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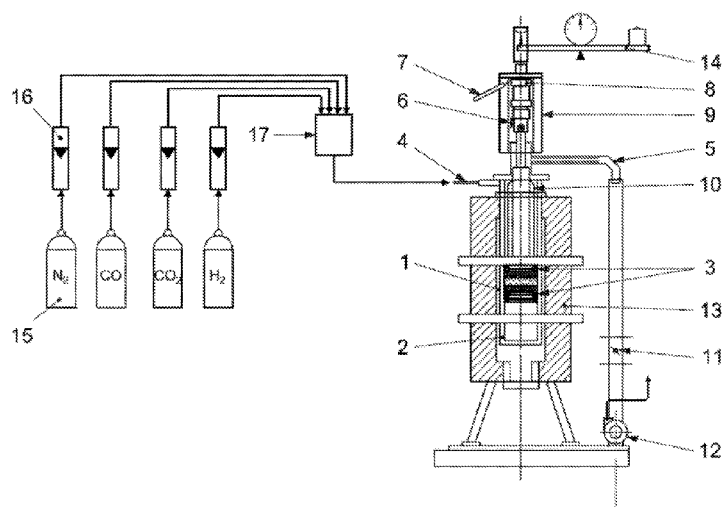
(54) Title: METHODS OF DETERMINING ADHESION CHARACTERISTICS OF COATING MATERIALS FOR IRON ORE  
PELLETS FOR USE IN DIRECT REDUCTION PROCESSES

FIG. 1

(57) Abstract: A method for determining adhesion characteristics of coatings disposed on the surfaces of iron ore pellets for use direct reduction processes is presented. A coating index is determined by measuring the percent reduction in the thickness of a coating layer after agitation forcibly contacting the coated iron ore pellets with each other. Coated iron ore pellets having optimized adhesion characteristics and reduced agglomeration tendencies for use in direct reduction processes are also provided.

**METHODS OF DETERMINING ADHESION CHARACTERISTICS OF COATING  
MATERIALS FOR IRON ORE PELLETS FOR USE IN DIRECT REDUCTION  
PROCESSES**

**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. Provisional Application No. 62/245,759, filed October 23, 2015, and U.S. Provisional Application No. 62/245,760, filed October 23, 2016. The contents of the referenced applications are incorporated into the present application by reference.

**BACKGROUND OF THE DISCLOSURE**

**A. Technical Field**

[0002] The present disclosure relates to a method for determining adhesion characteristics such as a coating index for a coating layer of iron ore pellets for use in direct reduction processes as well as iron ore pellets with optimized adhesion characteristics.

**B. Description of the Related Art**

[0003] Direct reduction (DR) of iron ores is a fundamental step in commercial manufacture of iron. Several direct reduction processes, including those using fine ore, lump ore, and pellets, have been developed. Some processes use natural gas as fuel reductant, whereas others are based on coal. Approximately 90% of directly reduced iron (DRI) in the world is produced by gas-based vertical shaft furnace processes owing to their low energy consumption and high productivity. Two of the common vertical shaft furnace processes are the Midrex (USA) and Tenova HYL (Mexico) processes, both of which use pellets and/or lumps of iron ores as feed stock.

[0004] The direct reduced iron (DRI) productivity is dependent on several factors including the iron ore pellet reduction properties, the reducing gasses concentration and the reaction temperature. Higher temperature, in general leads to higher productivity or faster reduction of the pellets but is limited by the sticking tendency of the pellets at high temperatures which leads to cluster formation and an uneven flow of ore pellets and gases. One drawback encountered with gaseous shaft furnaces is the sticking or agglomerating of iron ore pellets. This unintended agglomeration of pellets can make continuous operation difficult. In moving-bed shaft reduction processes, such as Midrex and HYL III, the avoidance of sticking is desired.

[0005] In direct reduction processes the product is freshly reduced iron in a solid state.

Therefore, it is crucial for the material flow in the reducing module that the solid product does not agglomerate or form aggregates that block the material flow within and out of the reactor [Direct reduced iron: Technology and Economics of Production and Use, ed. by J. Feinman and D. R. Mac Rae, ISS, Warrendale, PA, (1999). – incorporated herein by reference in its entirety]. If the pellets have little or no tendency to stick then the reduction temperature and therefore throughput can be increased. An increase of 100 °C in the reduction temperature can significantly increase throughput [Wong PLM, Kim MJ, Kim HS, Choi CH. Ironmaking Steelmaking, 1999: 26: 53–57. – incorporated herein by reference in its entirety]. High reduction temperature also minimizes degradation and re-oxidation of the reduced product.

**[0006]** Previous methods to prevent and/or lessen the tendency for agglomeration and lower sticking of iron ore pellets have included lower temperatures, higher basicity, and changes in gangue content. However, decreasing the reducing temperature of the DRI process to avoid this problem can cause a significant drop in throughput. As an example, a decrease from 850 to 750 °C can result in a decrease of 30-40% in throughput [L. G. Henderickson and J. A. Sandoval: Iron Steel Soc. AIME, 1980, 35–48. – incorporated herein by reference in its entirety]. High basicity and gangue content may also result in larger slag volume and less metal throughput leading to unfavorable economic and operation conditions.

**[0007]** One way to prevent pellet agglomeration is to coat the iron surfaces with a coating material that is inactive under the reducing conditions in the shaft furnace. However, a single coating has drawbacks such as ineffective agglomerate prevention during reduction and the loss of the coating prematurely during shipment or movement prior to reduction [Jerker Sterneland and Pär G. Jonsson ISIJ International, Vol. 43 (2003), No. 1, pp. 26–35.; and Cano JAM, Wendling F. Mining Eng 1993: 45: 633–636.; and Jianhua Shao, Zhancheng Guo, and Huiqing Tang, Steel research int., 84 (2013) No. 2, 111-118. – each incorporated herein by reference in its entirety]. For this reason, the iron ore pellets are often coated with materials to minimize adhesion tendencies. Usually these materials are sprayed in solution form so that a thin layer is formed and bonded with the surface of the pellets which then acts as a barrier between the surface of adjacent pellets during high temperature exposure, thus allowing for more free movement of the pellets during downward movement in the shaft and at the same time allowing for more uniform upward flow of the reducing gases during reduction processes. The suitability or effectivity of the coating is dependent on its ability to adhere with the pellet surface to such an extent that it is not removed during shipment,

movement on a conveyor belt or charging hopper as well as inside the shaft while rolling downwards and rubbing with each other.

### **BRIEF SUMMARY OF THE DISCLOSURE**

[0008] In view of the forgoing, an aspect of the present disclosure is to provide a method for ascertaining the quality of iron ore coatings by determining important adhesion characteristics, such as a coating index, and thus providing coatings and iron ore pellets having enhanced effectiveness as feedstock in direct reduction processes with optimized characterization of the coatings and the coating processes. A second aspect of the present disclosure is to provide iron ore pellets comprising an iron ore core that is coated with an inorganic coating material that may reclaim waste electric arc furnace dust and provides a suitable coating index and other adhesion characteristics for use in common commercial direct reduction processes.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0009] A more complete appreciation of the disclosure and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIG. 1 is a schematic diagram of the reduction under load apparatus.

FIG. 2A is a schematic diagram of the tumble drum apparatus in front view.

FIG. 2B is a schematic diagram of the tumble drum apparatus in side view.

FIG. 3 is an X-ray diffraction (XRD) analysis of iron ore pellets.

FIG. 4A is a scanning electron microscope (SEM) micrograph of iron ore pellets.

FIG. 4B is a SEM micrograph of iron ore pellets.

FIG. 5 is a SEM photo of electric arc furnace dust.

FIG. 6 is an energy-dispersive X-ray spectroscopy (EDX) analysis of electric arc furnace dust.

FIG. 7 is a SEM photo of the electric arc furnace dust coating layer of iron ore pellets.

FIG. 8 is an EDX analysis of the electric arc furnace dust coating layer of iron ore pellets.

FIG. 9 is a SEM photo of the electric arc furnace dust coating layer of iron ore pellets

after a rubbing test.

FIG. 10 is an EDX analysis of the electric arc furnace dust coating layer of iron ore pellets after a rubbing test.

FIG. 11 is a SEM photo of the cement coating layer of iron ore pellets.

FIG. 12 is an EDX analysis of the cement coating layer of iron ore pellets.

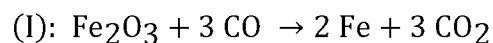
FIG. 13 is a SEM photo of the cement coating layer of iron ore pellets after a rubbing test.

FIG. 14 is an EDX analysis of the cement coating layer of iron ore pellets after a rubbing test.

### **DETAILED DESCRIPTION OF THE EMBODIMENTS**

[0010] Referring now to the drawings, wherein like reference numerals designate identical or corresponding parts throughout the several views.

[0011] The conventional route for making steel includes using one or more sintering or pelletization plants, coke ovens, blast furnaces, and basic oxygen furnaces. Such plants require high capital expenses and raw materials of stringent specifications. Direct reduction, an alternative route of iron making, has been developed to overcome some of these difficulties of conventional blast furnaces. Iron ore is reduced in solid state to form direct reduced iron (DRI). The most important reaction of iron (III) oxide is its carbothermal reduction, which gives iron used in steel-making (formula I):



[0012] The specific investment and operating costs of direct reduction plants are low compared to integrated steel plants. As used herein, direct-reduced iron (DRI), also known as sponge iron, is produced from the direct reduction of iron ore in the form of lumps, pellets, or fines by a reducing gas produced from natural gas or coal. The reducing gas is a mixture, the majority of which is hydrogen (H<sub>2</sub>) and carbon monoxide (CO) which act as reducing agents. Direct reduced iron has about the same iron content as pig iron, typically 90-94%.

[0013] The direct reduction of iron ore pellets at high temperature (*e.g.*, greater than 400 °C) may lead to the formation of agglomerates. As used herein, the term “agglomerates” or “agglomerated” refers to two or more iron ore pellets, either coated (*i.e.*, a first coating, a second coating, or both) or non-coated (*i.e.*, the iron ore core itself), which are attached to form a pellet cluster that has a longest length of at least 25 mm in any measurable direction.

For spherical or substantially spherical pellet agglomerates, longest length refers to the longest linear diameter of the pellet agglomerate. For non-spherical pellet agglomerates, such as pellet agglomerates that form a cubic shape, the longest length may refer to any of the length, width, or height of the agglomerate. The iron ore pellets may be attached to each other in any reasonable manner, including attached through surface coating interactions (*e.g.*, glued, tacked, cemented, pasted, *etc.*), attached by highly connected or integral interactions (*e.g.*, melted together, fused, amalgamated, *etc.*), or entrapped within a cluster (*e.g.*, sandwiched between a plurality of attached pellets). The iron ore pellets may also be attached as a result of interlocking fibrous iron precipitates (iron whiskers). For instance, growth of iron whiskers may lead to pellets that are hooked or entangled to each other through the fibrous iron whiskers. Therefore, one object of the present disclosure is to provide methods for evaluating the coatings for iron ore that prevents the formation of agglomerates before, during and/or after direct reduction processes as well as their adhesion to the iron ore core that prevents. The suitability or effectivity of the coating is dependent on its ability to adhere with the iron ore core surface to such an extent that it is not removed during transportation movements, movements on a conveyor belt, and movements on the charging hopper and/or inside the shaft while rolling downwards and rubbing with each other.

**[0014]** According to first aspect, the present disclosure relates to a method for determining a coating index of a coating layer. In one step, an iron ore core comprising iron ore is coated with a solution of a coating material to form coated iron ore pellets with a coating layer comprising the coating material.

**[0015]** The present disclosure relates to iron ore pellets including an iron ore core. Iron ores are rocks and minerals from which metallic iron can be economically extracted. The ores are typically rich in iron oxides and vary in color from dark grey, bright yellow, deep purple to rusty red. The iron itself is usually found in the form of magnetite ( $\text{Fe}_3\text{O}_4$ , 72.4% Fe), hematite ( $\text{Fe}_2\text{O}_3$ , 69.9% Fe), goethite ( $\text{FeO}(\text{OH})$ , 62.9% Fe), limonite ( $\text{FeO}(\text{OH}) \cdot n(\text{H}_2\text{O})$ ) or siderite ( $\text{FeCO}_3$ , 48.2% Fe), and mixtures thereof. Ores containing very high quantities of hematite or magnetite (greater than  $\sim 60\%$  iron) are known as natural ore or direct shipping ore. These ores can be fed directly into iron-making blast furnaces. Iron ore is the raw material used to make pig iron, which is one of the main raw materials to make steel.

**[0016]** Iron (III) oxide or ferric oxide is the inorganic compound with formula  $\text{Fe}_2\text{O}_3$ . It is one of the three main oxides of iron, the other two being iron (II) oxide ( $\text{FeO}$ ) which is rare,

and iron (II, III) oxide ( $\text{Fe}_3\text{O}_4$ ) which also occurs naturally as the mineral magnetite. As the mineral known as hematite,  $\text{Fe}_2\text{O}_3$  is the main source of iron for the steel industry.  $\text{Fe}_2\text{O}_3$  is ferromagnetic, dark red and readily attacked by acids.

[0017]  $\text{Fe}_2\text{O}_3$  can be obtained in various polymorphs. In the major polymorphs,  $\alpha$  and  $\gamma$ , iron adopts an octahedral coordination geometry, each Fe center is bound to six oxygen ligands.  $\alpha\text{-Fe}_2\text{O}_3$  has the rhombohedral corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) structure and is the most common form. It occurs naturally as the mineral hematite which is mined as the main ore of iron.  $\gamma\text{-Fe}_2\text{O}_3$  has a cubic structure, is metastable and converted to the alpha phase at high temperatures. It is also ferromagnetic. Several other phases have been identified, including the  $\beta$ -phase, which is cubic body centered, metastable, and at temperatures above 500 °C converts to alpha phase, and the epsilon phase, which is rhombic, and shows properties intermediate between alpha and gamma phase. This phase is also metastable, transforming to the alpha phase between 500 and 750 °C. Additionally, at high pressure an iron oxide can exist in an amorphous form. The ore in the iron ore core may have an  $\alpha$  polymorph, a  $\beta$  polymorph, a  $\gamma$  polymorph, an  $\epsilon$  polymorph or mixtures thereof.

[0018] The iron (III) oxide in the iron ore core may also be in the form of an iron hydrate. When alkali is added to solutions of soluble Fe(III) salts a red-brown gelatinous precipitate forms which is  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (also written as  $\text{Fe}(\text{O})\text{OH}$ ). Several forms of the hydrate oxide of Fe(III) exist as well.

[0019] The term “iron ore core” as used herein refers to an iron rich material (*i.e.*, greater than 40%, preferably greater than 50%, more preferably greater than 60% elemental iron by weight), onto which a single or a plurality of coatings are added to form a surface coated iron ore core or coated iron ore pellets.

[0020] In the present disclosure, the general shape and size of the iron ore core may dictate the shape and size of the coated iron ore pellets described herein. In a preferred embodiment, the iron ore cores of the present disclosure are in the form of a pellet, which is spherical or substantially spherical (*e.g.*, oval, oblong, *etc.*) in shape. However, the iron ore cores disclosed herein may have various shapes other than spheres. For instance, it is envisaged that iron ore cores may be in the shape of a “lump” or a “briquette.” Lumps or briquettes tend to have a more cubical or rectangular shape when compared to pellet forms. Therefore, the iron ore cores of the present disclosure may also be generally cubic or rectangular. The size of the iron ore core may also dictate the size of the iron ore pellets

herein. In one embodiment, the iron ore core has an average diameter of 5-20 mm, preferably 8-18 mm, more preferably 10-16 mm, although the size may vary from these ranges and still provide acceptable iron ore pellets.

**[0021]** In addition to iron and/or iron oxide, various non-ferrous materials (*i.e.*, metals and non-metals) may be present in the iron ore core including, but not limited to, aluminum, copper, lead, nickel, tin, titanium, zinc, bronze, metal oxides thereof, metal sulfides thereof, calcium oxide, magnesium oxide, magnesite, dolomite, aluminum oxide, manganese oxide, silica, sulfur, phosphorous, and combinations thereof. The total weight % of these non-ferrous materials relative to the total wt. % of the iron ore core is typically no more than 40%, preferably no more than 30%, preferably no more than 20%, preferably no more than 15%, preferably no more than 10%, preferably no more than 5%, preferably no more than 4%, preferably no more than 3%, preferably no more than 2%, more preferably no more than 1%.

**[0022]** “Coating”, “coat”, or “coated” as used herein, refers to a covering that is applied to a surface of the iron ore core or a coated iron ore core. The coating may “substantially cover” the surface, whereby the % surface area coverage of the surface being coated is at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%. In some cases, the coating may “incompletely cover”, or only cover portions of the surface being coated, whereby the % surface area coverage of the surface being coated is less than 75%, less than 65%, less than 60%, less than 55%, less than 50%, less than 45%, less than 40%, less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 10%. The “coating” or “coat” may refer to one material (*i.e.*, dolomite, bauxite, bentonite, electric arc furnace dust, lime, *etc.*) that covers a surface being coated, or alternatively, the coating may refer to a plurality of materials (*i.e.*, mixtures) that cover a surface being coated. The plurality of materials may be applied to a surface as a mixture or sequential applications of the individual materials. With sequential applications of individual materials, it may be possible to form distinct layers. These distinct layers may have a defined interface. The coating thickness of the present disclosure may be varied depending on the coating materials and the process for applying the coating. The term “coating” may also refer to a single application of a material, or a plurality of applications of the same material, or sequential applications of different materials.

**[0023]** In one embodiment, the coating substantially covers the iron ore core, where the first coating covers greater than 75%, preferably greater than 85%, preferably greater than 90%, preferably greater than 95% of the surface of the iron ore core. Alternatively, the first

coating may be applied to only a portion of the surface of the iron ore core (*i.e.*, incompletely cover), and the applied coating may still prevent agglomeration. One of two surfaces in contact coated may be sufficient to prevent agglomeration. In one embodiment, the iron ore pellets have a wt. % of the coating layer ranging from 0.05-2%, preferably 0.1-1.5%, more preferably 0.2%-1.0% relative to the total weight of the coated iron ore pellets.

**[0024]** Several methods may be used to coat the iron ore core including, but not limited to, spray coating, dip coating, brush coating, and spin coating. Spray coating is a process whereby the slurry is applied through the air to a surface as atomized particles using a spray coating device. A spray coating device may employ compressed gas, such as air, to atomize and direct the slurry. Dip coating is a process whereby the pellet is inserted and removed from a bath of the slurry. The pellet is immersed in the slurry and the coating deposits itself on the pellet while being removed from the bath. The excess liquid can be drained from the pellet during this process and the liquid of the slurry can then be evaporated. Brush coating is a process whereby a slurry is smoothed on the surface by a brush or by multiple brushes. Spin coating is a process whereby a slurry is applied to the center of the pellet and the pellet is then rotated at high speed to spread the coating material by centrifugal force. It is envisaged that the coating may be applied manually or through automation and that the applications of coatings may be done to individual iron ore cores or coated iron ore cores or in parallel to a plurality of iron ore cores or coated iron ore cores at the same time.

**[0025]** In a preferred embodiment, the process further comprises drying the coated iron ore core for 0.5-24 hours, preferably 0.5-12 hours, more preferably 1-8 hours, even more preferably 1-6 hours prior to applying the second coating. By drying a first coating prior to applying any additional coating(s), the formation of distinct coating layers may be obtained. The formation of distinct layers may be advantageous to prevent pellet agglomeration and to prevent premature removal of the coatings prior to an iron reduction process.

**[0026]** In one embodiment, the coating material is applied to the iron ore core as a solution or a slurry, preferably aqueous, comprising 10-30 wt. %, preferably 15-25 wt. %, more preferably 18-22 wt. % of coating material relative to the total weight of the slurry. "Slurry" as used herein refers to a semiliquid mixture typically of particles or particulates of the coating material suspended in liquid. The liquid used in the solution is not envisioned as particularly limiting and is preferably water. In one embodiment, the solution has a pH of 4-8, although the pH of the solution may be more acidic or more basic depending on the coating material and the application. The solution may also refer to a slurry, a suspension, a

dispersion or an emulsion, *etc.*

**[0027]** The solution preferably comprises a solids concentration of no more than 15 kg of coating material per ton of iron ore cores to be coated, preferably no more than 10 kg/ton, preferably no more than 5 kg/ton, preferably no more than 4 kg/ton, preferably no more than 3 kg/ton, preferably no more than 2 kg/ton, preferably no more than 1 kg/ton, preferably no more than 0.5 kg/ton, preferably no more than 0.25 kg/ton, most preferably 0.25-5 kg/ton.

**[0028]** In one embodiment, the solution may further comprise binder materials including, but not limited to, clay materials, cement materials, concrete materials, acrylic polymers or copolymers, polymers or copolymers of vinyl acetate or synthetic oils which can harden on the iron ore cores holding the coating mixture in place on the surface.

**[0029]** In one embodiment, the coating material is substantially granular and comprises grains with an average particle size of 0.5-20  $\mu\text{m}$ , preferably 1-15  $\mu\text{m}$ , more preferably 2-10  $\mu\text{m}$ .

**[0030]** In another step, the process comprises measuring a first coating thickness of the coating layer on the coated iron ore pellets. In one embodiment, the first coating thickness is measured using magnetic film thickness gages. Magnetic film thickness gages are used to nondestructively measure the thickness of a nonmagnetic coating on ferrous substrate and generally operate based on one of two principles: magnetic pull-off or magnetic/electromagnetic induction.

**[0031]** Magnetic pull-off gages use a permanent magnet, a calibrated spring, and a graduated scale. The attraction between the magnet and the magnetic steel pulls the two together. As the coating thickness separating the two increases, it becomes easier to pull the magnet away. Coating thickness is determined by measuring this pull-off force and is sensitive to surface roughness, curvature, core thickness and make-up of the coating material. Exemplary magnetic pull-off gages include, but are not limited to pencil-type models (*e.g.*, PosiPen) and rollback dial models (*e.g.*, PosiTest).

**[0032]** Magnetic induction instruments use a permanent magnet as the source of the magnetic field. A Hall-effect generator or magneto-resistor is used to sense the magnetic flux density at a pole of the magnet. Electromagnetic induction instruments use an alternating magnetic field. A soft, ferromagnetic rod wound with a coil of fine wire is used to produce a magnetic field. A second coiled wire is used to detect changes in magnetic flux. These electronic instruments measure the change in magnetic flux density at the surface of a

magnetic probe as it nears a steel surface. The magnitude of the flux density at the probe surface is directly related to the distance from the steel substrate. By measuring flux density the coating thickness can be determined. Electromagnetic gages (*e.g.*, PosiTector 6000 F Series, PosiTest DFT Ferrous) come in many shapes and sizes. They commonly use a constant pressure probe to provide consistent readings that are not influenced by different operators. Readings are typically shown on a liquid crystal display (LCD). They can have options to store measurement results, perform instant analysis of readings, and output results to a printer or computer for further examination.

**[0033]** In another embodiment, micrometers may be used to measure the first coating thickness. Micrometers have the advantage of measuring any coating/core combination but the disadvantage of requiring access to the bare core. The requirement to touch both the surface of the coating and the underside of the core can be limiting. Two measurements must be taken: one with the coating in place and the other without. The difference between the two readings, the height variation is taken to be the coating thickness. On rough surfaces, micrometers measure coating thickness above the highest peak.

**[0034]** In a preferred embodiment, the first coating thickness of the coating layer of the coated iron ore pellets is measured using destructive techniques. For example, one preferable destructive technique is to cut the coated iron ore pellet in a cross section and measure the film thickness by viewing the cut by visual inspection, optical microscopy and/or scanning electron microscopy at any appropriate standard magnification. Another cross sectioning technique uses a scaled microscope to view a geometric incision through the dry coating. A special cutting tool may be used to make a small, precise V-groove through the coating and into the iron ore core. Gages are available that come complete with cutting tips and illuminated scaled magnifiers. This method may be used to confirm nondestructive results.

**[0035]** In another embodiment, the first coating thickness of the coating layer may be measured by gravimetric analysis. By measuring the mass and area of the coating, thickness can be determined. The simplest method is to weight the iron ore core before and after coating. Once the mass and area have been determined, the thickness can be calculated with a known density. This is a preferred method of measuring the coating thickness when the iron ore core is smooth and the coating is even.

**[0036]** In another step, the method comprises testing the adherence properties of the coating, as well as the tendency for coatings to prevent or minimize agglomeration, the

coated iron ore pellets are agitated, tumbled, or rotated. Agitation involves processes that create contact between the surfaces of the pellets. The pellets can either be agitated against each other or a medium can be used to contact the pellets. Often a cyclical action is used to create this contact between surfaces. The agitation can be performed either dry or wet using liquid lubricants, cleaners, or abrasives. In a wet process a compound lubricant or barreling soap is added to aid the process. A wide variety of media is available to achieve the desired finished product. Common media material include: sand, granite, chips, slag, steel, ceramics, and synthetics. Moreover, these materials are available in a wide variety of shapes, and different shapes can be used in the same load to reach into every geometry of the pellet. In a preferred embodiment, tumbling is performed in a tumbling drum and rotating is performed in a disc pelletizer. It is envisaged that additional methods of agitation may be used to measure the agglomeration properties and the coating adherence properties of the coating layer. Other exemplary agitation techniques include, but are not limited to, sonication, vibration, shaking, stirring and stamping.

**[0037]** In one embodiment, the process further comprises rotating the coated iron ore pellets in a rotating pan or like device for a set time, at a set speed and at a set angle in a manner such that the rotation causes rubbing of the pellets against each other and the removal of any loose and/or un-adhered particles of coating material. As used herein “rotating” refers to an agitation process designed to measure the adherence properties of the coatings by forcibly contacting the pellets to one another. The rotating may be performed using a rotating apparatus, such as a centrifuge, or a disc pelletizer, or a similar device. In a preferred embodiment, the rotating is carried out with a disc pelletizer that is downwardly inclined at an angle of 40-60° with respect to the horizontal plane, preferably 41-55°, preferably 42-50°, preferably 45-50° with respect to the horizontal plane. In a preferred embodiment, the rotating is performed for a time of 0.5-15 min, preferably 2.5-14 min, preferably 5-13 min, preferably 8-12 min, or most preferably 10 min at a speed of 10-40 rpm, preferably 10-30 rpm, preferably 15-25 rpm, more preferably 18-22 rpm, most preferably 20 rpm. In a preferred embodiment less than 0.5 g of loose residual powder coating layer is recovered from the disc pelletizer after 10 min rotating at 20 rpm, preferably less than 0.25 g, preferably left than 0.2 g, preferably less than 0.1 g.

**[0038]** In another embodiment, the process further involves tumbling the coated iron ore pellets as the form of agitation. “Tumbling” as used herein, is a form of agitation designed to measure the agglomeration properties and adhesion characteristics of the iron ore pellets.

Tumbling may also be referred to as rumbling or barreling. As used herein, the tumbling process involves filling a vessel (*e.g.*, a barrel, a tumbling drum, *etc.*) with the iron ore pellets and then rotating the vessel. As the vessel is rotated the material rises until gravity causes the uppermost layer to landslide down to the other side. The vessel may additionally have vanes which run along the inside of the vessel. As the vessel turns the vanes catch and lift the pellets, which eventually slide down or fall. This tumbling process can be configured as a batch system where batches of pellets are added, run and removed before the next batch is run or as a continuous system where the pellets enter at one end and leave at the other end in a finished state.

**[0039]** As the iron ore pellets are tumbled, the % agglomeration will generally decrease. It is therefore advantageous to identify a first and second coating, both in amount of the coating and in terms of the composition, which provides the lowest, or a low level of % agglomeration relative to iron ore coatings without a coating.

**[0040]** In another step, according to the process of the present disclosure, a second coating thickness of coated iron ore pellets is measured following agitation (*e.g.*, rotating, tumbling and the like). The second coating thickness may be measured in any suitable manner as described herein for measuring the first coating thickness. In a preferred embodiment the first and second coating thickness values are measured by the same technique or multiple techniques. It is envisaged that the first and second coating thickness values may be measured using a different technique or multiple different techniques. Using this measurement the coating index of the coating layer may be determined according to formula (I):

$$(I): \text{Coating Index (\%)} = (T_2/T_1) \times 100\%$$

wherein,  $T_1$  is the first coating thickness and  $T_2$  is the second coating thickness.

**[0041]** In a preferred embodiment, coating material for the prevention of agglomeration before during or after direct reduction processes have a coating index of greater than 30%, preferably greater than 35%, preferably greater than 40%, preferably greater than 45%, preferably greater than 50%, preferably greater than 60%, preferably greater than 70%.

**[0042]** In one embodiment, the average first coating thickness is 50-300  $\mu\text{m}$ , preferably 50-250  $\mu\text{m}$ , preferably 50-200  $\mu\text{m}$ , preferably 55-150  $\mu\text{m}$ , preferably 60-100  $\mu\text{m}$ , more preferably 70-80  $\mu\text{m}$ . In one embodiment, the average second coating thickness is 15-210  $\mu\text{m}$ , preferably 15-175  $\mu\text{m}$ , preferably 15-140  $\mu\text{m}$ , preferably 16-105  $\mu\text{m}$ , preferably 18-70

μm, more preferably 20-55 μm. In one embodiment, the coating layer is uniform. Alternatively, the coating layer may be non-uniform. The term “uniform” refers to an average coating thickness that differs by no more than 50%, by no more than 25%, by no more than 10%, by no more than 5%, by no more than 4%, by no more than 3%, by no more than 2%, by no more than 1% at any given location on the surface of the coated material. The term “non-uniform” refers to an average coating thickness that differs by more than 5% at any given location on the surface of the coated material.

**[0043]** In one embodiment, the coating material of the present disclosure comprises at least one inorganic material selected from the group consisting of bauxite, bentonite, and dolomite and the coating index is in the range of 30-70%, preferably 35-70%, preferably 40-70%, preferably 45-70%, preferably 50-70%.

**[0044]** Bauxite is an aluminum ore and the predominant source of aluminum throughout the world. It consists mostly of the minerals gibbsite  $\text{Al}(\text{OH})_3$ , boehmite  $\gamma\text{-AlO}(\text{OH})$  and diasporite  $\alpha\text{-AlO}(\text{OH})$ , mixed with the two iron oxides goethite  $\text{FeO}(\text{OH})$  and hematite ( $\text{Fe}_2\text{O}_3$ ), the clay mineral kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  and small amounts of anatase  $\text{TiO}_2$ . Lateritic bauxites (silicate bauxites) are distinguished from karst bauxite ores (carbonate bauxites). In one embodiment, the coating material comprises bauxite and the bauxite coating material comprises 40-60%  $\text{Al}_2\text{O}_3$ , 10-30%  $\text{Fe}_2\text{O}_3$ , 0.1-10%  $\text{SiO}_2$  and 1-3%  $\text{TiO}_2$ . Other inorganic compounds may be present in the bauxite coating material including, but not limited to,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ , etc. These compounds are generally present in less than 5% relative to the total weight % of the bauxite, if at all.

**[0045]** Bentonite is an absorbent aluminum phyllosilicate, impure clay consisting primarily of montmorillonite. Phyllosilicates are sheet silicate minerals formed by parallel sheets of silicate tetrahedra with  $\text{Si}_2\text{O}_5$  or a 2:5 ratio, they may be hydrated with either water or hydroxyl groups attached. Montmorillonite generally comprises sodium, calcium, aluminum, magnesium and silicon and oxides and hydrates thereof. Other compounds may also be present in the bentonite of the present disclosure including, but not limited to, potassium-containing compounds and iron-containing compounds. There are different types of bentonite, named for the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca) and aluminum (Al). For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. Therefore, in terms of the present disclosure bentonite may refer to potassium bentonite, sodium bentonite, calcium bentonite, aluminum bentonite, and mixtures thereof, depending on the relative amounts of potassium, sodium,

calcium and aluminum in the bentonite first coating.

**[0046]** Dolomite is an anhydrous carbonate mineral composed of calcium magnesium carbonate, *e.g.*,  $\text{CaMg}(\text{CO}_3)_2$ . Dolomite can also describe the sedimentary carbonate rock composed primarily of mineral dolomite, known as dolostone or dolomitic limestone. The mineral dolomite crystallizes in the trigonal-rhombohedral system and forms white, tan gray or pink crystals. Dolomite is a double carbonate, having an alternating structural arrangement of calcium and magnesium ions. In one embodiment, the coating material comprises dolomite and the dolomite coating material comprises 15-25% Ca, 10-20% Mg, 10-20% C and 40-60% O, with the calcium and magnesium being present primarily as oxides or hydroxides. Other inorganic compounds may be present in the dolomite coating material including, but not limited to,  $\text{Al}_2\text{O}_3$ , MnO,  $\text{Fe}_2\text{O}_3$ , *etc.* These compounds are generally present in less than 5% relative to the total weight % of the dolomite, if at all.

**[0047]** It is envisioned that other types of sedimentary rock sources may be used in lieu of bauxite, bentonite, and dolomite as material in the coating material including, but not limited to, limestone, calcite, vaterite, aragonite, magnesite, taconite, gypsum, quartz, marble, hematite, limonite, magnetite, andesite, serpentinite, garnet, basalt, dacite, nesosilicates or orthosilicates, sorosilicates, cyclosilicates, inosilicates, phyllosilicates, tectosilicates and the like.

**[0048]** In one embodiment, the coating material comprises at least one inorganic material selected from the group consisting of electric arc furnace dust, lime, limestone, and cement and the coating index is in the range of 30-70%, preferably 35-70%, preferably 40-70%, preferably 45-70%, preferably 50-70%.

**[0049]** Electric arc furnace (EAF) dust, or lime dust, is the solid material recovered from the off-gases from the production of molten steel and/or iron including electric arc furnaces. An electric arc furnace is a furnace that heats charged material by means of an electric arc, it allows steel to be made from 100% scrap metal feedstock. EAF dust is generated during the melting of materials in an electric arc furnace and collected by a de-dusting system such as bag filters or electrostatic precipitators and stored. Generally, the EAF dust is a complex material comprising small fines of mostly metal oxides. The predominant material is iron oxide with the remainder comprising oxides of calcium, zinc, chromium, lead, magnesium, manganese, sodium, nickel and potassium. The composition of the dust is directly associated with the chemistry of the metallic charge used in the electric arc furnace. For example,

processes that recycle scrap metal from sources as varied as automobiles, railroad rails or discarded structural steel generate EAF dust with larger proportions of zinc, iron and lead and smaller proportions of tin, cadmium, chromium, copper, silica, lime, and alumina.

**[0050]** In one embodiment, the coating material comprises electric arc furnace dust that substantially comprises  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{CaCO}_3$ . In a preferred embodiment, other materials are present in less than 10 wt. %, preferably less than 5 wt. %, preferably less than 3 wt. %, preferably less than 2 wt. %, preferably less than 1 wt. %, preferably less than 0.5 wt. % relative to the total weight of the coating material and the electric arc furnace dust.

**[0051]** In one embodiment, the electric arc furnace dust of the coating material comprises greater than 40 wt. % of  $\text{Fe}_2\text{O}_3$ , preferably greater than 45%, preferably greater than 50%, preferably greater than 55%, preferably greater than 60%, preferably greater than 65%, preferably greater than 66%, preferably greater than 67%, preferably greater than 68%, preferably greater than 69 wt. % of  $\text{Fe}_2\text{O}_3$  relative to the total weight of the electric arc furnace dust. The  $\text{Fe}_2\text{O}_3$  present in the electric arc furnace dust is consistent with the preceding description of  $\text{Fe}_2\text{O}_3$  in the iron ore core.

**[0052]** Lime is a calcium-containing inorganic material in which carbonates, oxides, and hydroxides predominate. Lime may refer to quicklime or burnt lime, which is calcium oxide that has been derived from calcining limestone. Lime may also refer to hydrated lime or slaked lime, which is calcium hydroxide which has been derived from the hydration of quicklime. Therefore, “lime” as used herein, may refer to calcium carbonate, calcium oxide, or calcium hydroxide containing materials, limestone, and mixtures thereof. In one embodiment, the coating material comprises lime and the lime coating material comprises greater than 70%, preferably greater than 80%, preferably greater than 85%, preferably greater than 90%, preferably greater than 95% calcium-containing materials (*e.g.*,  $\text{CaO}$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , *etc.*). Other inorganic compounds may be present in the lime coating material, such as  $\text{MnO}$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ , *etc.*, with these compounds generally being present in less than 10% relative to the total weight % of the lime, if at all.

**[0053]** A cement is a binder that comprises at least one selected from the group consisting of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{CaO}$ , depending on the type of cement. There are many types of cements, including, Portland cement, siliceous fly ash, calcareous fly ash, volcanic ash, slag cement, silica fume, pozzolan, and the like. In one embodiment, the cement of the present disclosure is a Portland cement. Portland cement is made primarily of calcium oxide,

as well as a mixture of silicates and oxide. The four main components of Portland cement are belite ( $2\text{CaO}\cdot\text{SiO}_2$ ), alite ( $3\text{CaO}\cdot\text{SiO}_2$ ), celite ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ), and brownmillerite ( $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ ). In one embodiment, the cement is a slag cement. Slag cement is a type of cement produced by quenching molten iron slag (which is a byproduct of iron and steelmaking) from a blast furnace in water or steam to produce a granular cement product. The four main components of slag cement are CaO (30-50%),  $\text{SiO}_2$  (28-38%),  $\text{Al}_2\text{O}_3$  (8-24%), and MgO (1-18%). However, the chemical composition of slag cement varies considerably depending on the composition of the raw materials in the iron production process and therefore these percentages are given as just one example, and other % compositions may be used as the coating material in the present disclosure. As slag cement is a byproduct of iron making processes, the slag cement of the present disclosure may also contain iron or iron oxide materials.

**[0054]** In one embodiment, the method of the present disclosure further comprises measuring a surface area coverage of the coating layer on the iron ore core. In one embodiment, the surface area coverage is measured with at least one instrument selected from the group consisting of an optical microscope, an X-ray diffractometer, an X-ray fluorescence spectrometer, and a scanning electron microscope. Further, the surface area coverage may be measured upon visual inspection. In a preferred embodiment, the surface area coverage may be measured may be before the rotating, after the rotating, or both. In a preferred embodiment the surface area coverage of the coating layer is at least 75% before rotating, preferably at least 80%, preferably at least 85%, preferably at least 90% before rotating and the surface area coverage is at least 50% after rotating, preferably at least 55%, preferably at least 60%, preferably at least 65%, preferably at least 70% after rotating. In a preferred embodiment, the surface area coverage of the coating layer after rotating is at least 60% of the surface area coverage of the coating layer before rotating, preferably at least 65%, preferably at least 70%, preferably at least 75%, preferably at least 80%.

**[0055]** In one embodiment, the method of the present disclosure may further comprise performing an energy dispersive X-ray spectroscopy (EDX) analysis of the coating layer on the coated iron ore pellets before rotating, after rotating or both. In a preferred embodiment, elements unique to the coating layer (*i.e.*, Ca, C, Al, Si, *etc.*) have a higher percentage on the surface layer compared to the internal iron ore core confirming the formation of the coating layer on the iron ore core. After rotating a higher percentage is preferably still observed on the surface layer compared to the internal iron core confirming the maintained presence of the

coating layer after rotating.

**[0056]** In addition to measuring the coating layer thickness and surface area coverage, other coating characteristics may be measured before rotating, after rotating, or both to determine if an acceptable amount of coating with suitable adhesion characteristics has been applied and the uniformity of the coating layer. Further, the measuring may involve an analysis of the porosity and/or surface roughness of the coating surface, for instance by measuring a specific surface area (*i.e.*, BET surface area) through BET adsorption or gas permeability techniques. Further, the process of applying the coating and measuring the coating characteristics (*i.e.*, surface area coverage, thickness, etc.) can be repeated a plurality of times in an iterative fashion until an acceptable level of coating is achieved (*e.g.*, greater than 75% surface area coverage of the iron ore core).

**[0057]** In one embodiment, the method of the present disclosure involves a coating step that comprises a first coating step of coating the iron ore core with the solution of a first coating material to form green iron ore pellets having a first layer of a first coating material, optionally drying the green iron ore pellets, and a second coating step of coating the green iron ore pellets with a solution of a second coating material to form the coated iron ore pellets of the present disclosure having a first coating layer of the first coating material, and a second coating layer of the second coating material. In a preferred embodiment, the second coating material is of a different chemical composition than the first coating material. Thus, the “coating layer” formed on iron ore pellets and or the “coated iron core” in the method of the present disclosure may comprise one, two, and/or a plurality of individual layers of coating materials.

**[0058]** In one embodiment, the second coating layer substantially covers the first coating layer. In this scenario, the second coating covers at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99% of the surface of the first coating. Alternatively, the second coating may be applied to only a portion of the surface of the first coating (*i.e.*, incompletely cover the first coating). In the scenario where the first coating incompletely covers the iron ore core, the second coating may cover the iron ore core rather than, or in addition to covering the first coating.

**[0059]** In a preferred embodiment, the first and second coatings form distinct layers with distinct and identifiable interfaces between the two layers. In one embodiment, the first and second coatings form distinct layers, although the interface between the two layers is a

mixture of both the first and second layer. For example, in one embodiment the first layer can comprise or consist of at least one of bauxite, bentonite, and dolomite, and the second layer can comprise or consists of electric arc furnace dust. Preferably the major component of the first layer is not present in the second layer and the major component of the second layer is not present in the first layer. Thus, the rotating and determining of the coating index refers to determining the % reduction of a thickness of the total coating layer (*i.e.*, first and second coating, *etc.*) after the rotating, in terms of the average coating thickness of total coating layer (*i.e.*, the sum of the first and second coating, *etc.*).

**[0060]** In one embodiment, the thickness of the first and second coating decreases by no more than 60%, by no more than 50%, by no more than 40%, by no more than 30%, by no more than 20%, by no more than 10% after rotating the iron ore pellets at 10-30 rpm, in terms of the average coating thickness of the sum of the first and second coating. In one embodiment, the standard practice for measuring coating thickness by magnetic field of eddy current (ASTM E376) may be used as conditions or a standardized test for measuring coating thickness after rotation [ASTM E376 – incorporated herein by reference in its entirety].

**[0061]** According to a second aspect, the present disclosure is related to coated iron ore pellets comprising an iron ore core comprising iron ore and a coating layer comprising at least one inorganic material selected from the group consisting of bauxite, bentonite, dolomite, lime, limestone, cement, and electric arc furnace dust wherein the coating layer is disposed on the surface of the iron ore core comprising iron ore and wherein the coating layer has a coating index of greater than 40% as determined by the method of the present disclosure in any of its embodiments. In a preferred embodiment, the coating index is greater than 40%, preferably greater than 45%, preferably greater than 50%, preferably greater than 55%, preferably greater than 60%.

**[0062]** In one embodiment, the coating layer of the coated iron ore pellets comprises a first layer of a first coating material comprising at least one inorganic material selected from the group consisting of bauxite, bentonite, and dolomite; and a second layer of a second coating material comprising at least one inorganic material selected from the group consisting of lime, limestone, cement, and electric arc furnace dust wherein the first layer is disposed between a surface of the iron ore core comprising iron ore and the second layer. In a preferred embodiment, these iron ore pellets having a coating index of greater than 40% and a coating layer comprising a first and second material layer reduce the formation of agglomerated iron ore pellets compared to an iron ore core comprising iron ore without the

first layer of the coating layer, without the second layer of the coating layer, or without any coating layer. In one embodiment, the coated iron ore pellets have a % agglomeration of less than 5%, preferably less than 4%, preferably less than 3%, preferably less than 2%, preferably less than 1% in terms of the wt% of agglomerated iron ore pellets with a longest length of at least 25 mm relative to the total weight of the iron ore pellets.

**[0063]** In another embodiment, the present disclosure relates to a process for manufacturing reduced iron pellets involving i) applying at least one selected from the group consisting of bauxite, bentonite, and dolomite to an iron ore core to form a coated iron ore core coated with a first coating, ii) applying electric arc furnace (EAF) dust to the coated iron ore core to form the iron ore pellets coated with the first coating and the second coating and determining a coating index, and iii) reducing the iron ore pellets with a reducing gas to form reduced iron pellets. The techniques used to apply the first and second coating, as well as the measurement techniques used to analyze the coating characteristics of the applied coatings have been mentioned previously.

**[0064]** In one embodiment, the process further comprises drying the coated iron ore core for 0.5-24 hours, preferably 0.5-12 hours, more preferably 1-8 hours, even more preferably 1-6 hours prior to applying the second coating. By drying the first coating prior to applying the second coating, the formation of two distinct coating layers may be obtained. The formation of two distinct layers may be advantageous to prevent pellet agglomeration and to prevent premature removal of the coatings prior to an iron reduction process.

**[0065]** In one embodiment, the temperature for the reduction is up to 1100 °C, preferably up to 1000 °C, more preferably up to 950 °C. The reducing may be performed isothermally, or alternatively, a temperature gradient may be used to reduce the iron ore throughout the reduction process. In one embodiment, the reducing gas is hydrogen (H<sub>2</sub>). In one embodiment, the reducing gas is carbon monoxide (CO). In a preferred embodiment, the reducing gas comprises both hydrogen and carbon monoxide. In this scenario, other gases may be present in the reducing gas, including carbon dioxide, nitrogen and the like. The ratio of hydrogen to carbon monoxide may be about 10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9 or 1:10. The reducing gas of the present disclosure may be derived from natural gas, coal or both.

**[0066]** In one embodiment, the iron ore pellets are reduced in a direct reduction apparatus. In one embodiment, the direct reduction apparatus is a fixed-bed reactor. Alternatively, in

one embodiment, the direct reduction apparatus is a moving-bed shaft. In a preferred embodiment, the direct reduction apparatus is a vertical moving-bed shaft. In a vertical moving-bed shaft apparatus, the iron ore pellets, in one or more of their embodiments, are placed proximal to the top of the moving-bed shaft, where the iron ore pellets are heated and allowed to move towards the bottom of the moving-bed shaft gradually as they are reduced. The reducing gas is flowed countercurrent to the movement of the iron ore pellets. Then the reduced iron pellets are collected proximal to the bottom of the shaft apparatus. In a vertical moving-bed shaft reduction apparatus, the avoidance of agglomerated iron ore pellets is essential to allow the downward movement of the iron ore pellets for reduction and to allow for efficient flow of the reducing gas upwardly. Therefore, the first and second coating of the iron ore pellets may provide a more efficient direct reduction process by minimizing the formation of agglomerates. The wt. % of iron in the reduced iron pellets is greater than 90%, greater than 91%, greater than 92%, greater than 93%, greater than 94%, greater than 95%, relative to the total weight of the reduced iron pellet.

**[0067]** In one embodiment, the process further includes rotating the reduced iron pellets at 10-30 rpm and determining the % reduction of a thickness of the first and second coating after the rotating, in terms of the average coating thickness of the sum of the first and second coating.

**[0068]** It is envisaged that the reduced iron pellets of the present disclosure may be used for the manufacture of steel and steel related products. The type of steel produced using the reduced iron pellets of the present disclosure may vary depending on added alloying elements. Steel is an alloy of iron and carbon that is widely used in construction and other applications because of its high tensile strength and low cost. Carbon, other elements, and inclusions within iron act as hardening agents that prevent the movement of dislocations that naturally exist in the iron atom crystal lattices. The carbon in typical steel alloys may contribute up to 2.1% of its weight. The steel material of the present disclosure may be any of the broadly categorized steel compositions, including carbon steels, alloy steels, stainless steels and tool steels. Carbon steels contain trace amounts of alloying elements and account for 90% of total steel production. Carbon steels can be further categorized into three groups depending on their carbon content: low carbon steels/mild steels contain up to 0.3% carbon, medium carbon steels contain 0.3-0.6% carbon, and high carbon steels contain more than 0.6% carbon. Alloy steels contain alloying elements (*e.g.*, manganese, silicon, nickel, titanium, copper, chromium, and aluminum) in varying proportions in order to manipulate the

steel's properties, such as its hardenability, corrosion resistance, strength, formability, weldability or ductility. Stainless steels generally contain between 10-20% chromium as the main alloying element and are valued for high corrosion resistance. With over 11% chromium, steel is about 200 times more resistant to corrosion than mild steel. These steels can be divided into three groups based on their crystalline structure: austenitic steels, ferritic steels, and martensitic steels. Tool steels contain tungsten, molybdenum, cobalt and vanadium in varying quantities to increase heat resistance and durability, making them ideal for cutting and drilling equipment.

**[0069]** In one embodiment, the reduced iron pellets manufactured by the direct reduction process are maintained at or near the temperature used during the reducing, and are transferred at this elevated temperature to a steelmaking apparatus (*e.g.*, blast furnace, *etc.*), such that less heat is required to melt the reduced iron pellets during a steelmaking process.

**[0070]** The examples below are intended to further illustrate protocols for preparing, characterizing and assessing the coated iron ore pellets and reduced iron pellets described herein, and are not intended to limit the scope of the claims.

## **EXAMPLE 1**

### **Raw materials**

**[0071]** SAMARCO iron ore pellets were used in the experiments. This ore is practically used in iron making processes in the Saudi Iron and Steel Company (HADEED). Electric arc furnace (EAF) dust (lime dust) generated from an electric arc furnace during charging of dolo-lime, lump lime and special lime for slag formation was used. The iron ore and EAF dust were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM).

**[0072]** The various characterization tests of the iron ore pellets showed that iron oxide ( $\text{Fe}_2\text{O}_3$ ) is the major phase with the presence of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  as minor components (FIG. 3 and Table 1).

**Table 1**  
**X-ray fluorescence (XRF) chemical analysis of SAMARCO iron ore pellets**

| COMPOUNDS                          | Conc. %        | Elements  | Conc. %        |
|------------------------------------|----------------|-----------|----------------|
|                                    |                | O         | 30.8850        |
| Na <sub>2</sub> O                  | 0.1100         | Na        | 0.0835         |
| MgO                                | 0.1350         | Mg        | 0.0815         |
| Al <sub>2</sub> O <sub>3</sub>     | 0.3000         | Al        | 0.1615         |
| SiO <sub>2</sub>                   | 1.8150         | Si        | 0.8484         |
| P <sub>2</sub> O <sub>5</sub>      | 0.0710         | P         | 0.0315         |
| K <sub>2</sub> O                   | 0.0082         | K         | 0.0069         |
| CaO                                | 0.7810         | Ca        | 0.5655         |
| TiO <sub>2</sub>                   | 0.0345         | Ti        | 0.0210         |
| V <sub>2</sub> O <sub>5</sub>      | 0.0040         | V         | 0.0023         |
| Cr <sub>2</sub> O <sub>3</sub>     | 0.0328         | Cr        | 0.0226         |
| MnO                                | 0.0554         | Mn        | 0.0436         |
| <b>Fe<sub>2</sub>O<sub>3</sub></b> | <b>Balance</b> | <b>Fe</b> | <b>Balance</b> |
| NiO                                | 0.1040         | Ni        | 0.0827         |

[0073] The SEM photos for SAMARCO iron ore samples are shown in FIG. 4A and FIG. 4B. It was observed that grain coalescence with very low micropores and many macropores took place in a dense structure.

[0074] The characterization of EAF dust was also performed and is given in Table 2. The EAF dust is mainly Fe<sub>2</sub>O<sub>3</sub> (53.09%) with CaO and CaCO<sub>3</sub> (39.13%). The morphological examination under SEM with EDX analysis, as given in FIG. 5 and FIG. 6, show the average grain size of EAF dust as 2.0-10.0 µm while visual observation of the EAF dust indicates that it contains some coarse grains in the range of 1.0-9.0 mm.

**Table 2**  
**Chemical analysis for electric arc furnace (EAF) dust**

| PARAMETER                                  | METHOD                    | RESULT  | UNIT |
|--------------------------------------------|---------------------------|---------|------|
| Aluminum as Al <sub>2</sub> O <sub>3</sub> | Acid Digestion / ICP      | 0.29    | %    |
| Antimony (Sb)                              | Acid Digestion / ICP - MS | < 0.001 | %    |
| Arsenic (As)                               | Acid Digestion / ICP - MS | < 0.001 | %    |
| Barium (Ba)                                | Acid Digestion / ICP      | 0.041   | %    |
| Boron (B)                                  | Acid Digestion / ICP      | 0.014   | %    |
| Chromium (Cr)                              | Acid Digestion / ICP - MS | < 0.001 | %    |
| Copper (Cu)                                | Acid Digestion / ICP - MS | 0.0017  | %    |
| Lead (Pb)                                  | Acid Digestion / ICP - MS | < 0.001 | %    |
| Manganese (Mn)                             | Acid Digestion / ICP      | 0.48    | %    |
| Mercury (Hg)                               | Acid Digestion / ICP - MS | < 0.001 | %    |
| Nickel (Ni)                                | Acid Digestion / ICP - MS | 0.0011  | %    |
| Selenium (Se)                              | Acid Digestion / ICP - MS | 0.0056  | %    |
| Silver (Ag)                                | Acid Digestion / ICP - MS | < 0.001 | %    |

|                                              |                           |         |   |
|----------------------------------------------|---------------------------|---------|---|
| Zinc (Zn)                                    | Acid Digestion / ICP - MS | 0.0085  | % |
| Molybdenum (Mo)                              | Acid Digestion / ICP - MS | < 0.001 | % |
| Thorium (Th)                                 | Acid Digestion / ICP - MS | < 0.001 | % |
| Uranium (U)                                  | Acid Digestion / ICP - MS | < 0.001 | % |
| Vanadium (V)                                 | Acid Digestion / ICP - MS | 0.0127  | % |
| Strontium (Sr)                               | Acid Digestion / ICP      | 0.004   | % |
| Cadmium (Cd)                                 | Acid Digestion / ICP - MS | < 0.001 | % |
| Silica as SiO <sub>2</sub>                   | Gravimetry                | 3.02    | % |
| Lithium (Li)                                 | Acid Digestion / ICP      | < 0.001 | % |
| Iron Oxide as Fe <sub>2</sub> O <sub>3</sub> | Acid Digestion / ICP      | 53.09   | % |
| Calcium Oxide                                | Acid Digestion / ICP      | 14.03   | % |
| Magnesium Oxide                              | Acid Digestion / ICP      | 3.47    | % |
| Sulphate                                     | Water Extraction / IC     | 0.06    | % |
| Chloride                                     | Water Extraction / IC     | 0.05    | % |
| Sodium                                       | Water Extraction / IC     | 0.09    | % |
| Potassium                                    | Water Extraction / IC     | 0.04    | % |
| Carbonate as CaCO <sub>3</sub>               | Volumetry                 | 25.1    | % |
| Moisture                                     | ASTM D 2974               | 0.05    | % |
| Carbon Content                               | ASTM D 2974               | 0.18    | % |
| LOI @ 550 °C                                 | ASTM D 2974               | 0.38    | % |
| LOI @ 800 °C                                 | ASTM D 2974               | 0.64    | % |

## EXAMPLE 2

### Coating of Iron Ore Pellets and Adhesive Characterization

[0075] SAMARCO iron ore pellets were coated comparatively with various concentrations of cement and electric arc furnace (EAF) dust suspensions. 5000 g of SAMARCO iron ore pellets were used in each coating test. Pellets were placed in a disc pelletizer of 50 cm in diameter rotating at 20 rpm. The coating was applied by spraying a suspension of coating material (cement or EAF dust). Solid concentrations (2.0 Kg cement or EAF dust per ton of iron ore) using 20% suspension concentration were applied.

[0076] Coated pellets were left to air-dry for 4 hrs followed by rotation of the pellets in a disc pelletizer for 10 min at a predetermined speed (20 rpm) and angle to cause rubbing of the pellets against each other and removal of the loose and/or un-adhered particles. The remaining coating and its uniformity on the surface of the pellets was evaluated under a microscope at standard magnification. The coating index of the particles is expressed as the percentage of the remaining coating thickness after the rubbing test: Coating Index =  $(T_2/T_1) \times 100$ , wherein  $T_1$  = coating thickness before the rotation test and  $T_2$  = coating thickness after the rotation test.

[0077] For EAF dust coated pellets, SAMARCO pellets before and after the EAF dust

coating and after the rubbing test were visually inspected. The surface and internal layers of the coated pellets before and after rubbing were analyzed by energy-dispersive X-ray spectroscopy (EDX) as shown in FIG. 8 and FIG. 10 respectively. It was found that calcium and carbon have a higher percentage on the surface layer compared to the internal core confirming the formation of a coating layer comprising lime (FIG 8). Also, after the rubbing test a higher percentage of Ca and C are observed on the surface layer compared to the internal core to confirm the presence of the coating layer after rubbing. The residual powder of the EAF dust coating layer after rotation for 10 min in the disc pelletizer is less than 0.1 g.

**[0078]** Comparatively similar results were observed in the case of cement coating. SAMARCO pellets before and after the cement coating and after the rubbing test were visually inspected. The surface and internal layers of the coated pellets before and after rubbing were analyzed by EDX as shown in FIG. 12 and FIG. 14 respectively. It was found that calcium, aluminum, and silicon have a higher percentage on the surface layer compared to the internal one confirming the formation of a cement coating layer (FIG. 14). Also, after the rubbing test a higher percentage of Ca, Al, and Si are observed on the surface layer compared to the internal one confirming the presence of the coating layer after rubbing. The residual powder of the cement coating layer after rotation for 10 min in the disc pelletizer is less than 0.1 g.

**[0079]** Thus, the comparative results of the adhesive characterization reflected that EAF dust has relatively acceptable adhesive nature to be used as a coating material for iron ore pellets during production of direct reduced iron (DRI).

### **EXAMPLE 3**

#### **Determination of the Clustering Index (Reduction under load test) – ISO 11256**

**[0080]** ISO 11256 specifies a method to provide a relative measure for evaluating the formation of clusters of iron ore pellets when reduced under conditions resembling those prevailing in shaft direct-reduction processes [ISO 11256 – incorporated herein by reference in its entirety].

**[0081]** The clustering or sticking index was measured for SAMARCO iron ore pellets coated with various concentrations of electric arc furnace (EAF) dust slurry. A schematic diagram of the reduction under load (ISO 11256) apparatus is shown in FIG. 1. The apparatus comprises a reduction tube, a loading device, waste gas, a furnace and a gas supply system. The reduction tube comprises: an outer reduction tube **1**, an inner reduction tube **2**,

upper and lower perforated plates comprising a test portion **3**, a gas inlet **4**, a gas outlet **5** and a thermocouple exit **6**. The loading device comprises: a compressed air inlet **7**, a pressure cylinder **8**, a frame for the pressure cylinder **9** and a loading ram **10**. The waste gas comprises: a throttle valve **11** and a waste gas fan **12**. The gas supply system comprises: gas cylinders **15**, gas flowmeters **16** and a mixing vessel **17**.

**[0082]** The apparatus is constituted of a vertical oven divided into five heating zones starting from the bottom. One thermocouple is placed in the oven and a triple thermocouple is placed inside the reaction tube. Reducing gas and nitrogen flow rate is controlled by a mass flow meter and controller. The vertical electrical oven is equipped with a weighing system.

**[0083]** The system is capable of applying a total static load of 147 kPa on a bed of the test portion. The test portion is a 2000 g sample of pellets. The test portion comprises 50% pellets having a size in the range 16.0-12.5 mm and 50% having a size in the range of 12.5-10 mm. The pellet sample is isothermally reduced in a fixed bed at 850 °C under static load using a reducing gas consisting of 30% CO, 15% CO<sub>2</sub>, 45% H<sub>2</sub> and 10% N<sub>2</sub> in a flow rate of 40 L/min until a degree of reduction of 95% was achieved. A schematic diagram of the reduction under load- ISO 11256 apparatus is shown in FIG. 1.

**[0084]** The reduced test portion (cluster) is disaggregated by tumbling, using a specific tumbling drum. The percentage of clusters is determined on the cooled sample. The clustered pellets consisting of more than two pellets are applied to the tumbler test. A schematic diagram of the tumble drum apparatus is shown in FIG. 2A (front view) and FIG. 2B (side view). It comprises: a revolution counter **18**, a door with handle **19**, a stub axle **20** with no through shaft, two lifters **21** (50 mm x 50 mm x 5 mm), a direction of rotation **22**, and a plate **23**.

**[0085]** The tumble drum is made of a steel plate at least 5 mm in thickness, having an internal diameter of 1000 mm and an internal length of 500 mm. Two equally spaced L-shaped steel lifters, 50 mm flat by 50 mm high by 5 mm thick and 500 mm long are solidly attached longitudinally inside the drum by welding, so as to prevent accumulation of material between the lifter and drum. Each lifter is fastened so that it points towards the axis of the drum, with its attached leg pointing away from the direction of rotation, thus providing a clear unobstructed shelf for lifting the iron ore pellets sample. The door is constructed so as to fit into the drum forming a smooth inner surface. During the test, the door is rigidly

fastened and sealed to prevent any loss of sample. The drum is rotated on stub axles attached to its ends by flanges welded to provide smooth inner surfaces. The drum is replaced when the thickness of the plate is reduced to 3 mm in any area. The lifters are replaced when the height of the shelf is reduced to less than 47 mm.

**[0086]** All material is carefully removed from the reduction tube. The mass of the reduced material is determined ( $m_r$ ). During this operation, some individual pellets usually separate from the clustered material. These pellets are removed and the mass of the clustered material is recorded ( $m_c, 1$ ). This step is considered as the first disaggregation operation. The removal of the test portion from the reduction tube is a critical step and care must be taken to avoid its untimely disaggregation. The clustered material is placed inside the tumble drum and rotated for a total of 35 revolutions, divided into 7 disaggregation operations of 5 revolutions each. After each disaggregation operation, the mass of the remaining clusters is measured and recorded as a series ( $m_c, 2, m_c, 3 \dots m_c, 8$ ). Any individual pellets that are separated from the clustered material shall be removed prior to the next disaggregation operation.

**[0087]** The clustering index (CI) is expressed as a percentage and is calculated from the following equation where  $m_r$  is the total mass, in grams, of the test portion after reduction and  $m_c, i$  is the mass, in grams, of the clusters after the  $i^{\text{th}}$  disaggregation operation:

$$CI = \frac{100}{8 \times m_r} \times \sum_{i=1}^8 m_{c,i}$$

**[0088]** The clustering index measurement (ISO11256) was applied comparatively on SAMARCO iron ore pellets coated with various electric arc furnace (EAF) dust coating conditions, including 20% EAF slurry concentrations with a coated material amount of 0.5, 2.0 and 4.0 Kg per ton of iron ore. The results of the clustering index measurements are show in tables 3, 4 and 5.

**Table 3**

**Clustering index measurement for SAMARCO iron ore pellets coated with 20% electric arc furnace dust slurry concentration and 0.5 Kg electric arc furnace dust per ton of iron ore pellets**

| Nº | Cluster Mass (g)   |
|----|--------------------|
| 1  | 1114 (after Red.)  |
| 2  | 53 (after 05 rev.) |
| 3  | 29 (after 10 rev.) |
| 4  | 12 (after 15 rev.) |
| 5  | 5 (after 20 rev.)  |
| 6  | 5 (after 25rev.)   |
| 7  | 0 (after 30 rev.)  |
| 8  | 0 (after 35 rev.)  |

**Table 4**

**Clustering index measurement for SAMARCO iron ore pellets coated with 20% electric arc furnace dust slurry concentration and 2.0 Kg electric arc furnace dust per ton of iron ore pellets**

| Nº | Cluster Mass (g)   |
|----|--------------------|
| 1  | 900 (after Red.)   |
| 2  | 47 (after 05 rev.) |
| 3  | 32 (after 10 rev.) |
| 4  | 21 (after 15 rev.) |
| 5  | 21 (after 20 rev.) |
| 6  | 21 (after 25rev.)  |
| 7  | 21 (after 30 rev.) |
| 8  | 18 (after 35 rev.) |

**Table 5**

**Clustering index measurement for SAMARCO iron ore pellets coated with 20% electric arc furnace dust slurry concentration and 4.0 Kg electric arc furnace dust per ton of iron ore pellets**

| Nº | Cluster Mass (g)   |
|----|--------------------|
| 1  | 583 (after Red.)   |
| 2  | 17 (after 05 rev.) |
| 3  | 0 (after 10 rev.)  |
| 4  | 0 (after 15 rev.)  |
| 5  | 0 (after 20 rev.)  |
| 6  | 0 (after 25rev.)   |
| 7  | 0 (after 30 rev.)  |
| 8  | 0 (after 35 rev.)  |

**[0089]** It was noticed that the tendency for cluster formation decreased by increasing the coating amount from 0.5, 2.0 to 4.0 Kg per ton of iron ore. Also it was found that the coating

index measurement for iron ore pellets coated with 20% EAF dust slurry concentrations in 4.0 Kg per ton of iron ore achieved the Midrex process standard requirement. As used herein, this means the cluster mass comprising agglomerates of more than one pellet with a longest length of greater than 25 mm after 10 revolutions was zero or 0%. These obtained results confirm that the utilization of electric arc furnace (EAF) dust as a coating material for iron ore pellets is highly promising.

**[0090]** Thus, the foregoing discussion discloses and describes merely exemplary embodiments of the present invention. As will be understood by those skilled in the art, the present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. Accordingly, the disclosure of the present invention is intended to be illustrative, but not limiting of the scope of the invention, as well as other claims. The disclosure, including any readily discernible variants of the teachings herein, defines, in part, the scope of the foregoing claim terminology such that no inventive subject matter is dedicated to the public.

**CLAIMS**

1. A method for determining a coating index of a coating layer, comprising:  
coating an iron ore core comprising iron ore with a solution of a coating material to form coated iron ore pellets with a coating layer comprising the coating material;  
drying the coated iron ore pellets;  
measuring a first coating thickness of the coating layer on the coated iron ore pellets;  
then  
rotating the coated iron ore pellets to cause rubbing of the coated iron ore pellets against one another;  
measuring a second coating thickness of the coating layer on the coated iron ore pellets after the rotating; and  
determining the coating index of the coating layer according to formula (I):  
$$(I): \text{Coating Index (\%)} = (T_2/T_1) \times 100\%$$
  
wherein  $T_1$  is the first coating thickness and  $T_2$  is the second coating thickness.
2. The method of claim 1, wherein the coating material comprises granular inorganic material with an average grain size of 0.5-20  $\mu\text{m}$ .
3. The method of claim 1, wherein the solution comprises 10-30 wt% of the coating material relative to the total weight of the solution.
4. The method of claim 1, wherein the solution comprises 0.25-5 kg of the coating material per ton of iron ore cores.
5. The method of claim 1, wherein the rotating is carried out with a disc pelletizer that is downwardly inclined at an angle of 40-60° with respect to the horizontal plane.
6. The method of claim 1, wherein the rotating includes rotating the coated iron ore pellets in a disc pelletizer for 0.5-15 minutes at 10-40 rpm.
7. The method of claim 1, wherein the first coating thickness and the second coating thickness are measured using an optical microscope and/or a scanning electron microscope.
8. The method of claim 1, wherein the first coating thickness is 50-300  $\mu\text{m}$  and the second coating thickness is 15-210  $\mu\text{m}$ .
9. The method of claim 1, wherein the coating material comprises at least one inorganic

material selected from the group consisting of bauxite, bentonite, and dolomite and wherein the coating index is in the range of 30-70%.

10. The method of claim 1, wherein the coating material comprises at least one inorganic material selected from the group consisting of lime, limestone, cement, and electric arc furnace dust and wherein the coating index is in the range of 30-70%.
11. The method of claim 1, further comprising measuring a surface area coverage of the coating layer on the coated iron ore pellets with at least one instrument selected from the group consisting of an optical microscope, an X-ray diffractometer, an X-ray fluorescence spectrometer, and a scanning electron microscope before rotating, after rotating, or both.
12. The method of claim 11, wherein the surface area coverage of the coating layer is at least 85% before rotating and the surface area coverage of the coating layer is at least 50% after rotating.
13. The method of claim 11, wherein the surface area coverage of the coating layer after rotating is at least 60% of the surface area coverage of the coating layer before rotating.
14. The method of claim 1, further comprising performing an energy dispersive X-ray spectroscopy elemental analysis of the coating layer on the coated iron ore pellets before rotating, after rotating or both.
15. The method of claim 1, wherein the coating comprises:
  - a first coating step of coating the iron ore core with the solution of the first coating material to form green iron ore pellets having a first layer of the first coating material; and
  - a second coating step of coating the green iron ore pellets with a solution of a second coating material to form the coated iron ore pellets having a second layer of the second coating material,wherein the second coating material is of a different chemical composition than the first coating material.
16. The method of claim 1, further comprising tumbling the coated iron ore pellets and weighing agglomerated coated iron ore pellets with a longest length of greater than 25 mm relative to the total weight of the coated iron ore pellets to determine a % agglomeration.

17. The method of claim 16, wherein the coating index is greater than 40% and the % agglomeration is less than 5% in terms of the wt. % of agglomerated coated iron ore pellets with a longest length of greater than 25 mm relative to the total weight of the coated iron ore pellets.
18. Coated iron ore pellets, comprising:
  - an iron ore core comprising iron ore; and
  - a coating layer comprising at least one inorganic material selected from the group consisting of bauxite, bentonite, dolomite, lime, limestone, cement and electric arc furnace dust,wherein the coating layer is disposed on a surface of the iron ore core comprising iron ore, and  
wherein the coating layer has a coating index of greater than 40% as determined by the method of claim 1.
19. The coated iron ore pellets of claim 18, wherein the coating layer comprises:
  - a first layer of a first coating material comprising at least one inorganic material selected from the group consisting of bauxite, bentonite and dolomite; and
  - a second layer of a second coating material comprising at least one inorganic material selected from the group consisting of lime, limestone, cement and electric arc furnace dust,wherein the first layer is disposed between a surface of the iron ore core comprising iron ore and the second layer.
20. The coated iron ore pellets of claim 19, wherein the coating layer having a coating index of greater than 40% reduces the formation of agglomerated iron ore pellets compared to an iron ore core comprising iron ore without the coating layer.

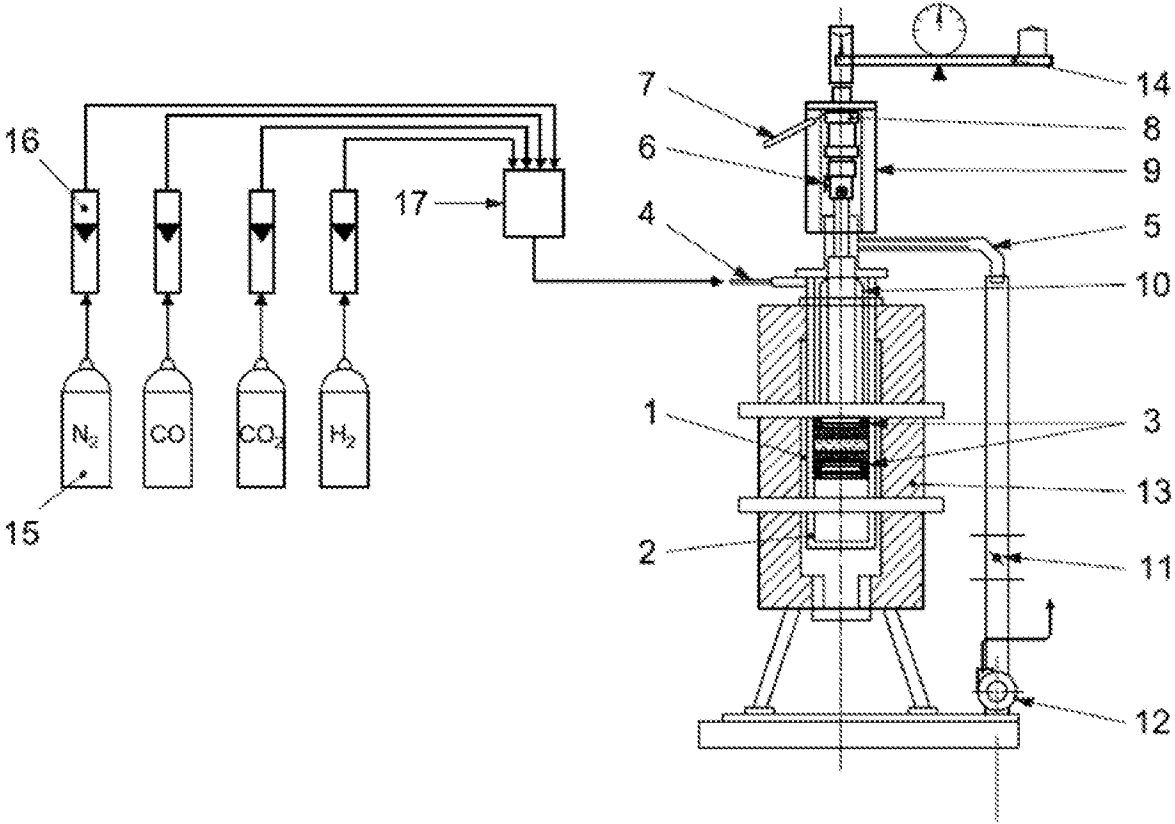


FIG. 1

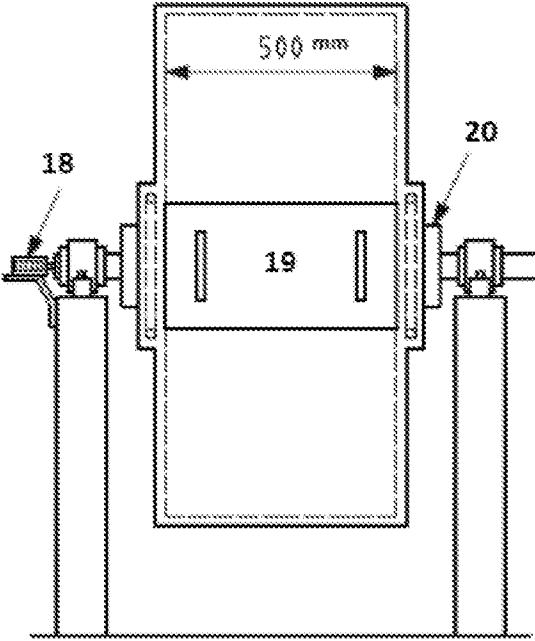


FIG. 2A

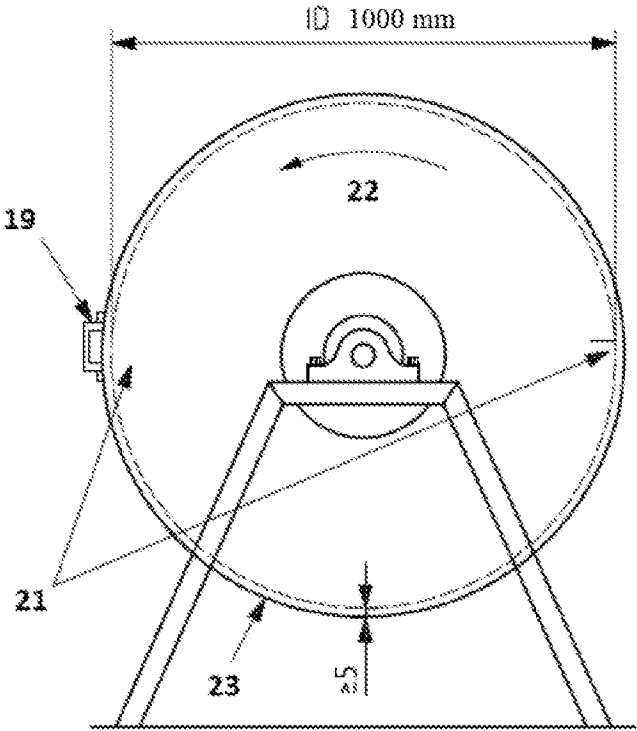


FIG. 2B

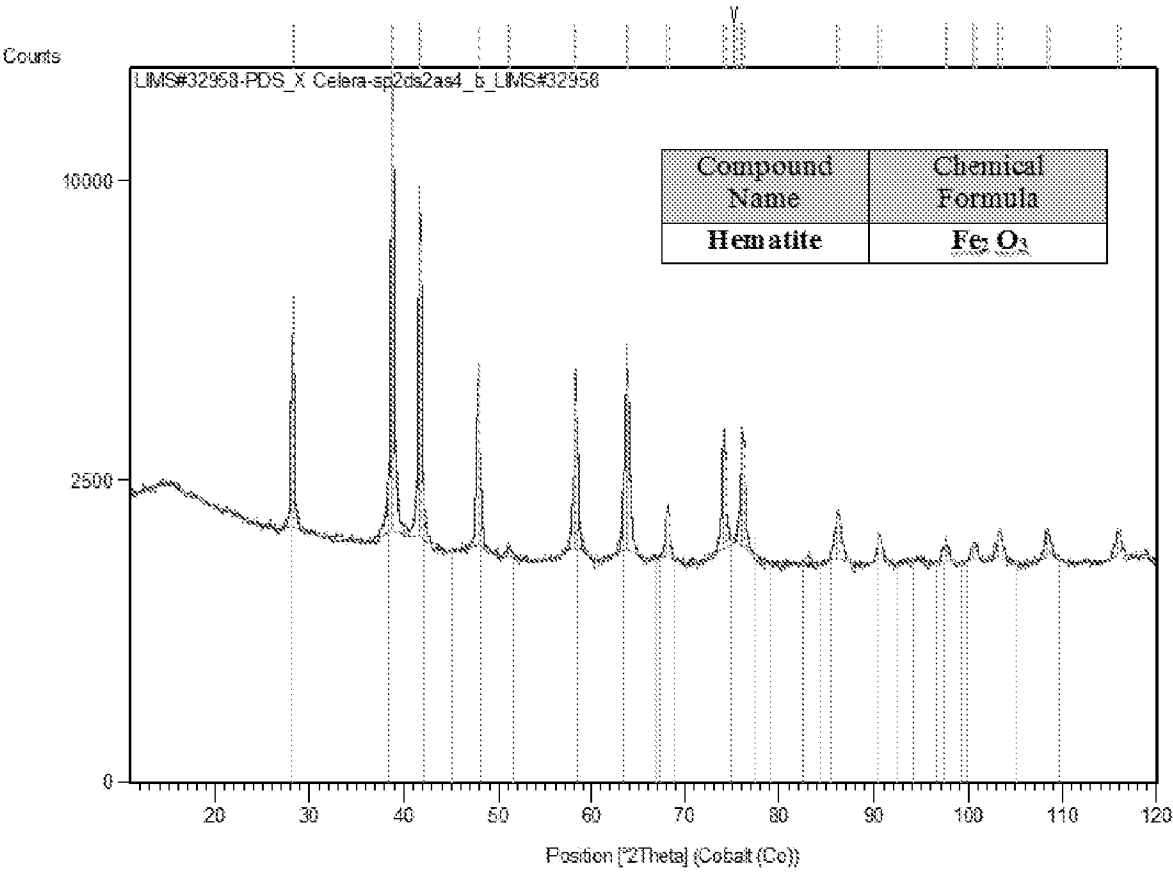


FIG. 3

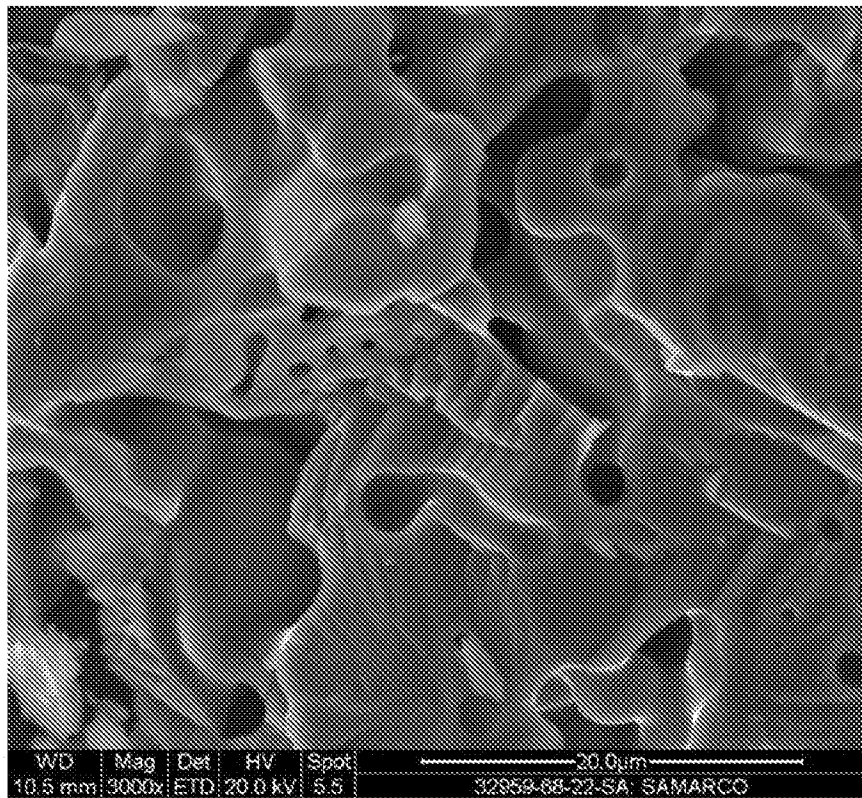


FIG. 4A

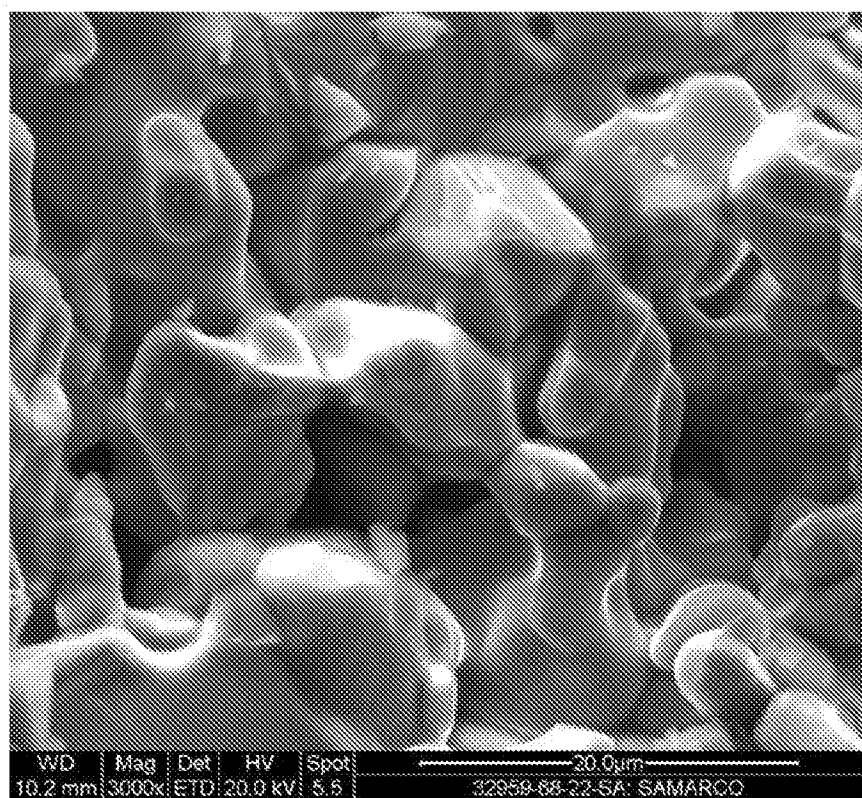


FIG. 4B

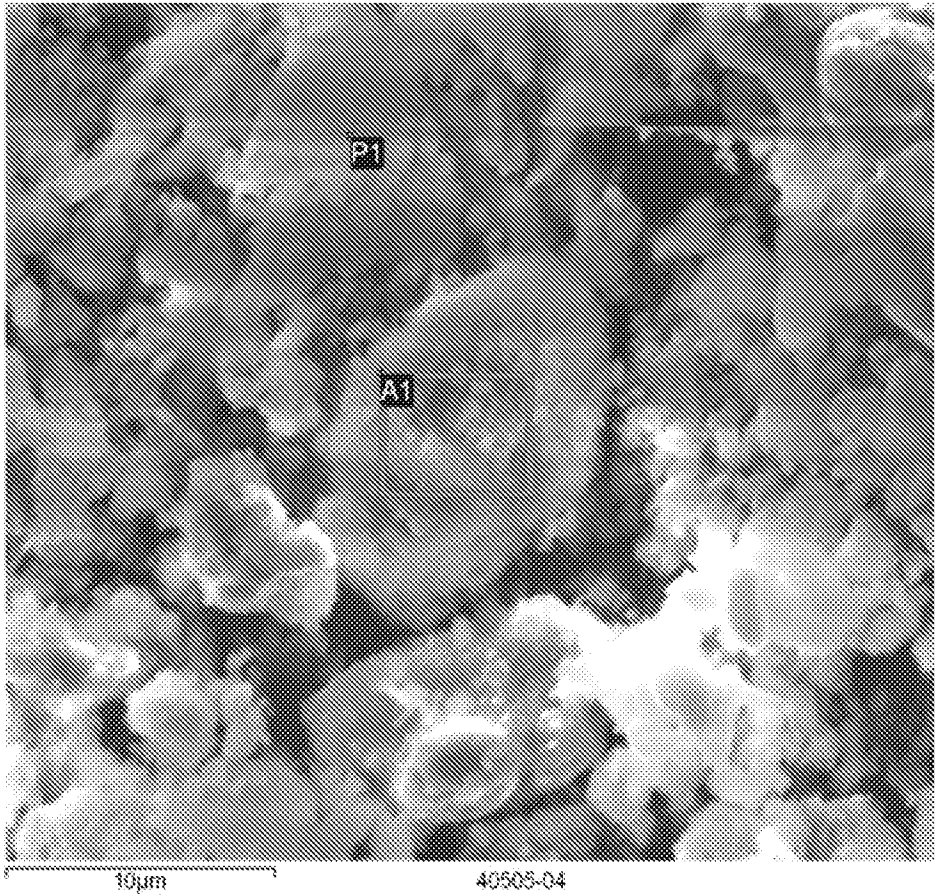


FIG. 5

| Spectrum | C    | O     | Na   | Mg   | Al   | Si   | S    | Cl   | Ca    | Ti   | Mn   | Fe    | Total  |
|----------|------|-------|------|------|------|------|------|------|-------|------|------|-------|--------|
| A1       | 4.98 | 50.25 | 0.36 | 1.80 | 4.37 | 2.50 | 0.34 | 0.37 | 20.76 | 0.76 | 0.18 | 13.34 | 100.00 |

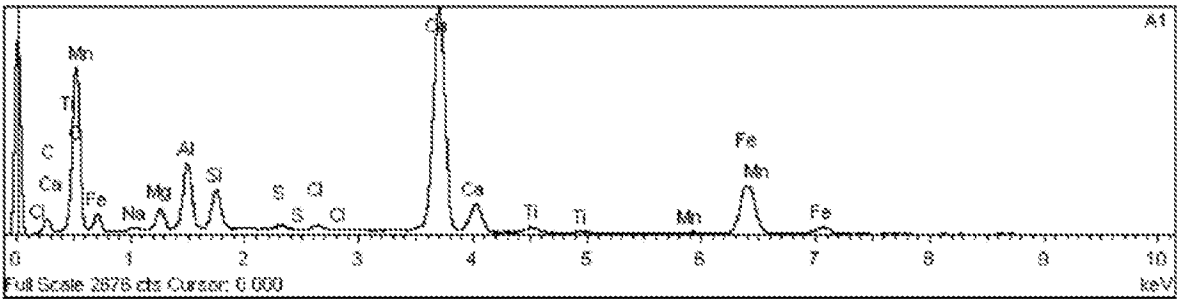


FIG. 6



FIG. 7

| Spectrum | C     | O     | Mg   | Al   | Si   | Ca    | Fe    | Total  |
|----------|-------|-------|------|------|------|-------|-------|--------|
| P1       | 11.02 | 51.29 | 1.19 | 0.30 | 0.68 | 18.92 | 16.61 | 100.00 |
| P2       | 1.70  | 35.13 |      | 0.19 |      |       | 62.98 | 100.00 |

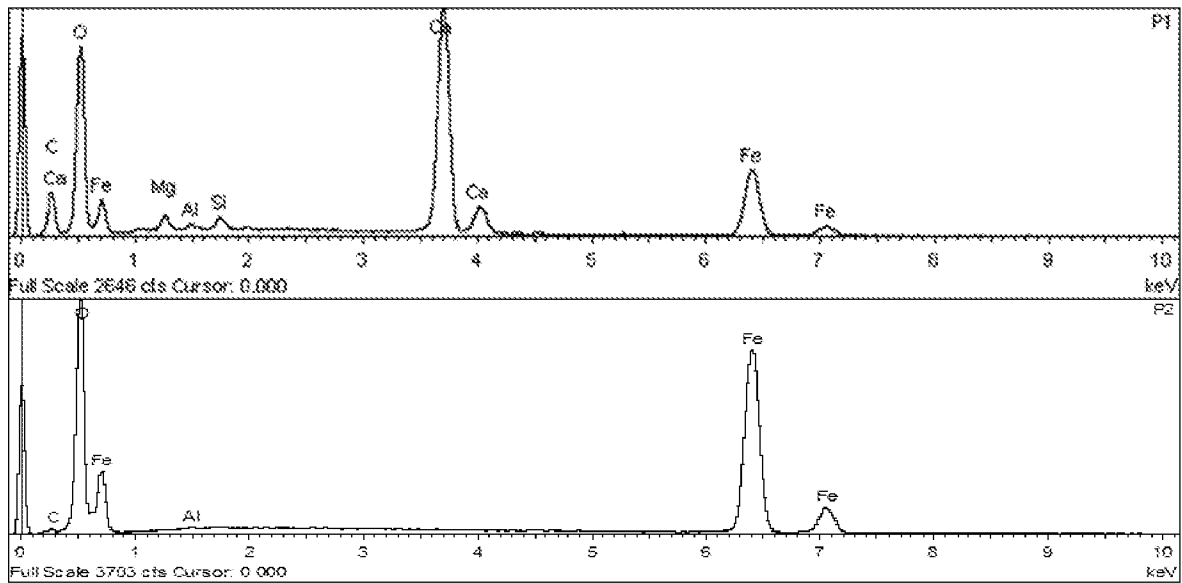


FIG. 8

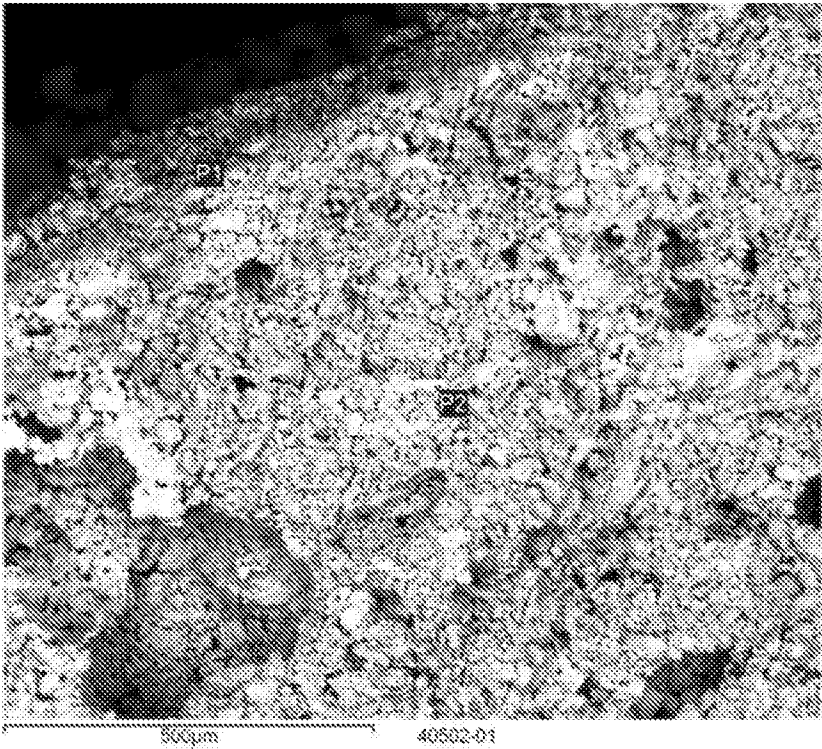


FIG. 9

| Spectrum | C     | O     | Mg   | Al   | Si   | Ca    | Fe    | Total  |
|----------|-------|-------|------|------|------|-------|-------|--------|
| P1       | 11.02 | 51.29 | 1.19 | 0.30 | 0.68 | 15.92 | 18.61 | 100.00 |
| P2       | 1.70  | 35.13 |      | 0.19 |      |       | 62.98 | 100.00 |

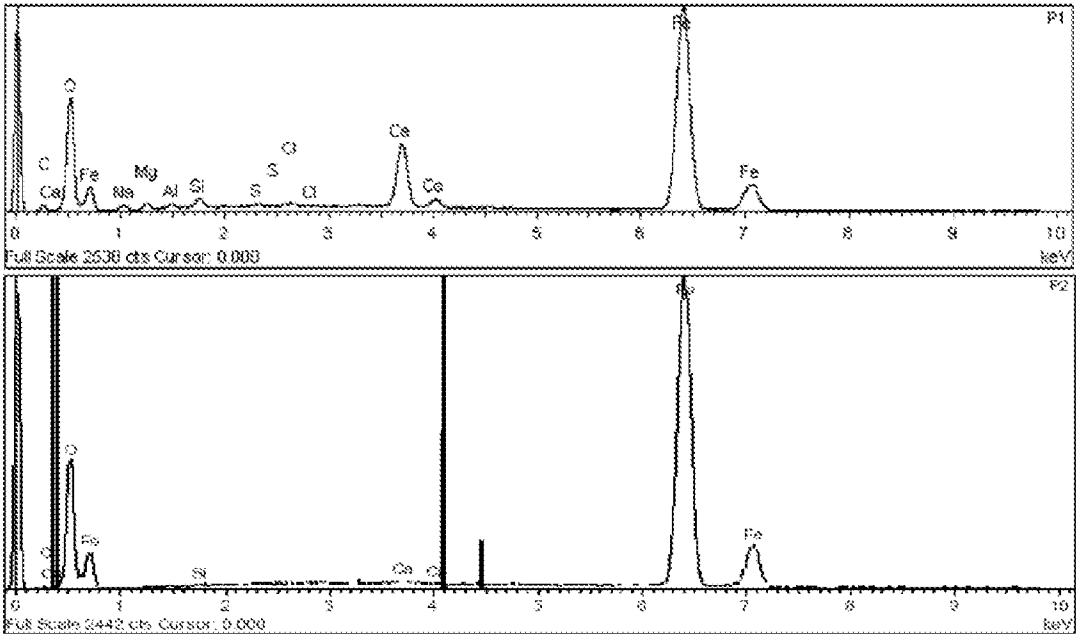


FIG. 10

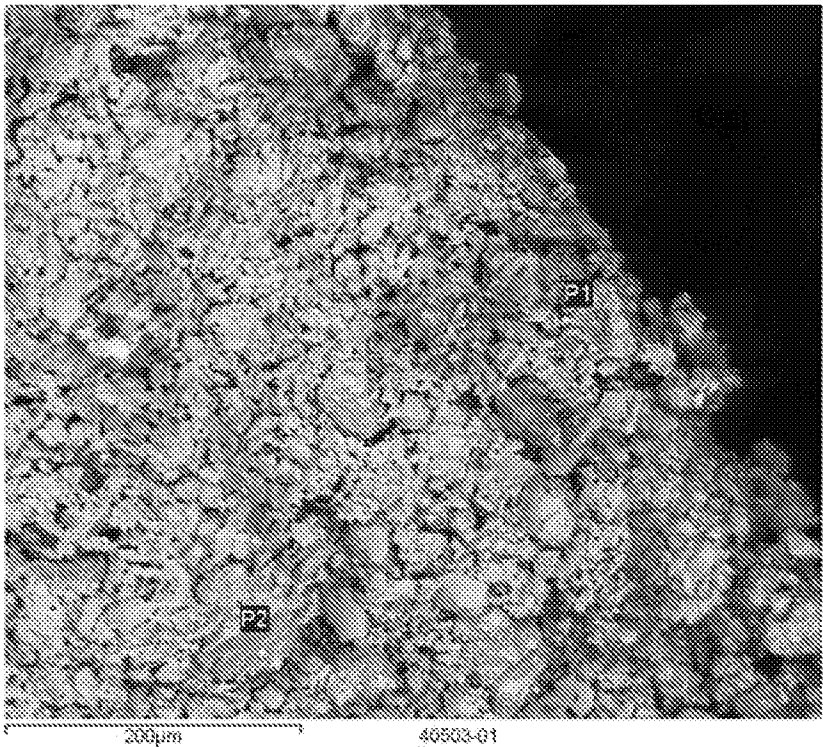


FIG. 11

| Spectrum | C    | O     | Na   | Mg   | Al   | Si   | S    | Cl   | K    | Ca    | Fe    | Total  |
|----------|------|-------|------|------|------|------|------|------|------|-------|-------|--------|
| P1       | 1.09 | 39.52 | 0.81 | 0.92 | 7.03 | 5.28 | 2.43 | 0.17 | 0.20 | 35.52 | 7.04  | 100.00 |
| P2       | 1.07 | 28.12 |      |      |      | 0.39 |      |      |      |       | 70.43 | 100.00 |

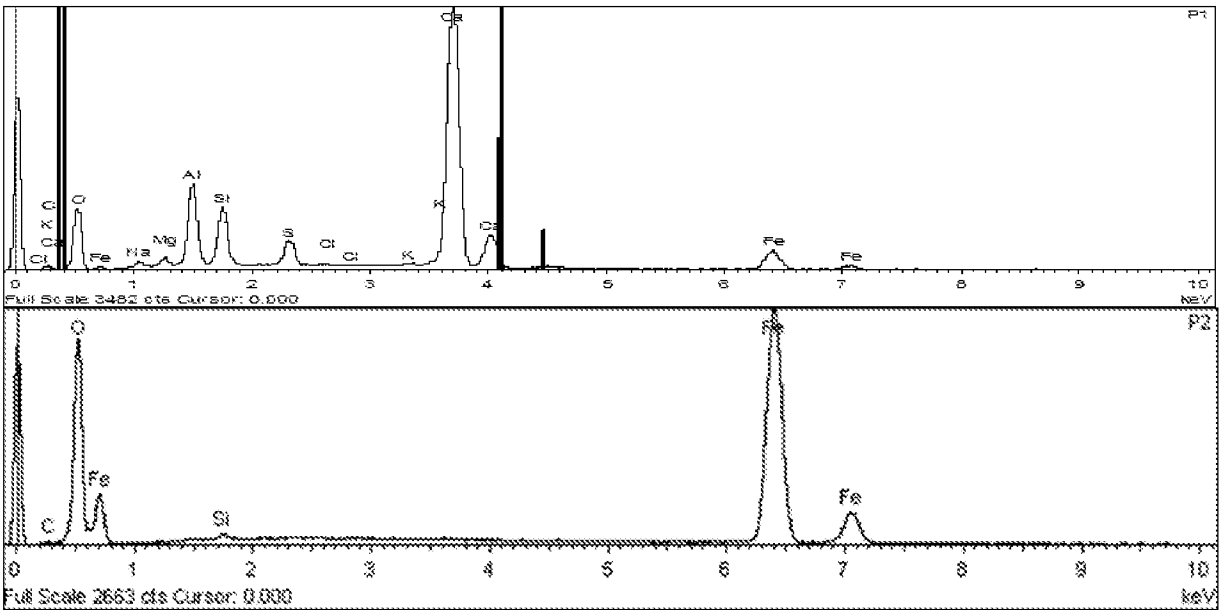


FIG. 12

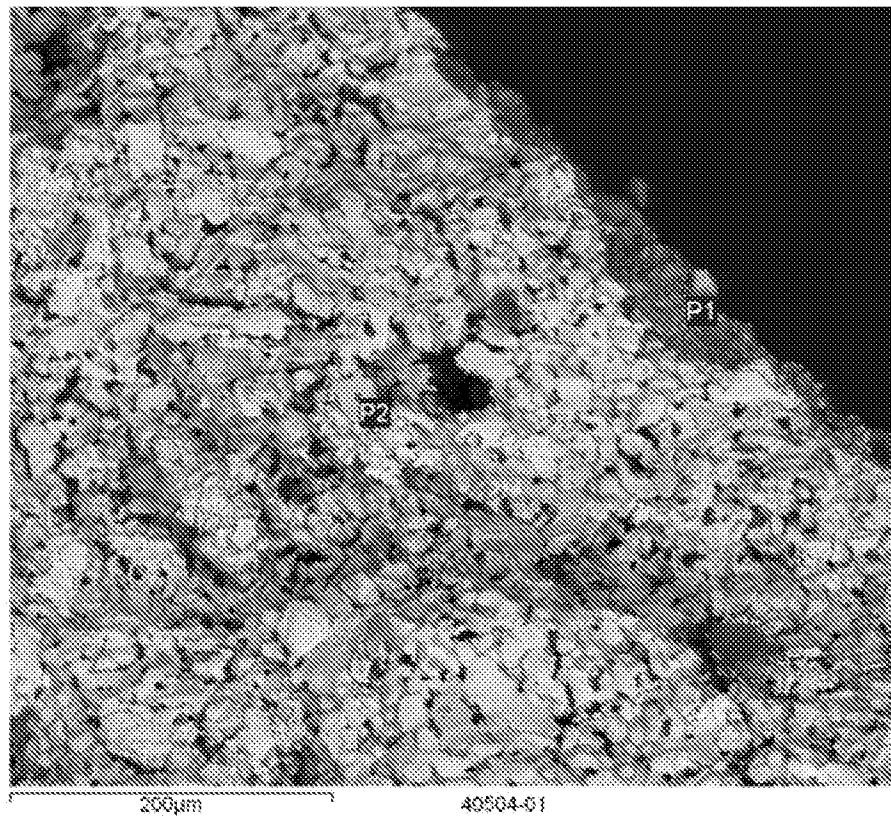


FIG. 13

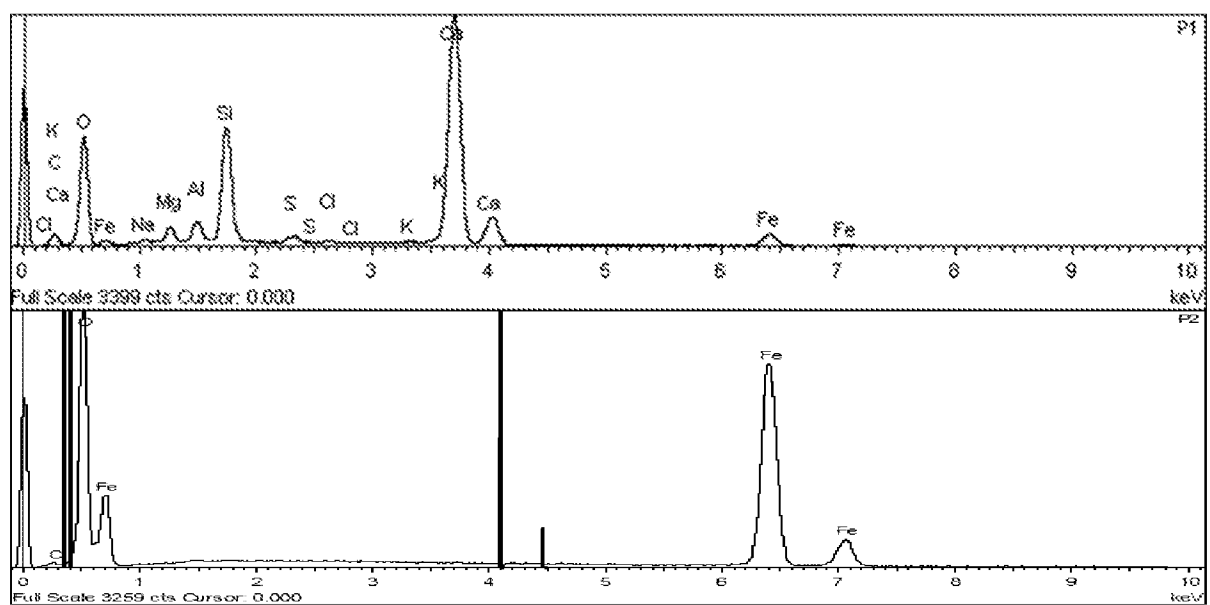
[illegible]

FIG. 14

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2016/055783

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C22B1/24  
ADD.

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)  
C22B

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

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

EPO-Internal, COMPENDEX, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                             | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 7 226 495 B1 (MOURAO JOSE MURILO [BR] ET AL) 5 June 2007 (2007-06-05)                                                                                                                                                       | 18-20                 |
| A         | the whole document                                                                                                                                                                                                             | 1-17                  |
| X         | DE 20 61 346 A1 (HÜTTENWERKE OBERHAUSEN AG, 4200 OBERHAUSEN) 22 June 1972 (1972-06-22)                                                                                                                                         | 18-20                 |
| A         | the whole document                                                                                                                                                                                                             | 1-17                  |
| X         | CASTRO P A ET AL: "Effect of different coatings on the adherence of direct reduction pellets", IRONMAKING CONFERENCE PROCEEDINGS, XX, XX, vol. 4, 11 November 2003 (2003-11-11), pages 195-202, XP009122851, figure 8; table 3 | 18-20                 |
|           | -----<br>-/--                                                                                                                                                                                                                  |                       |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

11 January 2017

Date of mailing of the international search report

30/01/2017

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer

Juhart, Matjaz

## INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2016/055783

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                     |                       |
|------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                  | Relevant to claim No. |
| A                                                    | <p>ANONYMOUS: "Iron ores for blast furnace and direct reduction feedstocks - Determination of the tumble and abrasion indices",<br/>ISO,<br/>no. 3271:2007, 1 October 2007 (2007-10-01)<br/>, pages i-6, XP002765793,<br/>-----</p> | 1-17                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/055783

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| US 7226495                                | B1                  | 05-06-2007                 | NONE                |
| DE 2061346                                | A1                  | 22-06-1972                 | NONE                |