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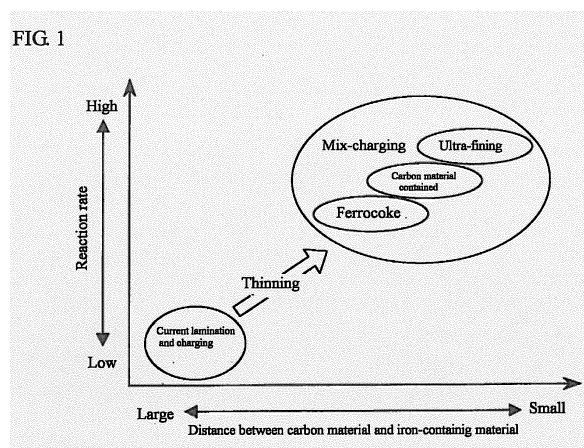
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(54) **CARBON MATERIAL-CONTAINING GRANULATED PARTICLES FOR MANUFACTURING SINTERED ORE, PRODUCTION METHOD THEREFOR, AND PRODUCTION METHOD FOR SINTERED ORE**

(57) Small lump coke having a particle size of 3-15 mm as a carbon material core, iron ore powder having a particle size of not more than 250 μm to be an outer layer and CaO-containing raw material are charged into a pelletizer and mixed and granulated therein to obtain quasi particles formed by coating the carbon material core with the outer layer (carbon material-containing granulated particles). Also, a sintering raw material obtained by mixing the carbon material-containing granulated particles with normal granulated particles is charged onto a pallet of a sintering machine to form a charged layer, and a sintered ore (carbon material-containing sintered ore) is produced by sintering heat of a carbon material included in the normal granulated particles. Thus, the carbon material-containing sintered ore having the iron-containing raw material and the carbon material arranged close to each other is obtained without using metallic iron-containing iron oxide powder such as iron-making dust, mill scale or the like and without restricting production volume.

FIG. 1



Description

TECHNICAL FIELD

[0001] This invention relates to a production technique of sintered ore used as an iron-making material for a blast furnace or the like, and more particularly to carbon material-containing granulated particles used in the production of sintered ore, a method for producing the same and a production method for sintered ore using the carbon material-containing granulated particles.

RELATED ART

[0002] In the iron-making method with a blast furnace are mainly used iron-containing materials such as iron ores, sintered ores and the like as an iron source at the moment. The sintered ore is a type of agglomerated ores obtained by adding a proper amount of water to a raw granulating material made from iron ores having a particle size of not more than 10 mm, an auxiliary raw material of SiO₂-containing material such as silica stone, serpentinite, refined nickel slag or the like and CaO-containing raw material such as limestone, quicklime or the like, and a solid fuel (carbon material) of a coagulating material such as coke breeze, anthracite or the like, mixing and granulating them with a drum mixer or the like to form a sintering raw material of quasi particles, charging the sintering raw material onto a circularly moving pallet in a sintering machine, burning the carbon material contained in the quasi particles to perform sintering, crushing and granulating the resulting sintered cake and then recovering particles of not less than a given particle size as a product.

[0003] As the agglomerated ore are recently watched ones formed by closely arranging an iron source such as iron ores, dusts or the like to a carbon material such as coke or the like. It is because when the iron source such as iron ores or the like and the carbon material are closely arranged in one agglomerated ore, reduction reaction (exothermic reaction) at the side of the iron source and gasification reaction (endothermic reaction) at the side of the carbon material are repeatedly caused at a faster rate, whereby not only an iron-making efficiency can be increased but also a temperature inside a furnace such as blast furnace or the like can be decreased.

[0004] For example, Patent Document 1 discloses an agglomerated ore formed by adding a carbon material such as coal, coke or the like and starch to an iron-containing powder generated in iron-making steps such as blast furnace/converter dust, rolling scale, slug, iron pore powder or a mixture thereof, mixing and kneading them, feeding a starch solution in a granulating machine and granulating them. In the agglomerated ore disclosed in Patent Document 1, however, the carbon material in pellets is burnt out in the production of sintered ore, so that the close arrangement of the iron-containing material such as iron ore or the like to the carbon material is not actually attained. When the particle sizes of the iron ore and the carbon material are merely made small for the purpose of closely arranging them, a moving resistance of a gas propagating heat becomes too large, and hence slowdown in the reaction rate is inversely caused to deteriorate the iron-making efficiency.

[0005] There are proposed some techniques for the purpose of closely arranging the iron ores and the carbon material (see, for example, Patent Documents 2-5). In these techniques, the iron-containing material such as iron ores or the like is mixed with the carbon material such as coke or the like and agglomerated by hot forming and then used as a raw iron-making material in a blast furnace or the like at raw particle state without firing. However, these agglomerates are lacking in the strength and are violent in the powdering because they are non-fired ones comprised of a uniform mixture or multi-stratified granulates, so that there is a problem that when the agglomerates are charged into a blast furnace or the like, powdering formation through degradation through dehydration or reduction degradation is caused to block air permeability in the blast furnace and hence the use amount is restricted.

[0006] As a technique for solving the problems in the techniques of Patent Documents 2-5, for example, Patent Document 6 proposes an agglomerated ore for iron-making formed by making cores from a starting material containing not less than 5 wt% of metallic iron and/or not less than 5% of carbon, enveloping the cores with a starting material containing not less than 10 wt% of metallic iron and not more than 5 wt% of carbon to form one or more outer peripheral layers and firing in an oxidizing atmosphere of 300-1300°C. In the agglomerated ore disclosed in Patent Document 6, however, metallic iron is necessary to be used as a starting material, so that there is a quantitative restriction in the starting material used, and there is a problem that there is a restriction in an amount capable of producing the agglomerated ore for iron-making.

[0007] Therefore, a technique on a carbon material-containing agglomerated ores is proposed as a technique for overcoming the problems of Patent Documents 1-6. For example, Patent Document 7 discloses a technique wherein a carbon material-containing agglomerated ore is obtained by coating a carbon material core of small lump coke with a metallic iron-containing iron oxide powder such as iron-making dusts, mill scale or the like with a granulating machine to form iron oxide shells having a low oxidation degree, subjecting to an oxidation treatment by heating in air at a temperature of not lower than 200°C but lower than 300°C for 0.5-5 hours to form a hard thin layer made of iron oxide having a high oxidation degree onto only the surfaces of the iron oxide shells, and Patent Document 8 discloses a

technique of producing an agglomerated ore containing coke breeze of not more than 3 mm at a dispersed state in iron oxide powder or iron ore powder by mixing and granulating iron oxide powder or iron ore powder such as iron-making dusts or mill scale and a carbon material in a granulating machine and coating outer surfaces of the granulates with metallic iron-containing iron oxide powder to form iron oxide shells with a low oxidation degree.

[0008] Also, Non-patent Document 1 reports evaluation results of reactivity in an atmosphere inside a blast furnace on carbon material-containing sintered ore obtained by coating anthracite as a core with pellet feeds to form a green ball, applying anthracite onto a surface of the green ball, charging the green balls onto ores placed on a floor of a pan type testing device and charging a sintering raw material thereon to perform sintering.

PRIOR ART DOCUMENTS

PATENT DOCUMENTS

[0009]

Patent Document 1: JP-A-2001-348625

Patent Document 2: Japanese Patent No. 3502008

Patent Document 3: Japanese Patent No. 3502011

Patent Document 4: JP-A-2005-344181

Patent Document 5: JP-A-2002-241853

Patent Document 6: JP-A-H10-183262

Patent Document 7: JP-A-2011-195943

Patent Document 8: JP-A-2011-225926

NON-PATENT DOCUMENT

[0010] Non-patent Document 1: CAMP-ISIJ vol. 24(2011), 194

SUMMARY OF THE INVENTION

TASK TO BE SOLVED BY THE INVENTION

[0011] According to the techniques disclosed in Patent Documents 7 and 8 can be obtained carbon material-containing agglomerated ores having a proper size and a sufficient strength as an iron-making material and having a structure in which an iron-containing material and a carbon material are closely arranged and iron-making reaction is easily caused and a low-temperature reduction can be performed. However, these techniques have problems that the wettability to the carbon material becomes poor when the amount of metallic iron is large, so that the coating of surfaces of carbon material cores with the metallic iron-containing iron oxide powder is difficult, and the iron oxide shells with a low oxidation degree are formed, and an oxidation treatment is required after the granulation to increase the production cost, and further there is a restriction in the production volume because the generation amount of the metallic iron-containing iron oxide powder such as iron-making dusts, mill scale or the like is small.

[0012] Also, the technique of Non-patent Document 1 has a problem that since the sintering raw material is not existent around the green ball but anthracite is applied onto the surface of the green ball, the pellet feed layer coated with anthracite are melted to expose anthracite therein, which is burn out and dispensed.

[0013] This invention is made in view of the above problems inherent to the conventional techniques and is to provide carbon material-containing granulated particles capable of providing carbon material-containing agglomerated ore (sintered ore), in which iron-containing raw material and carbon material are arranged close to each other, without using metallic iron-containing iron oxide powder such as iron-making dusts, mill scale and the like and hence restricting production volume, and a method for producing the same as well as a method for producing sintered ore by using the carbon material-containing granulated particles.

SOLUTION FOR TASK

[0014] The inventors have made various studies for solving the above task. As a result, it has been found that as carbon material-containing granulated particles in the production of sintered ore are granulated quasi particles by using a small lump coke as a carbon material core in a central part of the particle and using iron ore powder added with CaO-containing material of a melting point conditioner and having a particle size of not more than 250 μm (pellet feed (PF)) as an outer layer starting material and hence it is effective to produce sintered ore (agglomerated ore) by charging these

particles into a sintering machine as a part of a sintering raw material, and the invention has been accomplished.

[0015] The invention lies in carbon material-containing granulated particles in the production of sintered ore being quasi particles comprised of a carbon material core and an outer layer formed around the carbon material core and composed mainly of iron ore powder and CaO-containing raw material.

[0016] In the carbon material-containing granulated particles according to the invention; the iron ore powder is a pellet feed having a particle size of 10-1000 μm .

[0017] The pellet feed in the carbon material-containing granulated particles according to the invention has a particle size of not more than 250 μm .

[0018] In the carbon material-containing granulated particles according to the invention, the outer layer has a melting point of not lower than 1200°C but not higher than 1500°C.

[0019] Also, in the carbon material-containing granulated particles according to the invention, a carbon material as the carbon material core is coke particles having a particle size of not less than 3 mm.

[0020] The outer layer in the carbon material-containing granulated particles according to the invention has a thickness of not less than 2 mm.

[0021] The carbon material-containing granulated particles according to the invention have a particle size of not less than 8 mm.

[0022] Further, the invention is a method for producing the carbon material-containing granulated particles described in any of the above, i.e. a method for producing carbon material-containing granulated particles in the production of sintered ore, which comprises charging a carbon material core, iron ore powder to be an outer layer and CaO-containing raw material as a melting point conditioner into a pelletizer and mixing and granulating them to obtain quasi particles formed by coating the carbon material core with the outer layer.

[0023] Moreover, the invention is a method for producing a carbon material-containing sintered ore, which comprises mixing the carbon material-containing granulated particles described in any of the above with normal granulated particles to form a sintering raw material, charging it on a pallet of a sintering machine to form a charged layer, and producing a sintered ore by combustion heat of a carbon material included in the normal granulating particles.

[0024] In the production method of the carbon material-containing sintered ore according to the invention, a large number of the carbon material-containing granulated particles are charged into a lower layer side of the charged layer.

[0025] Also, in the production method of the carbon material-containing sintered ore according to the invention, the normal granulated particles are granulated in a drum mixer and have a particle size smaller than that of the carbon material-containing granulated particles.

EFFECT OF THE INVENTION

[0026] According to the invention, the cheap iron ore powder having a high purity (pellet feed (PF)) is used instead of iron oxide powder having a low oxidation degree such as various iron-making dusts, mill scale and the like generated in an iron foundry and having limits in the production volume, so that the carbon material-containing granulated particles can be produced cheaply without limiting the production volume and requiring oxidation treatment. Also, the carbon material-containing granulated particles according to the invention can be converted to a sintered ore with the conventional sintering machine, so that a large amount of carbon material-containing sintered ore can be produced cheaply. Further, the carbon material-containing sintered ore according to the invention has a sufficient strength for use as a raw material for a blast furnace or the like and a structure of arranging iron-containing material and carbon material close to each other, so that it contributes to the increase of iron-making reaction efficiency, the lowering of the temperature inside the furnace, the reduction of fuel ratio and the decrease of production cost.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

FIG. 1 is a view explaining an influence of a distance between iron-containing material and carbon material upon a reaction rate.

FIG. 2 is a view explaining an iron-making reaction between iron-containing material and carbon material (reduction reaction, gasification reaction) in comparison with phenomenon inside the conventional blast furnace and use of carbon material-containing sintered ore according to the invention.

FIG. 3 is a view explaining reduction reaction and gasification reaction in carbon material-containing sintered ore.

FIG. 4 is a Fe_2O_3 -CaO binary phase diagram.

FIG. 5 is a view explaining reaction in an outer layer during the sintering of carbon material-containing granulated particles.

FIG. 6 is SiO_2 - Fe_2O_3 -CaO ternary phase diagram.

FIG. 7 is a view illustrating an example of a method for producing carbon material-containing granulated particles and carbon material-containing sintered ore according to the invention.

FIG. 8 is a view illustrating a sintering test pan used in Examples.

FIG. 9 is appearance photographs of sintered ore (agglomerated ore) obtained in sintering experiments of Examples.

FIG. 10 is a photomicrograph of a section of carbon material-containing sintered ore according to the invention.

FIG. 11 is a view showing EPMA analytical results of a section of carbon material-containing sintered ore according to the invention.

FIG. 12 is a view illustrating reducibility index RI and reduction degradation index RDI of carbon material-containing sintered ore according to the invention in contrast with the normal sintered ore.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0028] For example, according to an iron-making method with a blast furnace, pig iron is produced by heating and reducing an iron-containing material such as iron ore, sintered ore or the like by combustion heat of a carbon material such as coke or the like. In this case, it is common to charge iron-making materials from a top of the blast furnace by charging the iron-containing material and the carbon material, each of which being granulated to a size of about 20-40 mm, in a laminated state separately. It is considered that as the thickness of each of the iron-containing material layer and the carbon material layer is made thinner, the distance between the iron-containing material and the carbon material becomes smaller, and hence the reduction reaction rate can be increased. As previously mentioned, however, when the iron-containing material and the carbon material are simply mixed and charged, moving resistance of a gas as a heat transfer means becomes larger and rather the reaction rate becomes slower.

[0029] As a method of increasing the reaction rate is recently examined a technique for ferrocoke, carbon material-containing agglomerated ore, ultra-fining and so on as shown by a conceptual diagram in FIG. 1. Here, the ferrocoke is a technique wherein a carbon material and iron ores (iron-containing material) are mixed and baked to form an iron-making raw material, and the carbon material-containing agglomerated ore is a technique wherein a carbon material is filled and included into iron ore to form an iron-making raw material, and the ultra-fining is a technique wherein a carbon material is mainly fined and used.

[0030] The thinking for these techniques is based on a theory shown in FIG. 2. In FIG. 2 is shown a relationship among heat exchange, reduction reaction of iron ores and gasification reaction of carbon material (coke) when the iron ores and carbon material are arranged closely to each other. At the side of the iron ores is caused reduction reaction by reacting Fe_2O_3 with CO to produce Fe and CO_2 . This reaction is an exothermic reaction. On the other hand, a gasification reaction (gas reforming reaction), which is called as "Boudoir reaction" by reacting CO_2 with C to produce CO , is caused at the side of the carbon material. This reaction is an endothermic reaction. (Hereinafter, both the reactions are called as "iron-making reaction".)

[0031] As shown in FIG. 2(a), when the iron-containing material and the carbon material are charged into a blast furnace in a laminated state, the reduction reaction as an exothermic reaction and the gasification reaction as an endothermic reaction are caused at separate places, so that the movement of a gas is necessary for heat transfer required for the above reactions and supply of CO and CO_2 . On the contrary, as shown in FIG. 2(b), when the iron ore are arranged close to the carbon material, the reduction reaction as an exothermic reaction and the gasification reaction as an endothermic reaction are repeated at a faster rate, whereby the iron-making reaction efficiency is improved.

[0032] Therefore, it is considered that it is effective to locate the iron-containing material and the carbon material close to each other or closely arrange the iron-containing material and the carbon material for enhancing the iron-making reaction. Under such a thinking, a carbon material-containing agglomerated ore formed by previously mixing the iron-containing material and the carbon material so as to embed the carbon material in the iron-containing material is an ultimate form.

[0033] In the carbon material-containing agglomerated ore formed by closely arranging the carbon material and the iron-containing material, when heat required for the gasification reaction arrives at the inside of the carbon material-containing agglomerated ore, as shown in FIG. 3, reduction reaction of reducing Fe_nO_m with CO generated by the gasification reaction is caused and next gasification reaction is caused with CO_2 generated by the reduction reaction, whereby the reactions are caused serially from the inside of the agglomerated ore toward the outside thereof and consequently Fe_nO_m inside the ore is sequentially self-reduced to produce Fe (metallic iron). As mentioned above, the reduction reaction and the gasification reaction are promoted at the inside of the agglomerated ore, so that heat supply from exterior is reduced and hence the temperature inside the furnace can be lowered.

[0034] In order to achieve the above thinking, however, it is necessary that the carbon material-containing agglomerated ore (sintered ore) can be produced stably. In the production of the carbon material-containing agglomerated ore, however, there is a problem that small lump coke included in granulated particles (quasi particles) is burnt and lost during the sintering. The carbon material-containing sintered ore cannot be obtained stably as long as this problem cannot be solved.

[0035] In the invention, therefore, the above problem is solved by using quasi particles, in which small lump coke is

included in its central portion as a carbon material core and coated around the periphery thereof with iron ore powder with an adjusted melting point, as carbon material-containing granulated particles in the production of a carbon material-containing agglomerated ore or in the production of sintered ore.

[0036] That is, the carbon material-containing agglomerated ore according to the invention is the same as the carbon material-containing agglomerated ore of the prior art in a point that small lump coke is used as a carbon material core in a central portion of granulated particles (quasi particles). However, the invention is different from the prior art in a point that the burning and losing of the carbon material core during the sintering is prevented by coating the periphery of the carbon material core with the iron ore powder and adding quicklime to the iron ore powder to lower a melting point and form a dense outer layer during the sintering.

[0037] As the iron ore powder, it is desirable to use pellet feed having a particle size of 10-1000 μm , preferably not more than 250 μm . The pellet feed contains not less than 90% of fine ores having a particle size of not more than 1 mm and is mainly composed of hematite or magnetite having a high quality (high Fe, low gangue) and is excellent in a point that it can be obtained cheaply in large volume.

[0038] As the iron ore powder used in the invention are used mill scale, dust recovered from converter exhaust gas (OG dust), tailing generated in ore dressing and so on in addition to the pellet feed, or a mixture thereof with the pellet feed, as long as the particle sizes thereof are within the above range.

[0039] However, a melting point of magnetite, particularly high-quality magnetite is as high as about 1580°C as seen from Fe_2O_3 -CaO binary phase diagram shown in FIG. 4, which is considerably higher than a sintering temperature suitable for obtaining a high quality sintered ore, so that it is not melted at a normal sintering temperature or it does not cause sintering reaction.

[0040] Therefore, the invention lies in that the iron ore powder is added with CaO-containing material to lower a melting point of the outer layer and early fused at a temperature of the sintering (not lower than 1200°C) to form a fusion layer and the burning and losing of the carbon material core included in the carbon material-containing granulated particles is prevented by making the fusion layer act as an oxygen blocking layer to leave the carbon material core.

[0041] By taking the above structure can be retained the carbon material core included even if air is penetrated in the firing of the sintered ore. That is because it is considered that as shown in FIG. 5, the inside of the outer layer is basically kept by CO gas of a reducing atmosphere generated by a reaction of C forming a central core with penetrated O_2 through an oxygen blocking effect of the outer layer formed around central core of the carbon material-containing granulated particles (quasi particles), and hence the retaining of the carbon material is made possible.

[0042] The melting point to be adjusted is preferably within a range of 1200-1500°C, and more preferably within a range of 1200-1400°C from a viewpoint of promoting fusion in a sintering machine. When it is lower than 1200°C, a melt is not formed and also calcium ferrite having a highest strength and a relatively high reducing property among constituent minerals of the sintered ore is not produced. While when it exceeds 1500°C, the outer layer is not melted in the sintering machine and is not fused with a sintered ore structure composed mainly of calcium ferrite.

[0043] The addition amount of quicklime CaO added as a melting point conditioner may be determined from the Fe_2O_3 -CaO binary phase diagram shown in FIG. 4, for example, when ones having a small gangue ingredient (hematite (Fe_2O_3) is 97.7 mass%) such as Anglo American-PF is used as pellet feed (PF) of the outer layer. While, when PF having a large gangue ingredient is used, the addition amount of CaO may be determined with SiO_2 - Fe_2O_3 -CaO ternary phase diagram shown in FIG. 6 considering SiO_2 as a gangue ingredient. Moreover, quicklime acts not only as the melting point conditioner but also as a binder.

[0044] In the carbon material-containing granulated particles (quasi particles) according to the invention, it is preferable that the size of the carbon material core is not less than 3 mm and the thickness of the outer layer formed around the carbon material core is not less than 2 mm and the particle size is controlled to a proper range. Here, the size of the carbon material means a major axis of the carbon material.

[0045] That is, as the carbon material core used as a granulating core in the carbon material-containing granulated particles according to the invention, it is preferable to use a carbon material having a small volatile matter such as small lump coke and/or anthracite such as Hongay coal or the like. Particularly, the small lump coke is preferable because it is easily available and does not generate a gas even in the heating. Also, the particle size of the carbon material as a core is not fine for preventing the burning and losing of the carbon material core in the sintering process and is preferably not less than 3 mm. It is more preferably not less than 4 mm, further preferably not less than 5 mm.

[0046] The outer layer formed around the carbon material core is preferable to have a thickness of not less than 2 mm. When it is less than 2 mm, even if the dense outer layer is formed by melting in the sintering, there is a fear of not sufficiently functioning as an oxygen blocking layer and also there is a fear of not completely covering the carbon material core because many irregularities are existent in the carbon material core. In general, the granulated particles are heated from exterior, so that it is more difficult to raise the temperature toward the central side by the heating. Therefore, as the thickness of the outer layer is thicker, it is preferable to adjust the melting point of the outer layer to be lower. To this end, it is more preferably within a range of 3-7 mm.

[0047] Further, the particle size of the carbon material-containing granulated particles using the carbon material as a

core according to the invention (quasi particles) becomes 7 mm in minimum from a minimum size of the carbon material core and a minimum thickness of the outer layer but is preferable to be not less than a particle size sufficiently raising a temperature up to a particle center in the sintering process in view of a temperature distribution inside the granulated particles from a viewpoint of suppressing the reaction of the carbon material in the sintering machine because the heating of the carbon material core is not required, i.e. not less than 8 mm. It is more preferably not less than 10 mm, further preferably not less than 20 mm.

[0048] Furthermore, it is preferable to make the particle size larger than that of the normal sintering raw material (granulated particles) from a viewpoint of segregation-charging toward a lower layer side of the sintered layer when the sintering material is charged into the sintering machine as mentioned later. Here, the normal granulated particles mean quasi particles formed by granulating a raw granulating material of iron ore powder, carbon material and CaO-containing material as an auxiliary material to a particle size of 2-4 mm (arithmetic mean size) with a drum mixer, pelletizer or the like (the same hereinafter). Also, the particle size in the invention means a particle size measured by sieving.

[0049] There will be described the carbon material-containing granulated particles according to the invention and a method for producing sintered ore by using the granulated particles as a sintering raw material.

[0050] FIG. 7 shows an example of carbon material-containing granulated particles and a method for producing carbon material-containing sintered ore according to the invention. Coke particles having a size of not less than 3 mm ϕ as a nuclear particle, pellet feed (PF) comprised of iron ore powder of not more than 250 μ m and quicklime CaO as a melting point conditioner are charged into a pelletizer and mixed and granulated to form carbon material-containing granulated particles (quasi particles) having a size of not less than 8 mm ϕ . These starting materials may be added simultaneously because the granulation is performed by using a coke particle having a large size as a nucleus. Also, the charging ratio of the coke particle to PF is determined so as to render the thickness of PF layer as an outer layer to the coke particle as a nuclear particle into not less than 2 mm.

[0051] Then, the thus obtained carbon material-containing granulated particles (quasi particles) are converged with the normal granulated particles for sintering (quasi particles) obtained by agitating and granulating the normal starting materials in a drum mixer or the like, and the resulting mixture of both granulated particles is carried into a surge hopper of a sintering machine and charged from the surge hopper onto a circularly moving pallet of the sintering machine. Since the particle size of the carbon material-containing granulated particles (quasi particles) is larger than that of the normal granulated particles for sintering (quasi particles), most of the former particles are included in middle layer and lower layer sides having a sintering temperature higher than that of upper layer side due to segregation in the charging, whereby sintering reaction can be promoted sufficiently.

[0052] As mentioned above, the carbon material-containing sintered ore (agglomerated ore) according to the invention can be produced by utilizing the actual sintering machine, so that the mass production can be performed cheaply. Also, the pellet feed (PF) as a starting material for the outer layer can be obtained cheaply in large volume, so that there is no restriction in the production.

EXAMPLE 1

[0053] A sintering experiment is performed by using carbon material-containing granulated particles according to the invention obtained by coating lump coke with PF and normal granulated particles as a sintering raw material with a sintering test pan shown in FIG. 8.

[0054] The normal granulated particles (quasi particles) used in the sintering raw material are obtained by charging iron ore powder as a raw granulating material, limestone corresponding to 10 mass% of CaO as an auxiliary material and coke breeze corresponding to 5 mass% as a carbon material into a drum mixer and agitating and mixing them and granulating into particles having an arithmetic mean particle size of 2.9 mm.

[0055] As the carbon material-containing granulated particles (quasi particles) are used quasi particles T1-T7 shown in Table 1, which are obtained by charging three kinds of small lump coke each having particles sizes of 3 mm, 4 mm and 8 mm as a carbon material core, Anglo American-PF having a particle size of not more than 250 μ m (hematite (Fe₂O₃): 97.7%) as a raw material for outer layer (iron ore powder) and CaO (quicklime) as a melting point conditioner into a pelletizer and mixing them and granulating into particles having an outer layer thickness of not less than 2 mm and a particle size of 8-20 mm.

Table 1

	T1	T2	T3	T4	T5	T6	T7
Coke diameter (mm)	3	4	8	8	8	8	8
Addition amount of CaO (mass%)	10	10	10	17	17	5	-
Addition amount of coal (mass%)	-	-	-	2	-	-	-

(continued)

	T1	T2	T3	T4	T5	T6	T7
Outer layer thickness (mm)	2.5	3	6	6	6	6	6
Particle size of granulated particles (mm)	8	10	20	20	20	20	20

[0056] In the production of the carbon material-containing granulated particles, the addition amount of CaO (quicklime) is 5 mass% (T6) when a melting point is set to 1500°C, 10 mass% (T1-T3) when a melting point is set to 1450°C and 17 mass% (T4, T5) when a melting point is set to 1300°C in a Fe_2O_3 -CaO binary phase diagram shown in FIG. 5, respectively, because hematite (Fe_2O_3) of PF used as a raw material for outer layer is approximately 100%. Moreover, the granulated particles T4 in Table 1 are a comparative example that 2 mass% of a carbon material is incorporated into PF of the outer layer like the normal granulated particles. Also, T7 in Table 1 is a comparative example that the adjustment of a melting point in the outer layer is not performed (no addition of CaO, melting point: 1580°C).

[0057] The sintering experiment is performed with a sintering pan having an inner diameter of a starting material charging portion of 300 mm ϕ and a height of 400 mm shown in FIG. 8, in which the carbon material-containing granulated particles and the normal granulated particles are uniformly mixed at a mass ratio of 1:1 so as to embed the carbon material-containing granulated particles into the normal granulated particles and charged into a lower layer side 1/3 (133 mm) of the starting material charged portion, while the normal granulated particles are charged into an upper layer side 2/3 thereof (267 mm), and thereafter the upper layer surface of the charged layer is ignited, and air is sucked and introduced into the charged layer from above the test pan through a blower arranged beneath the test pan to combust the carbon material in the sintering raw material. The reason why the carbon material-containing granulated particles are embedded in the normal granulated particles and charged into the lower layer side 1/3 is due to the fact that a carbon material-containing sintered ore is obtained by promoting the sintering reaction between the normal granulated particles and the outer layer of the carbon material-containing granulated particles through only combustion heat of the normal granulated particles without combusting the carbon material as a central core. To this end, the lower layer side 1/3 is advantageous because the temperature easily rises during the sintering.

[0058] In FIG. 9 is shown an appearance photograph of the sintered ore (agglomerated ore) obtained in the above sintering experiment.

[0059] As seen from this figure, the granulated particles T1-T3, T5 and T6 adapted to the invention provide the carbon material-containing sintered ore but also are properly fused to the normal sintered ore surrounding them. In this example, it is guessed that since the sintered ore is obtained at a state of including the carbon material therein and integrally uniting with the surrounding sintered ore, there is no bad influence even if it is charged into the actual sintering machine as a sintering raw material.

[0060] On the contrary, the sintered ore obtained from the granulated particles T7 not performing the melting point adjustment are retained alone without being fused to the surrounding normal sintered ore and maintained at a raw state. Therefore, it is anticipated that when the carbon material-containing granulated particles not performing the melting point adjustment of the outer layer are charged into the actual sintering machine, the carbon material-containing sintered ore is not obtained and the firing to the surrounding sintered ore is not promoted, so that they form a breaking point of the sintered ore and hence the dusting rate is increased to largely lower the yield.

[0061] In the case of the granulated particles T4 obtained by incorporating 2 mass% of coke into the outer layer, an over-fusion state is generated and pellets are not retained in the resulting sintered ore.

[0062] In FIG. 10 is shown a photomicrograph of the carbon material-containing sintered ore T5 integrally united with the surrounding sintered ore by proper sintering. As seen from this figure, the carbon material core is coated with the PF layer in the sintered ore obtained by proper sintering, and also a fusion layer is observed between PF and the other sintering material in the surface portion of the PF layer, i.e. the PF layer is fused to the surrounding sintering raw material while coke forming the central core is retained. Therefore, there is no fear of decreasing the strength of the sintered ore due to the presence of the carbon material-containing sintered ore.

[0063] In FIG. 11 are shown results of elemental mapping with EPMA on the section of the carbon material-containing sintered ore T5 obtained by proper sintering. As seen from these results, carbon remains in the residual pellets inside the sintered ore, i.e. the included carbon material is existent. Also, Fe concentration is locally increased around the carbon and hence metallic iron is produced by reduction.

[0064] The reason of causing such a reduction reaction is considered as follows.

[0065] In the case of the carbon material-containing granulated particles, a carbon material core made from small lump coke particle is located in its central portion to form a complete carbon material-containing structure. Therefore, it is considered that reduction reaction between iron oxide powder and coke particles existing close to each other and gasification reaction of coke are simultaneously caused inside the granulated particles like the iron-making reaction of

the sintered ore shown in FIG. 2(b) and metallic iron is produced at a stage of producing the sintered ore.

[0066] Accordingly, when the carbon material-containing sintered ore according to the invention is charged into a blast furnace, it is expected that the iron-making reaction is promoted at a higher rate in a higher efficiency and at a lower temperature as compared to the normal sintered ore.

EXAMPLE 2

[0067] The sintering experiment is performed by charging the carbon material-containing granulated particles T5 produced in Example 1 and the normal granulated particles into the sintering test pan shown in FIG. 8 in the same manner as in Example 1. The reducibility index (reducibility) RI defined in JIS M8713 and reduction degradation index RDI defined in JIS M8720 are measured on the carbon material-containing sintered ore obtained from a lower layer side 1/3 of the starting material charged part (133 mm) and the normal sintered ore obtained from an upper layer side 2/3 of the starting material charged part (267 mm), respectively.

[0068] FIG. 12(a) shows a change of the reducibility index (reducibility) RI with a reduction time, from which it can be seen that the carbon material-containing sintered ore according to the invention is higher in the reducibility as compared to the normal sintered ore, or the reduction reaction rate becomes higher.

[0069] FIG. 12(b) shows a relation between the reducibility index RI and the reduction degradation index RDI of the carbon material-containing sintered ore according to the invention in comparison with a relation between the reducibility index RI and the reduction degradation index RDI of the normal sintered ore, from which it can be seen that the carbon material-containing sintered ore according to the invention is excellent in the reducibility index RI as well as reduction degradation index RDI as compared to the normal sintered ore.

INDUSTRIAL APPLICABILITY

[0070] The technique of the invention is not limited to the aforementioned examples and can be applied, for example, to a sintering technique of supplying a gaseous fuel in addition to the carbon material added to the sintering raw material as a heat source for sintering or further a sintering technique of enriching and supplying oxygen.

Claims

1. Carbon material-containing granulated particles in the production of sintered ore being quasi particles comprised of a carbon material core and an outer layer formed around the carbon material core and composed mainly of iron ore powder and CaO-containing raw material.
2. Carbon material-containing granulated particles in the production of sintered ore according to claim 1, wherein the iron ore powder is a pellet feed having a particle size of 10-1000 μm .
3. Carbon material-containing granulated particles in the production of sintered ore according to claim 2, wherein the pellet feed has a particle size of not more than 250 μm .
4. Carbon material-containing granulated particles in the production of sintered ore according to any one of claims 1-3, wherein the outer layer has a melting point of not lower than 1200°C but not higher than 1500°C.
5. Carbon material-containing granulated particles in the production of sintered ore according to any one of claims 1-4, wherein a carbon material as the carbon material core is coke particles having a particle size of not less than 3 mm.
6. Carbon material-containing granulated particles in the production of sintered ore according to any one of claims 1-5, wherein the outer layer has a thickness of not less than 2 mm.
7. Carbon material-containing granulated particles in the production of sintered ore according to any one of claims 1-6, which have a particle size of not less than 8 mm.
8. A method for producing carbon material-containing granulated particles in the production of sintered ore as claimed in any one of claims 1-7, which comprises charging a carbon material core, iron ore powder to be an outer layer and CaO-containing raw material as a melting point conditioner into a pelletizer and mixing and granulating them to obtain quasi particles formed by coating the carbon material core with the outer layer.

9. A method for producing a carbon material-containing sintered ore, which comprises mixing the carbon material-containing granulated particles as claimed in any one of claims 1-7 with normal granulated particles to form a sintering raw material, charging it into a pallet of a sintering machine to form a charged layer, and producing a sintered ore by combustion heat of a carbon material included in the normal granulated particles.

5 10. The method for producing a carbon material-containing sintered ore according to claim 9, wherein a large number of the carbon material-containing granulated particles are charged into a lower layer side of the charged layer.

10 11. The method for producing a carbon material-containing sintered ore according to claim 9 or 10, wherein the normal granulated particles are granulated in a drum mixer and have a particle size smaller than that of the carbon material-containing granulated particles.

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FIG. 1

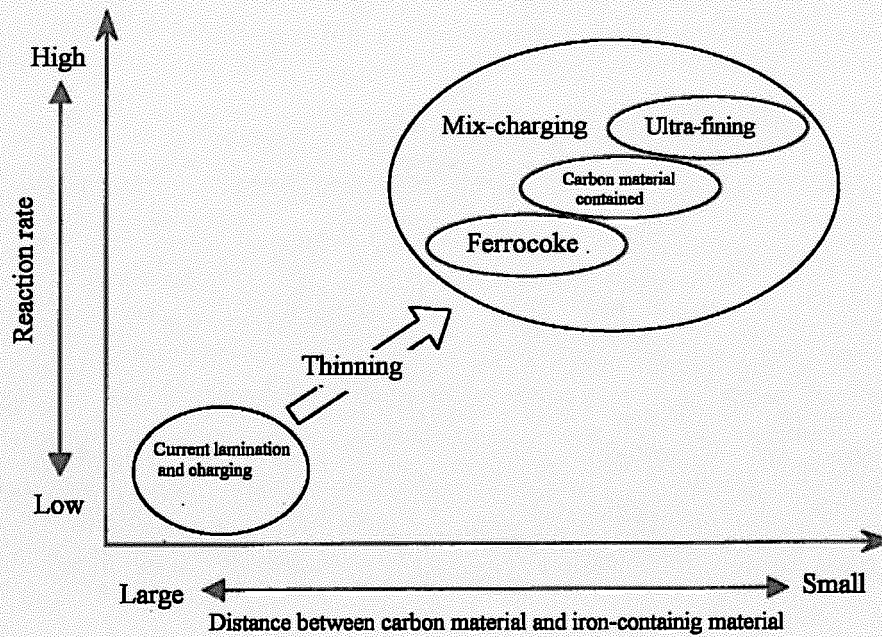


FIG. 2

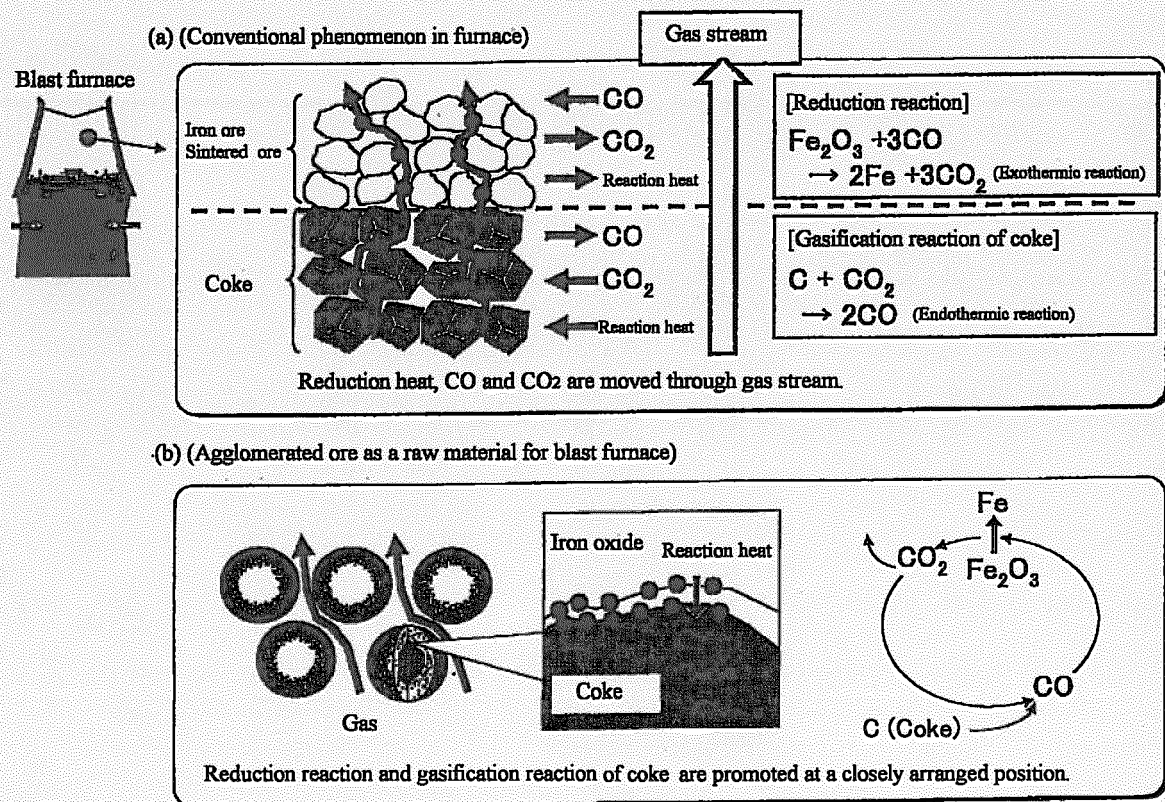


FIG. 3

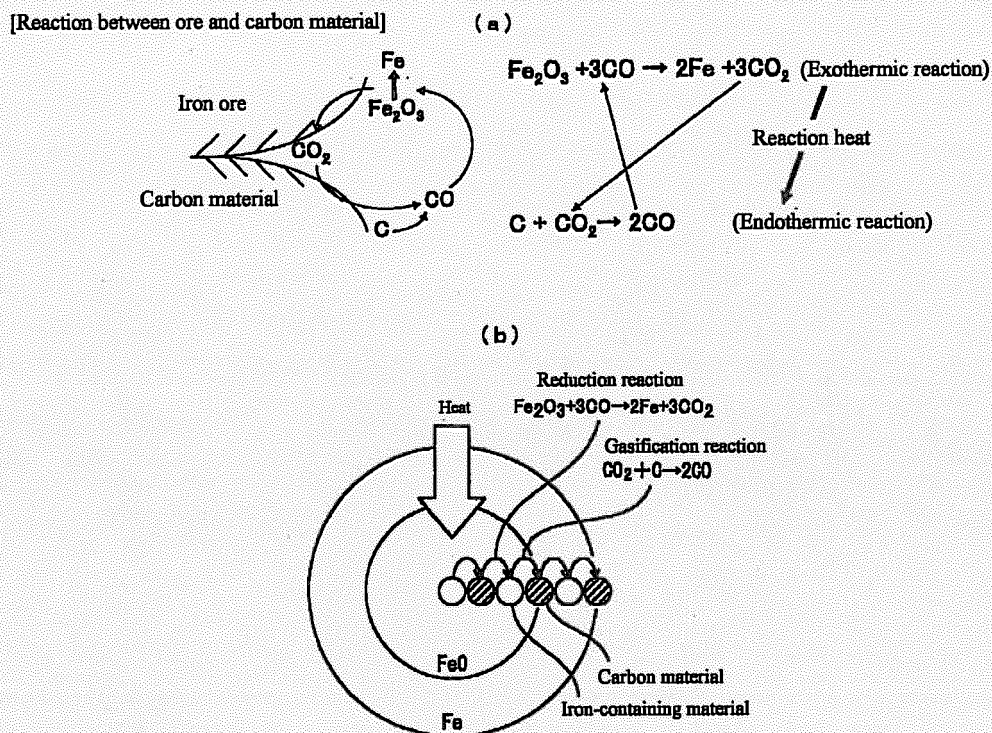


FIG. 4

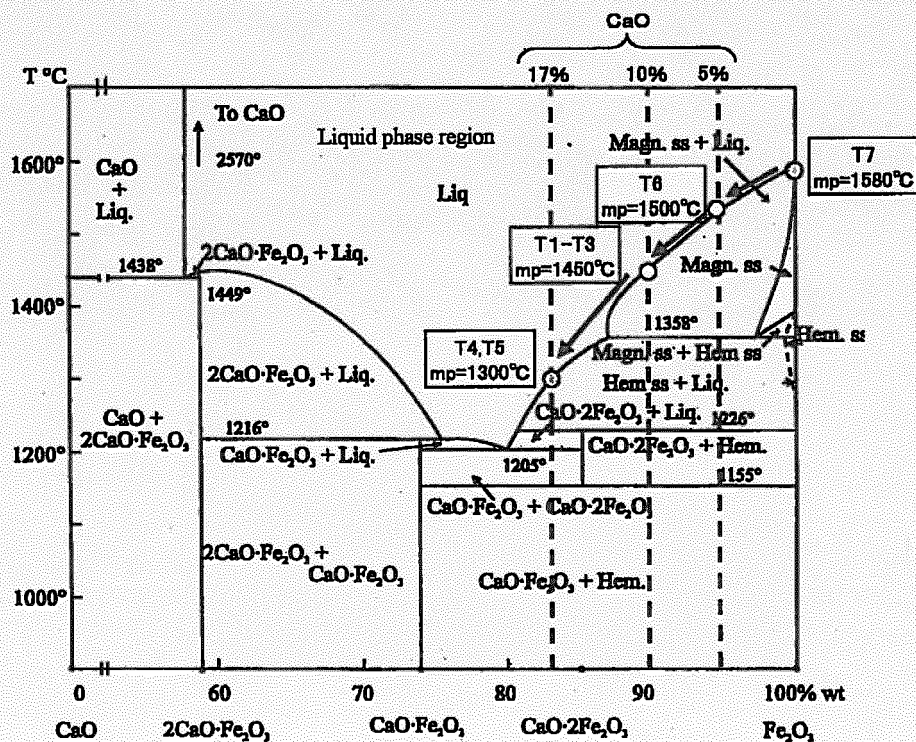


FIG. 5

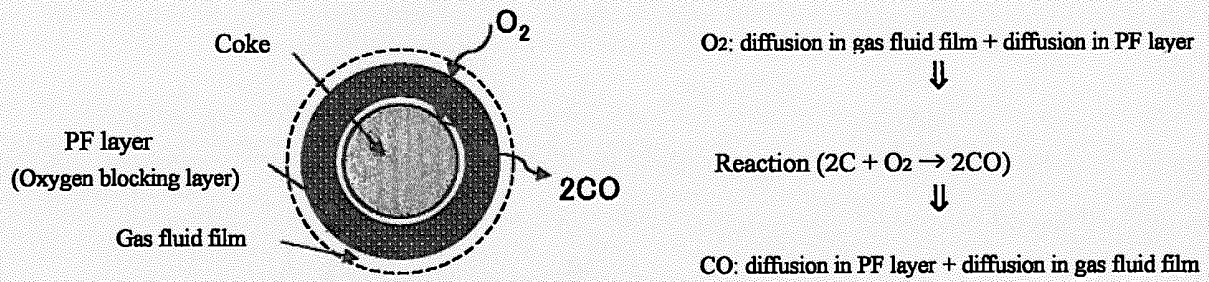


FIG. 6

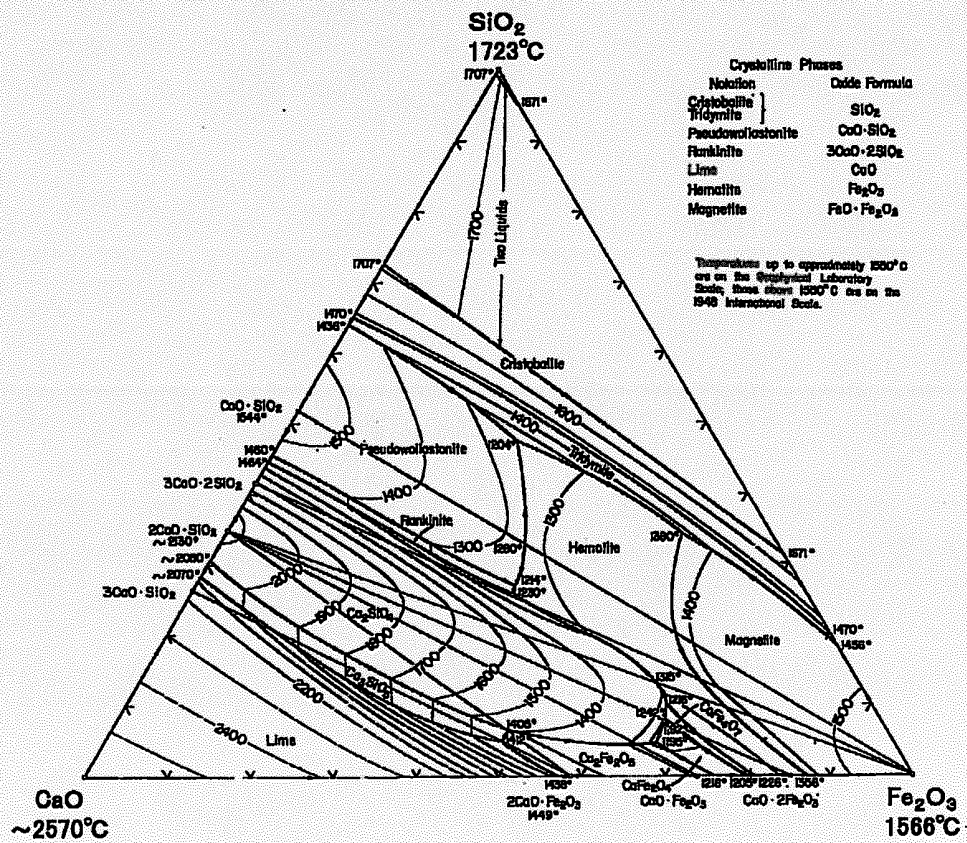


FIG. 7

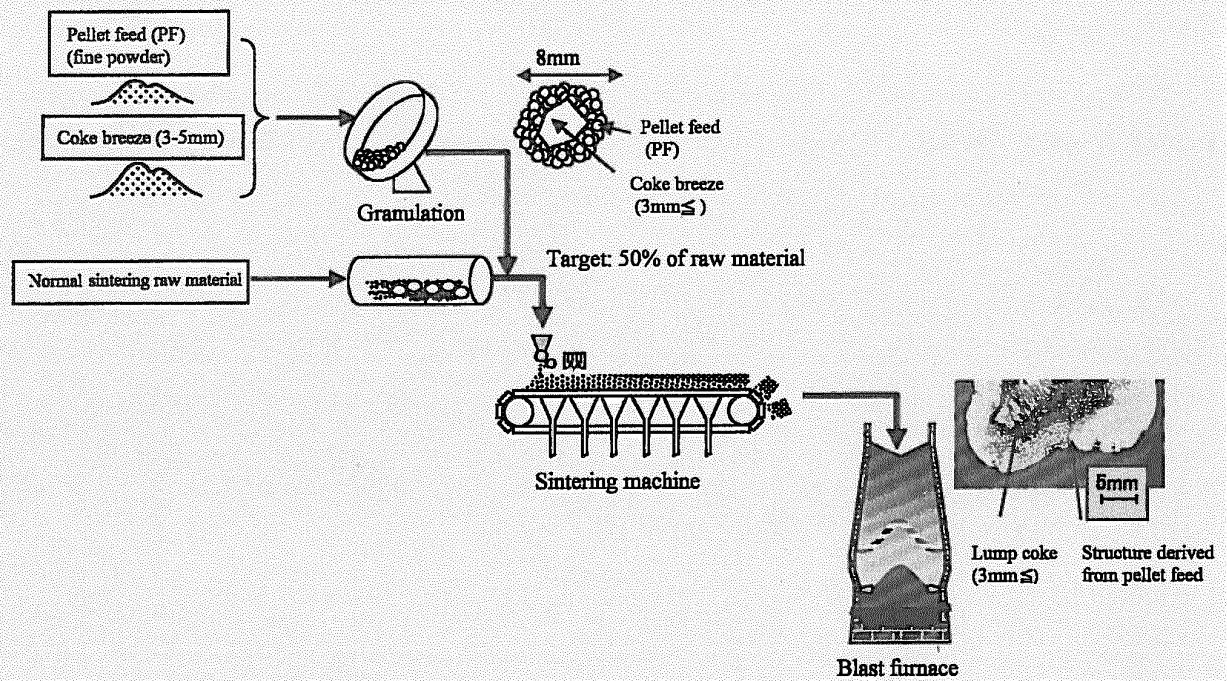


FIG. 8

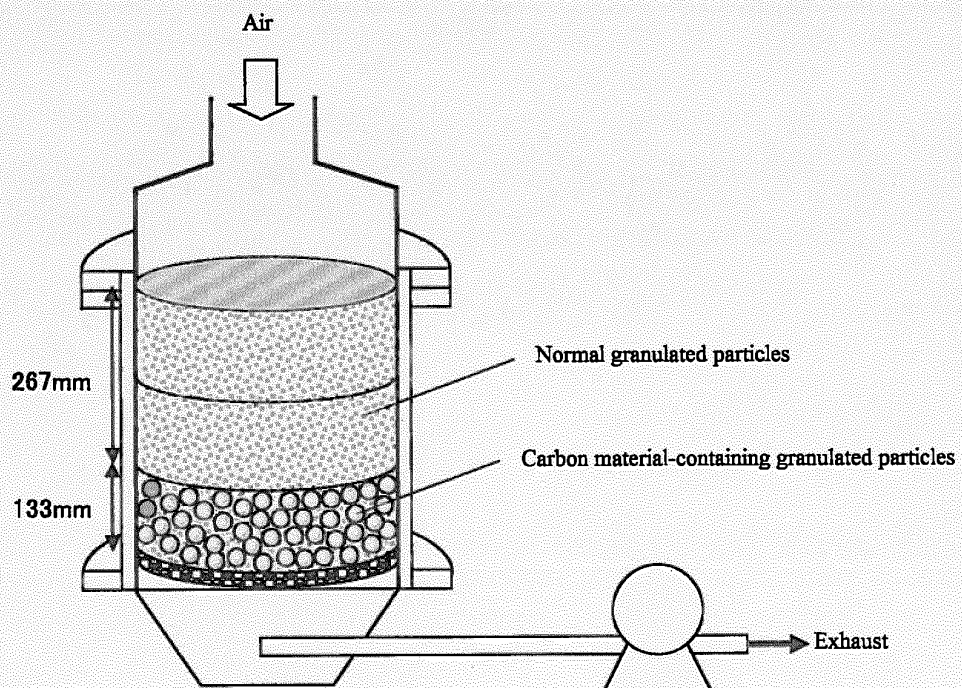


FIG. 9

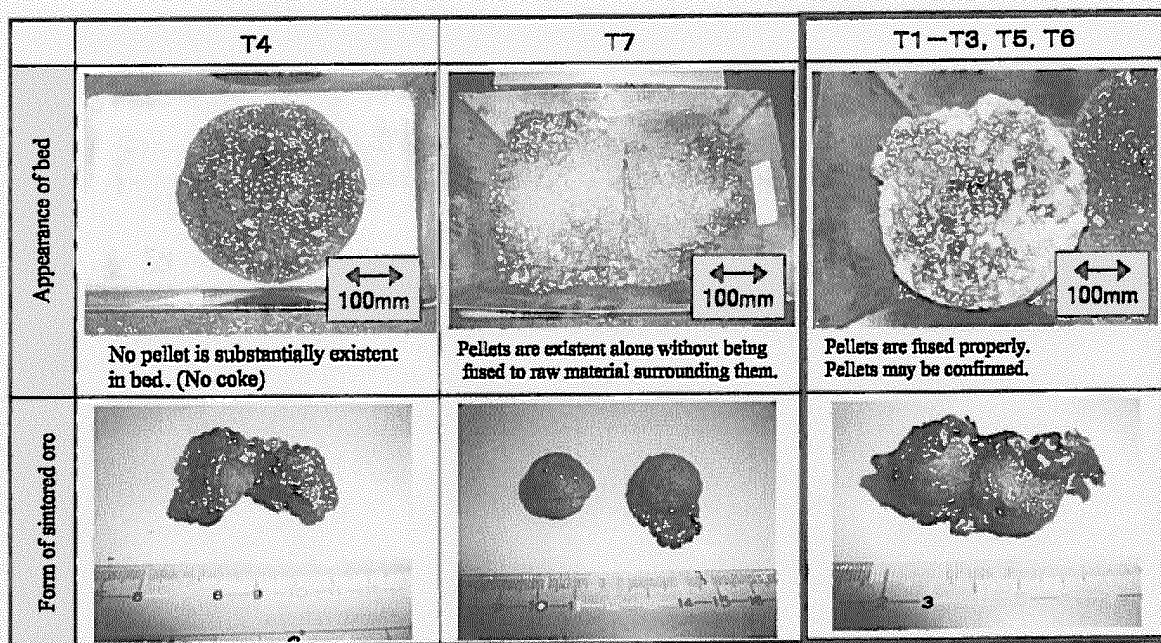


FIG. 10

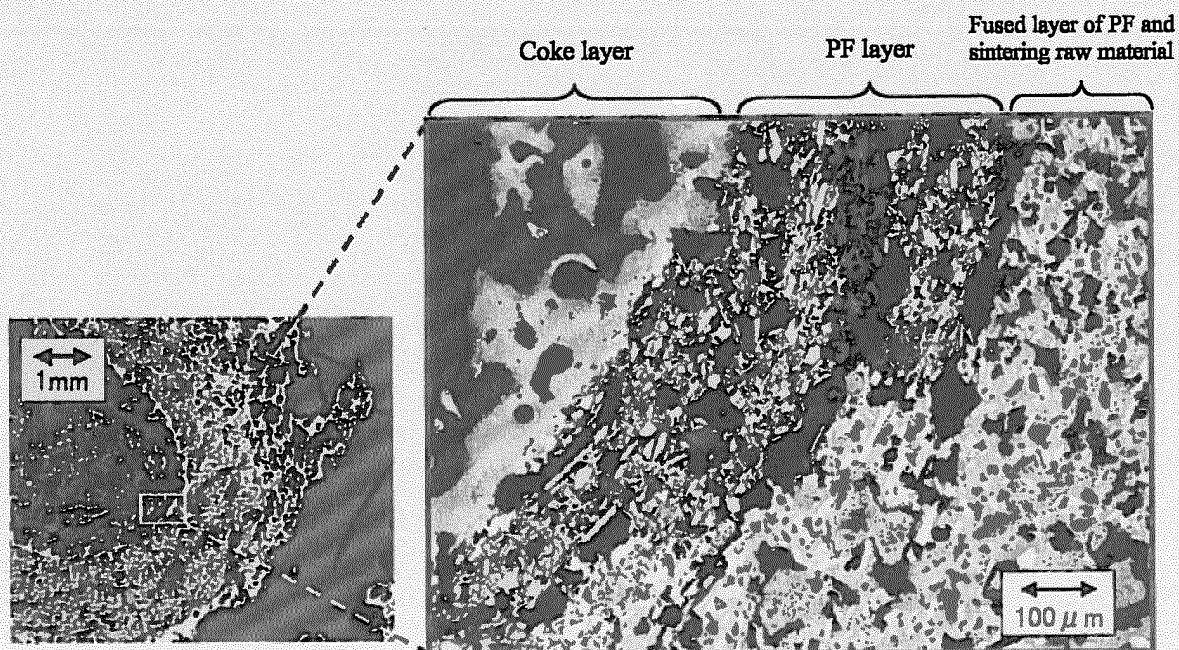


FIG. 11

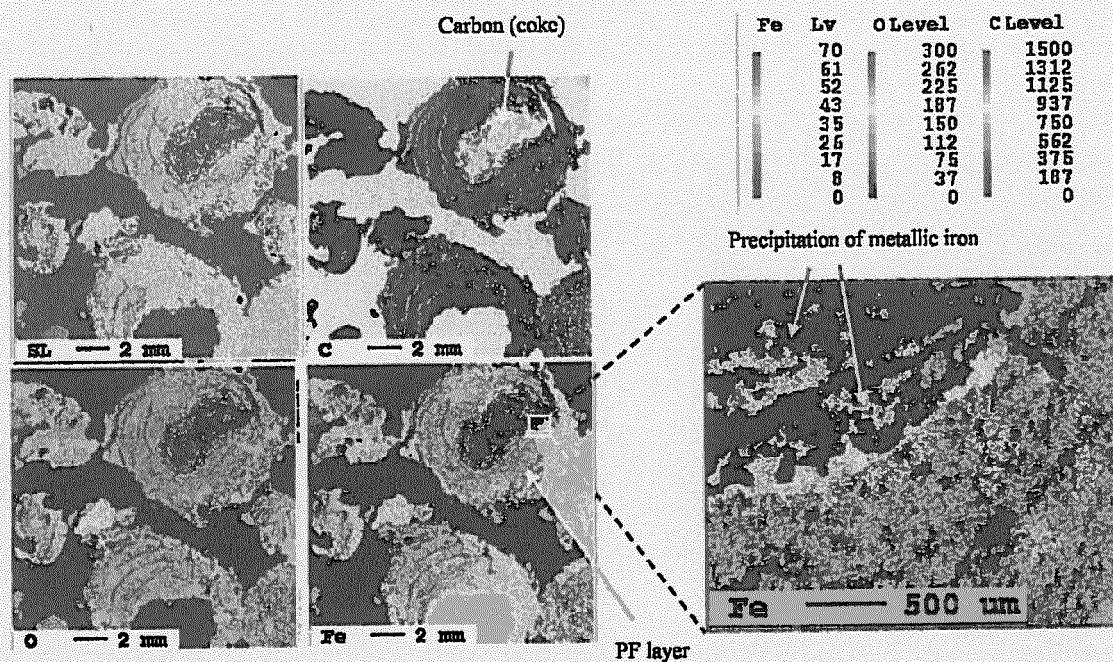
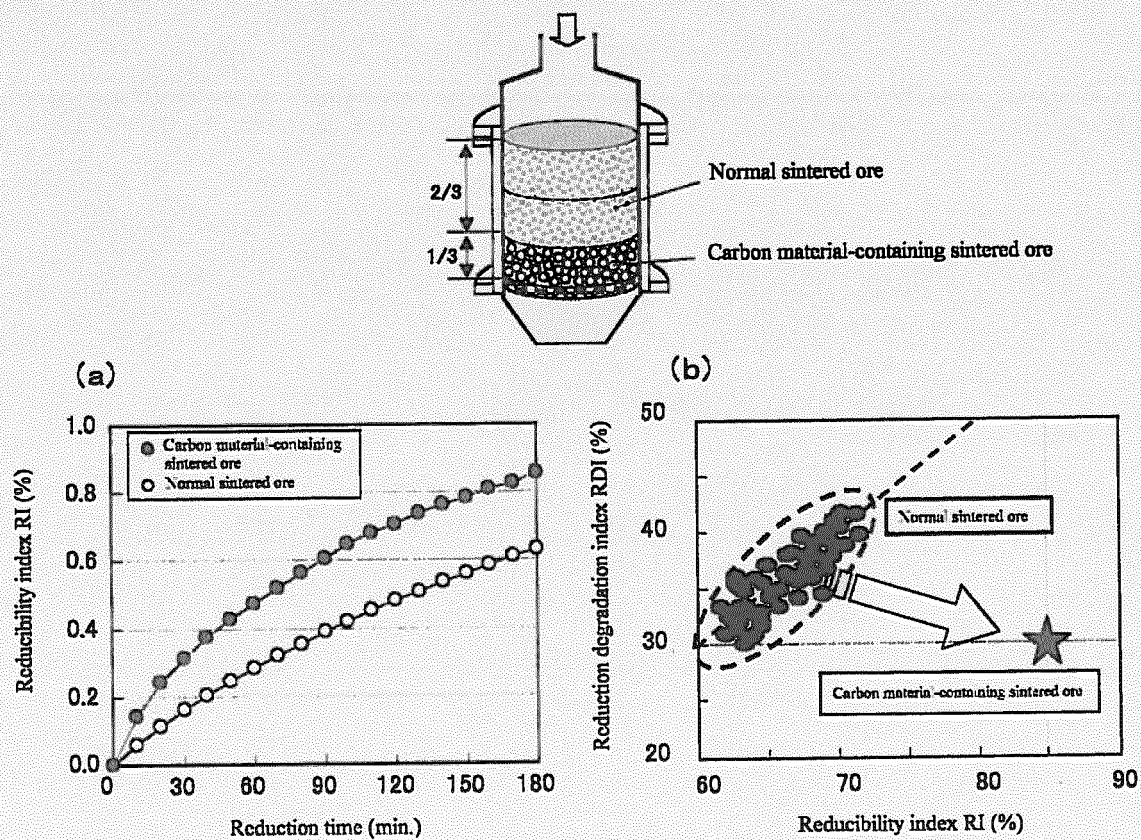


FIG. 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2014/067656

A. CLASSIFICATION OF SUBJECT MATTER
C22B1/16 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B1/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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 A	JP 4-210432 A (Nippon Steel Corp.), 31 July 1992 (31.07.1992), fig. 4 and the relevant passage thereof (Family: none)	1-9, 11 10
A	JP 2005-194544 A (JFE Steel Corp.), 21 July 2005 (21.07.2005), all pages; all drawings (Family: none)	1-11

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
26 August, 2014 (26.08.14)

Date of mailing of the international search report
02 September, 2014 (02.09.14)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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