, hydrogen gas supply was shut off at the switching valve 93, the switching valve 91 was switched to the exhaust gas processor side and the switching valve 98 was switched to the nitrogen gas introduction side, and all exhaust gas remaining in the reduction furnace 10 was discharged to the exhaust gas processor. The reduction furnace 10 was then dismantled to check the condition of the furnace interior.

[0084] Of the total of 10 kg of lump ore, 3.3 kg of coke, and 2.8 kg of slow-cooled blast furnace slag in the raw material blocks A and B, almost nothing was observed on the tungsten mesh. A mixture of ferrite (α -Fe) and cementite (Fe₃C), as well as slag deposited on top of the mixture, was observed at the bottom of the furnace, separated by the tungsten mesh. That the mixture was composed of ferrite and cementite was confirmed by X-ray diffraction. The carbon content in the mixture measured by a combustion-type carbon-sulfur analyzer was approximately 4.3 mass%, and a comparison of the carbon content at the top and bottom of the mixture indicated an increase of about 0.3 mass% at the bottom.

[0085] Through the above experiment, it was confirmed that the entire amount of lump ore fed as raw material can be reduced in the reduction process of the raw material block B, which corresponds to 50 % carbonless operation using slag as gas permeable material, after the entire amount of the raw material block A, which corresponds to blast furnace mode, has been reduced.

(Inventive Example 4)

[0086] The configuration of the experimental circulating reduction system according to Inventive Example 4 is illustrated in FIG. 12. This is the same as the circulating reduction system of Inventive Example 3 illustrated in FIG. 11, except that the electric tube furnace 40 was a single unit and a dehumidifier was not disposed downstream of the electric tube furnace 40. The electric tube furnace 40 was set to an internal temperature of 900 °C using a thermocouple (TC) around the catalyst. Other conditions were the same as in Inventive Example 3.

[0087] Representative compositions of the exhaust gas produced by the reduction of lump ore in the raw material block A and the mixed gas after passing through the electric tube furnace 40 (without hydrogen replenishment at the inlet of the electric tube furnace 40) are listed in Table 1. It can be seen that, after passing through the electric tube furnace 40, CO increased by 1.8 % and CO₂ and H₂ decreased by 1.8 % each due to the reverse water-gas shift reaction caused by excess H₂ in the exhaust gas.

[0088] At the end of the test, as in Inventive Example 3, almost no lump ore, coke, or slow-cooled blast furnace slag was found on the tungsten mesh. A mixture of ferrite (α -Fe) and cementite (Fe₃C), as well as slag deposited on top of the mixture, was observed at the bottom of the furnace, separated by the tungsten mesh. That the mixture was composed of ferrite and cementite was confirmed by X-ray diffraction. The carbon content in the mixture measured by a combustion-type carbon-sulfur analyzer was approximately 4.3 mass%, and a comparison of the carbon content at the top and bottom of the mixture indicated an increase of about 0.3 mass% at the bottom.

[0089] Through the above experiment, it was confirmed that the entire amount of lump ore fed as raw material can be reduced in the reduction process of the raw material block B, which corresponds to 50 % carbonless operation using slag as gas permeable material, after the entire amount of the raw material block A, which corresponds to blast furnace mode, has been reduced.

[Table 1]

[0090]

Table 1

Classification	Gas	CO	CO ₂	H ₂	N ₂	H ₂ O
		vol%	vol%	vol%	vol%	vol%
Inventive Example 3	Exhaust gas	22.0	22.8	4.2	51.0	-
	Mixed gas	24.7	20.1	1.5	51.0	0.8
Inventive Example 4	Exhaust gas	22.0	22.8	4.2	51.0	-
	Mixed gas	23.8	21.0	2.4	51.0	1.8

REFERENCE SIGNS LIST

[0091]

100 circulating reduction system
 200 circulating reduction system
 10 reduction furnace
 12 furnace top
 14 tuyere
 20 first dehumidifier
 30 hydrogen gas supply apparatus
 40 catalytic apparatus
 42 reaction chamber
 44 heating apparatus
 50 second dehumidifier
 60 gas heating apparatus
 70 third dehumidifier
 81 first piping
 82 second piping
 83 third piping
 84 fourth piping
 85 fifth piping
 86 sixth piping
 87 seventh piping
 90 switching valve

Claims

1. A circulating reduction system comprising:

a reduction furnace configured to reduce an oxide contained therein;
 first piping configured to recover from the reduction furnace exhaust gas generated in the reduction furnace that contains CO₂, wherein the exhaust gas is passed through the first piping;
 a hydrogen gas supply apparatus connected to a point along the first piping and configured to add hydrogen gas to the exhaust gas to produce hydrogen-added gas;
 a catalytic apparatus to which an end of the first piping is connected and which comprises a reaction chamber containing a catalyst for the reverse water-gas shift reaction, configured so that the hydrogen-added gas introduced into the reaction chamber from the first piping comes into contact with the catalyst to convert CO₂ in the hydrogen-added gas to CO by the reverse water-gas shift reaction to produce a CO-rich gas having an increased CO concentration; and
 second piping extending from the catalytic apparatus and connected to the reduction furnace, wherein the CO-rich gas is passed through the second piping and supplied to the inside of the reduction furnace as reducing gas, wherein no separation apparatus is disposed at any point along the first piping nor the second piping to separate and either recover or remove a specific gas component other than water vapor from gas passing through the first piping or gas passing through the second piping.

2. The circulating reduction system according to claim 1, further comprising a gas heating apparatus disposed at a point

along the second piping and configured to heat the CO-rich gas.

3. The circulating reduction system according to claim 2, further comprising third piping that branches off from the second piping at a position upstream of the gas heating apparatus and is connected to the gas heating apparatus, wherein a portion of the CO-rich gas is supplied to the gas heating apparatus as combustion gas via the third piping.

4. The circulating reduction system according to claim 2 or 3, further comprising fourth piping extending from the gas heating apparatus and connected to a point along the first piping, wherein combustion exhaust gas generated from the gas heating apparatus is merged with the exhaust gas in the first piping via the fourth piping.

5. The circulating reduction system according to any one of claims 1 to 3, wherein

the catalytic apparatus further comprises a heating apparatus configured to heat the reaction chamber, and the circulating reduction system further comprises fifth piping that branches off from the second piping and is connected to the heating apparatus, wherein a portion of the CO-rich gas is supplied to the heating apparatus as combustion gas via the fifth piping.

6. The circulating reduction system according to claim 5, further comprising sixth piping extending from the heating apparatus and connected to a point along the first piping, wherein combustion exhaust gas generated from the heating apparatus is merged with the exhaust gas in the first piping via the sixth piping.

7. The circulating reduction system according to any one of claims 1 to 3, further comprising a first dehumidifier disposed at a point along the first piping, upstream from the site where the hydrogen gas supply apparatus is connected, and configured to remove water vapor from the exhaust gas.

8. The circulating reduction system according to any one of claims 1 to 3, further comprising a second dehumidifier disposed at a point along the second piping and configured to remove water vapor from the CO-rich gas.

9. The circulating reduction system according to any one of claims 1 to 3, further comprising:

a switching valve disposed at a point along the second piping; and seventh piping extending from the switching valve, wherein a portion of the CO-rich gas is recovered via the seventh piping.

10. The circulating reduction system according to claim 9, further comprising a third dehumidifier disposed at a point along the seventh piping and configured to remove water vapor from the CO-rich gas passing through the seventh piping.

11. The circulating reduction system according to any one of claims 1 to 3, wherein the reduction furnace is a smelting furnace and the oxide is iron ore.

12. The circulating reduction system according to claim 11, wherein the smelting furnace is a blast furnace.

13. An iron ore reduction method using the circulating reduction system according to any one of claims 1 to 3, wherein the CO-rich gas obtained by reforming the exhaust gas is recycled as the reducing gas to reduce iron ore as the oxide.

14. A smelting furnace operation method using the circulating reduction system according to claim 11, the smelting furnace operation method comprising alternately charging, from the furnace top of the smelting furnace, (I) at least one of the iron ore selected from sintered ore, lump ore, iron ore pellets, and fine ore, and (II) gas permeable material consisting of crushed slag obtained by crushing solidified slag obtained by slow cooling molten slag discharged from the bottom of the smelting furnace, or a mixture of the crushed slag and coke, in layers to secure gas permeability in the furnace for the reducing gas.

15. The smelting furnace operation method according to claim 14, further comprising:

supplying the reducing gas and air to the inside of the smelting furnace as blown gas from a tuyere disposed at a bottom portion of the smelting furnace; and gradually increasing a ratio of the crushed slag to the coke in the gas permeable material and a ratio of the reducing gas to the air in the blown gas to gradually decrease the amount of the coke.

FIG. 1

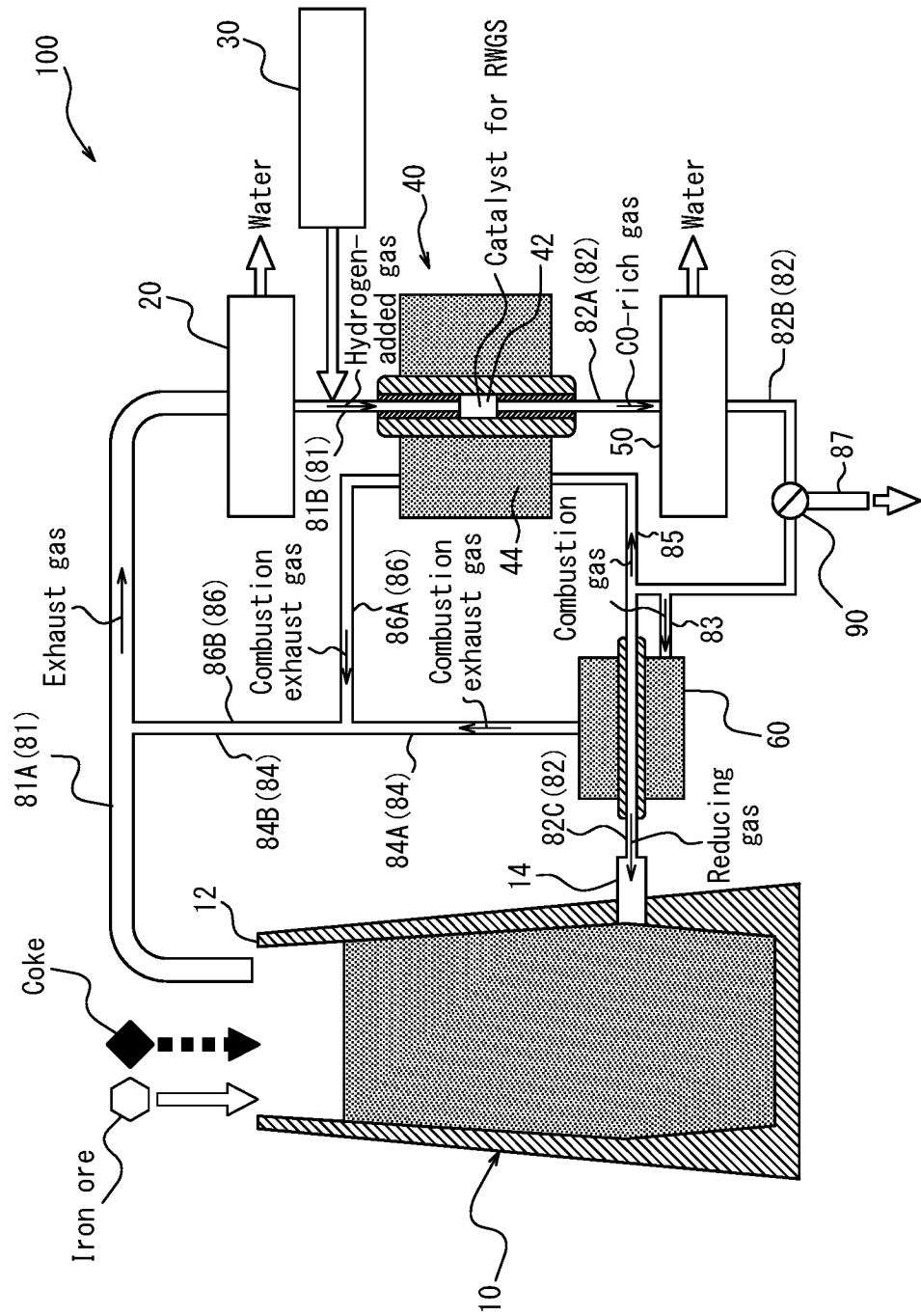


FIG. 2

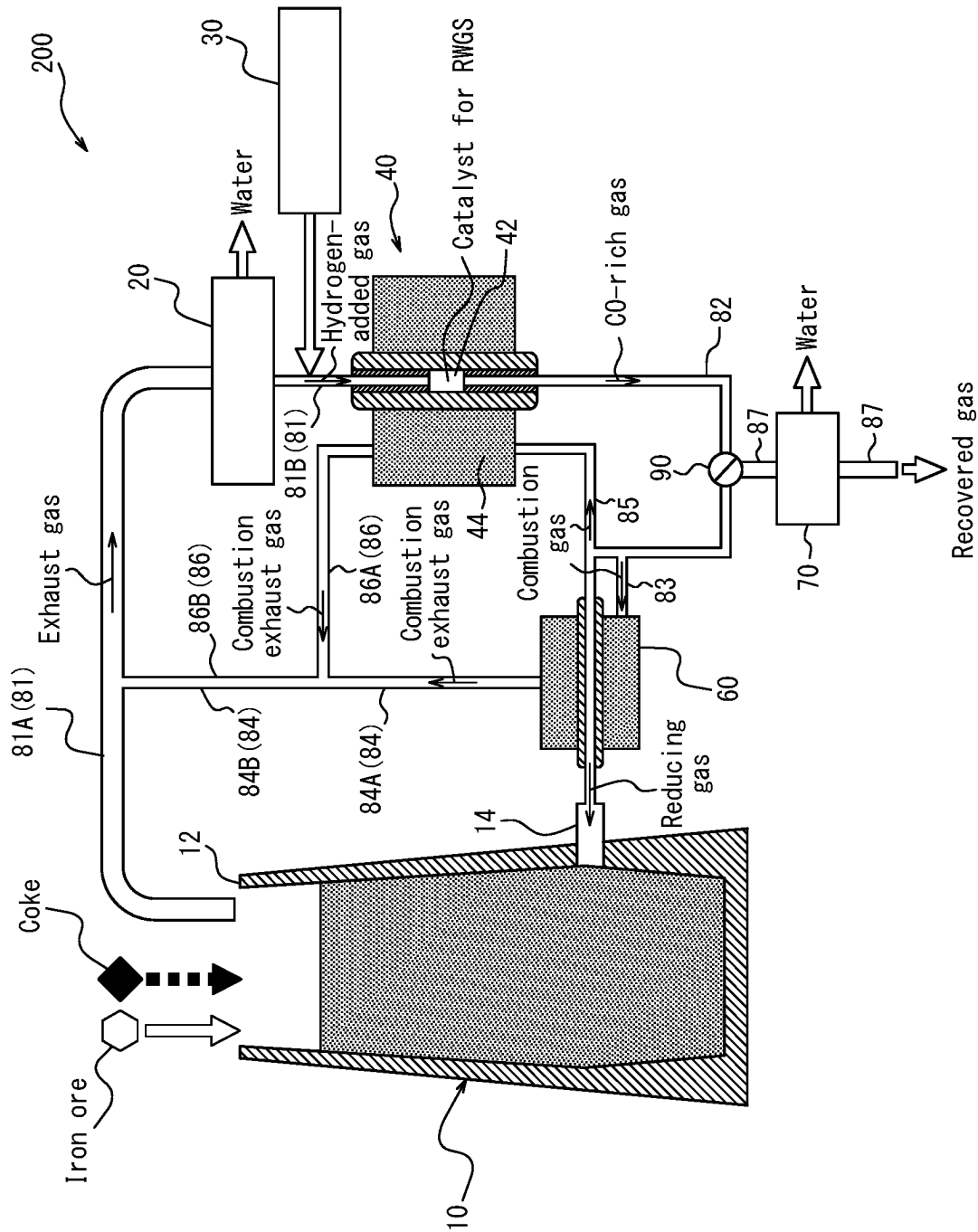


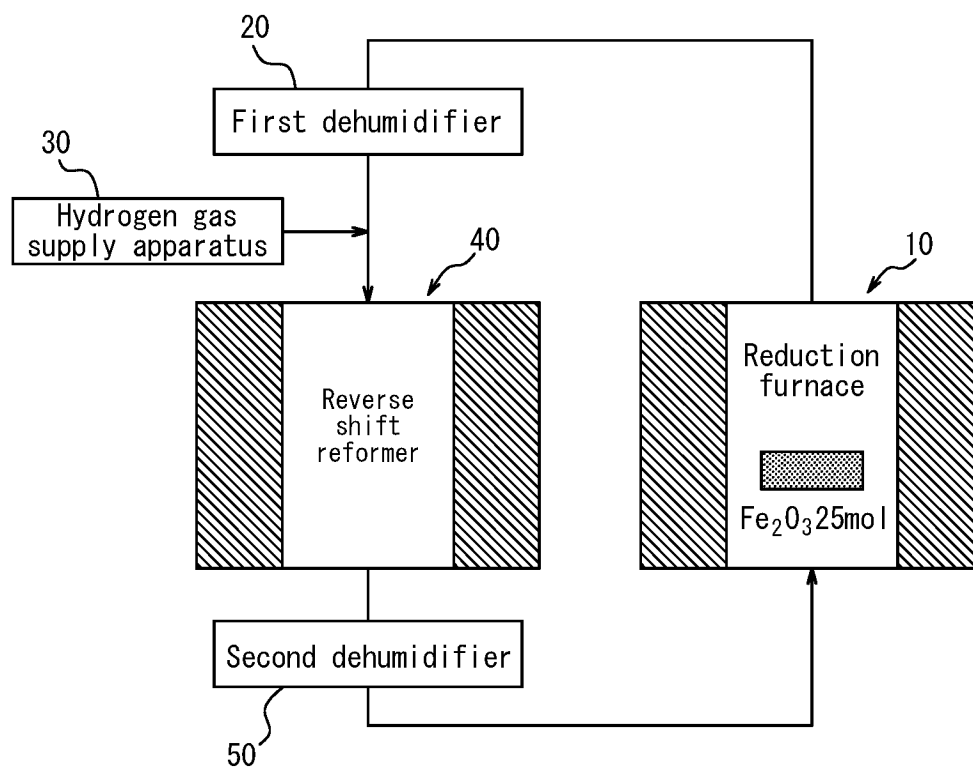
FIG. 3

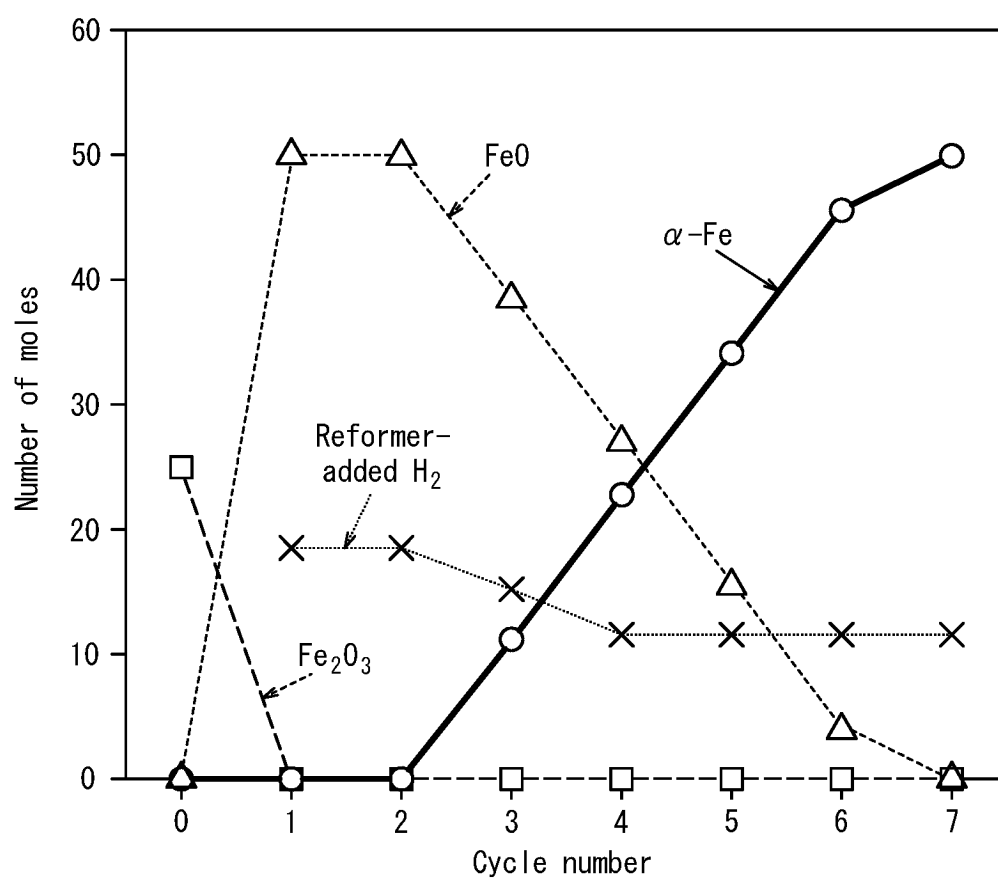
FIG. 4

FIG. 5

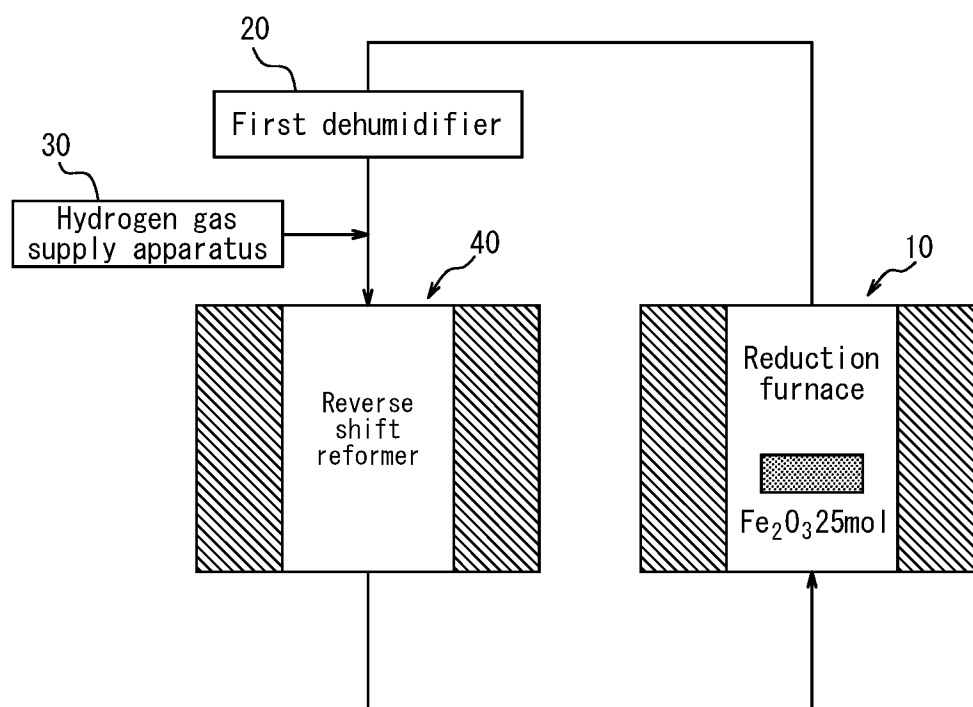


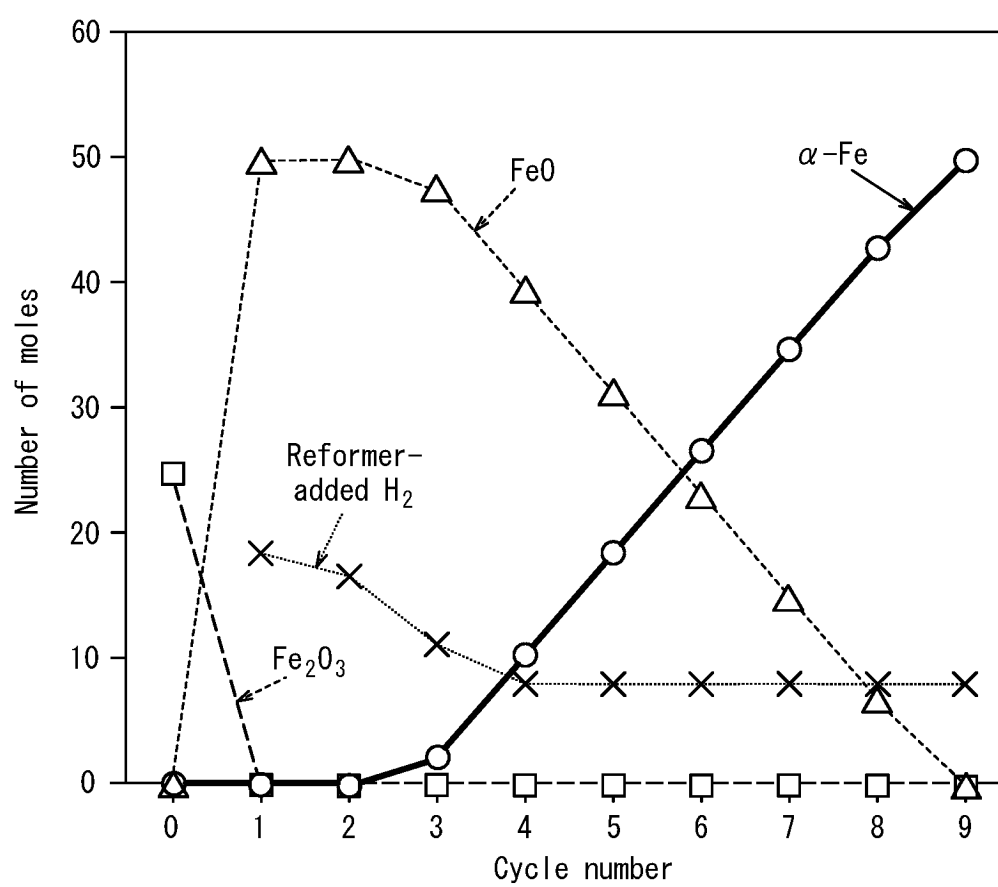
FIG. 6

FIG. 7

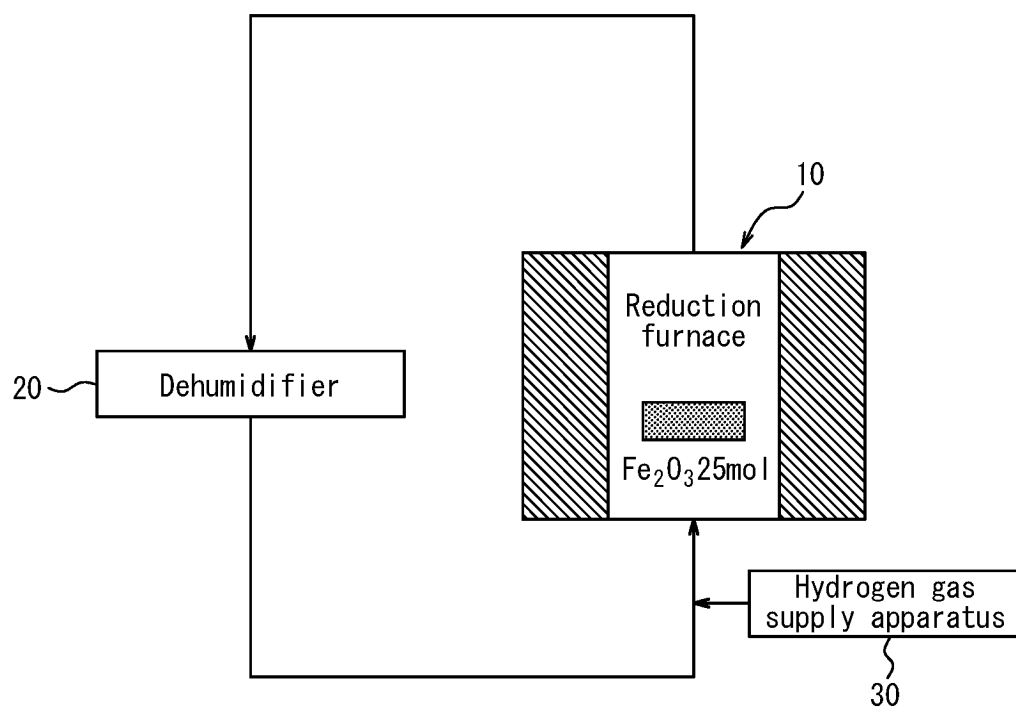


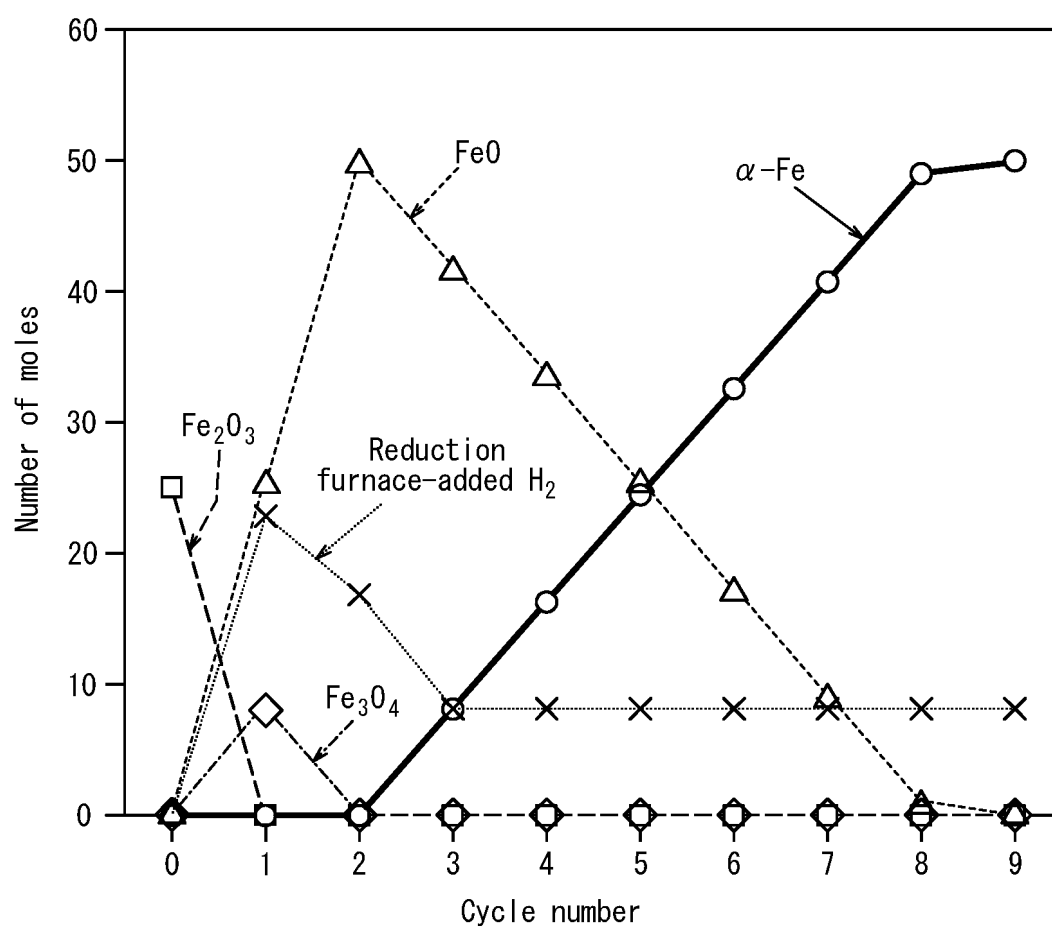
FIG. 8

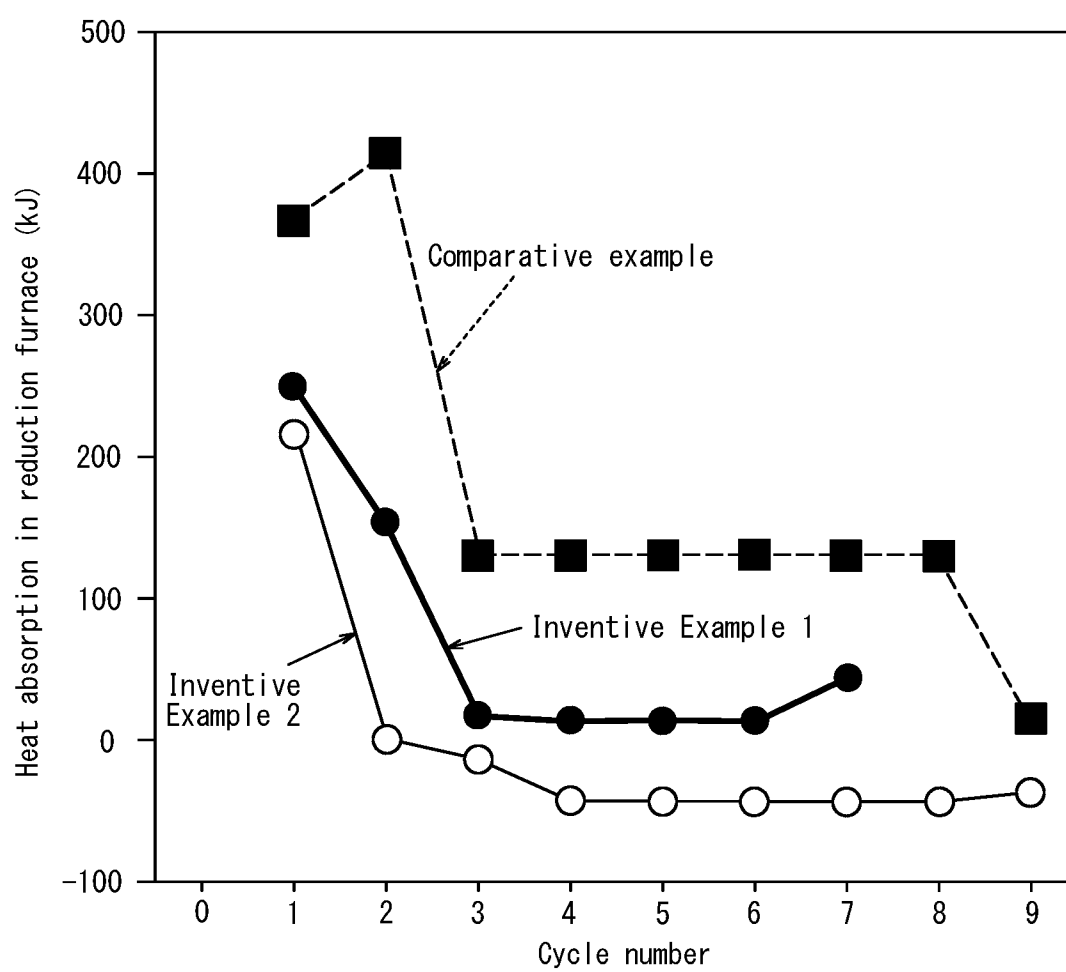
FIG. 9

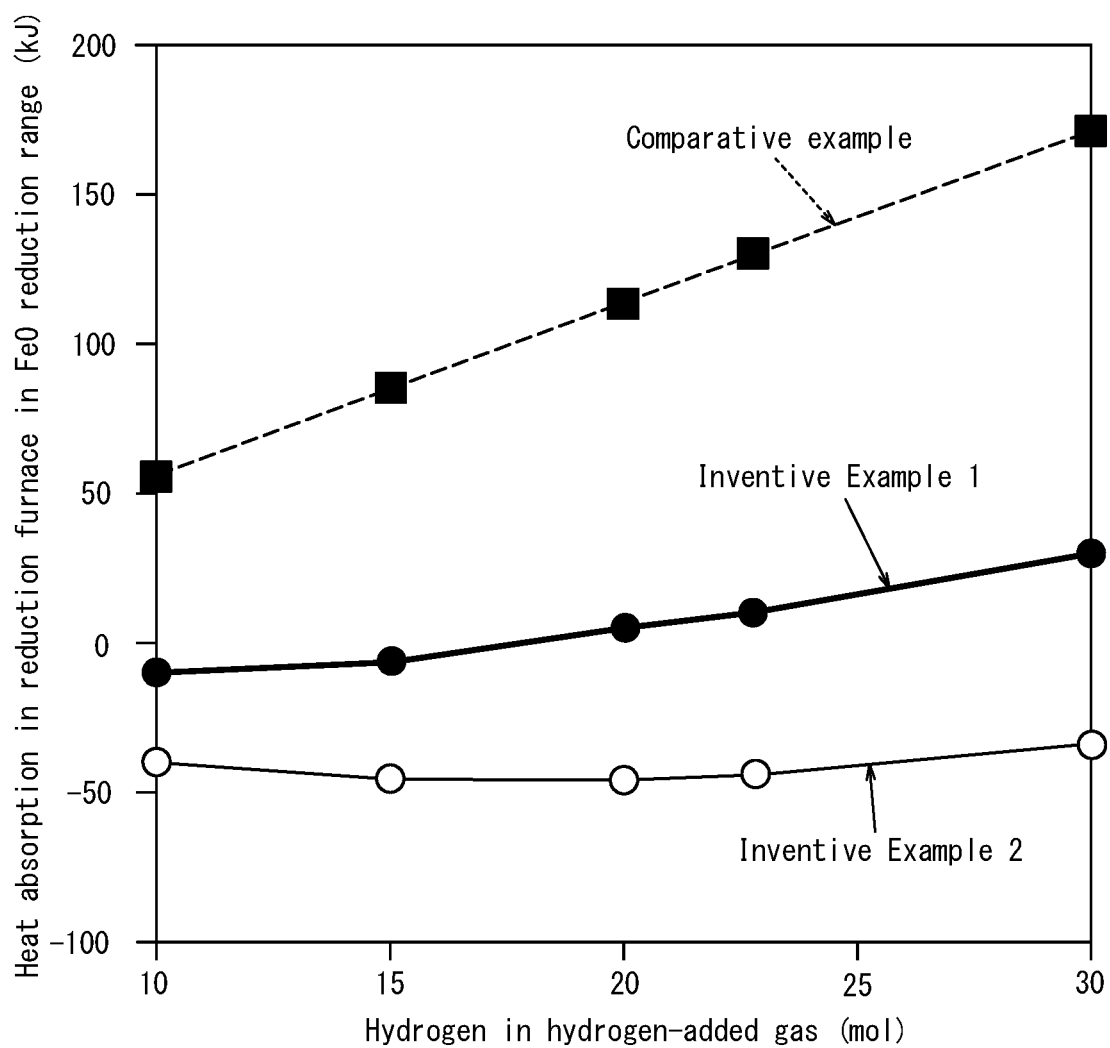
FIG. 10

FIG. 11

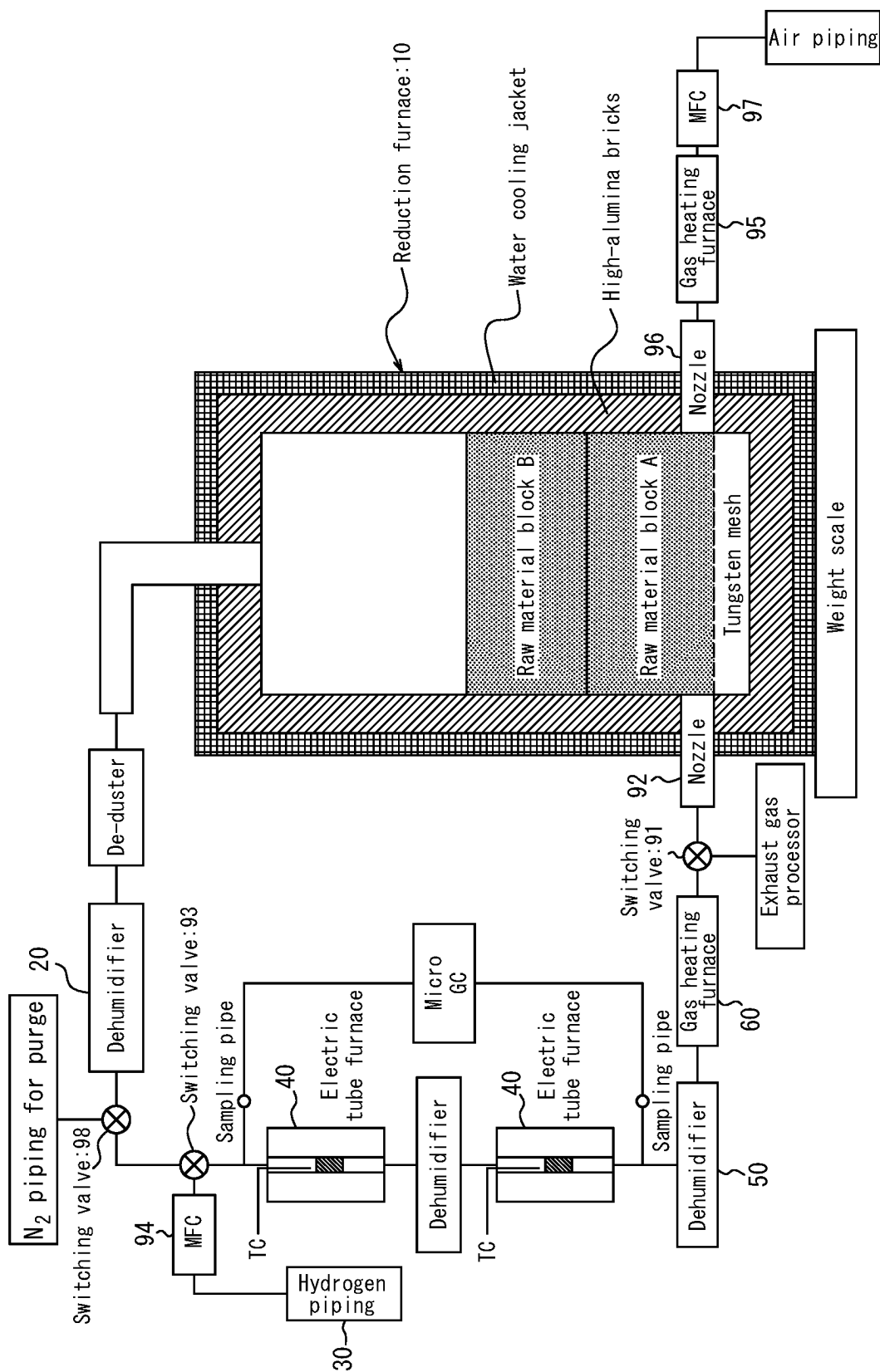
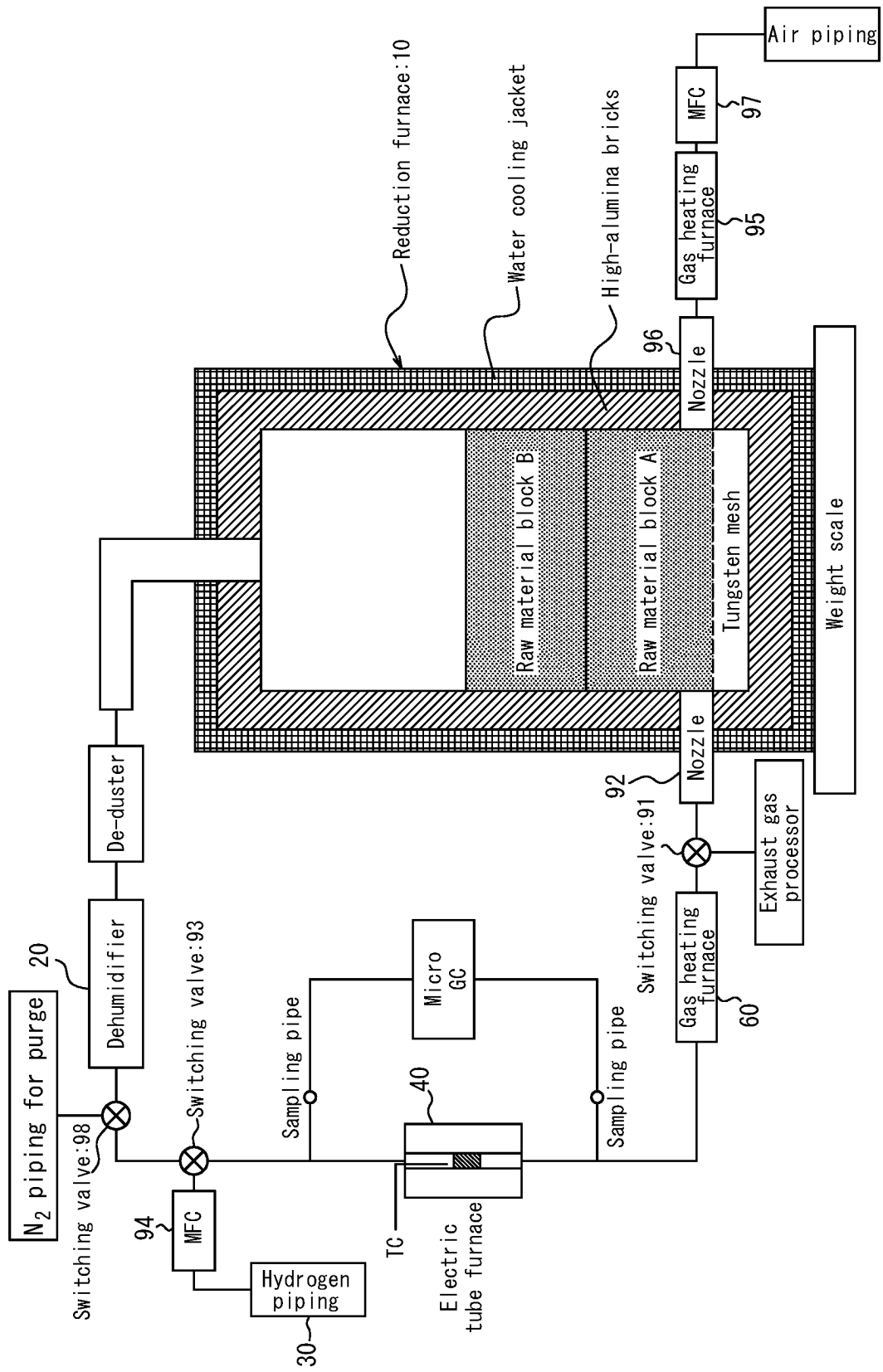


FIG. 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/030590

A. CLASSIFICATION OF SUBJECT MATTER

C21B 5/06(2006.01)i; *C21B 5/00*(2006.01)i; *C21B 11/00*(2006.01)i

FI: C21B5/06; C21B11/00; C21B5/00 321; C21B5/00 311

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)

C21B5/06; C21B5/00; C21B11/00

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2023

Registered utility model specifications of Japan 1996-2023

Published registered utility model applications of Japan 1994-2023

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.
X	JP 6843490 B1 (SEKISUI CHEMICAL CO., LTD.) 17 March 2021 (2021-03-17) claims, paragraphs [0015]-[0021], [0040]-[0047], [0054]-[0071], [0085], fig. 1-5	1, 2, 11-13
Y		3-13
A		14, 15
X	CN 106399617 A (JIANGSU PROVINCE METALLURGICAL DESIGN INSTITUTE CO., LTD.) 15 February 2017 (2017-02-15) claims, paragraphs [0032]-[0065], fig. 1	1, 2, 11, 13
A		3-10, 12, 14, 15
Y	JP 9-100108 A (COSMO ENGINEERING CO., LTD.) 15 April 1997 (1997-04-15) claims, paragraph [0007], fig. 1	3-13
A	JP 2016-524654 A (CCP TECHNOLOGY GMBH) 18 August 2016 (2016-08-18) entire text, all drawings	1-15
A	US 4265868 A (KOPPERS COMPANY, INC.) 05 May 1981 (1981-05-05) entire text, all drawings	1-15

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

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“&” document member of the same patent family

Date of the actual completion of the international search

06 November 2023

Date of mailing of the international search report

14 November 2023

Name and mailing address of the ISA/JP

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Japan

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Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/030590

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2012-72473 A (JFE STEEL CORP.) 12 April 2012 (2012-04-12) claims	14, 15

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/030590

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JP 6843490 B1	17 March 2021	US 2022/0305439 A1 claims, paragraphs [0030]- [0054], [0103]-[0120], [0139]- [0187], [0228]-[0230], fig. 1-5 WO 2022/029886 A1 EP 3978434 A1 CN 114302970 A	
CN 106399617 A	15 February 2017	(Family: none)	
JP 9-100108 A	15 April 1997	(Family: none)	
JP 2016-524654 A	18 August 2016	US 2016/0083810 A1 WO 2014/198635 A1 EP 3008218 A1 DE 102013009993 A TW 201510227 A AU 2014280344 A CA 2913725 A CN 105283562 A KR 10-2016-0018813 A EA 201690017 A AR 96605 A MX 2015017131 A ZA 201508565 B BR 112015031150 A	
US 4265868 A	05 May 1981	CA 1106178 A1	
JP 2012-72473 A	12 April 2012	(Family: none)	

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

REFERENCES CITED IN THE DESCRIPTION

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