Title: METHOD AND APPARATUS FOR REDUCING METALLIFEROUS MATERIAL TO A REDUCTION PRODUCT

Abstract: The present invention relates to a method for reducing metalliferous material to a reduction product. The invention also relates to an apparatus for reducing metalliferous material to a reduction product.
METHOD AND APPARATUS FOR REDUCING METALLIFEROUS MATERIAL TO A REDUCTION PRODUCT.

The present invention relates to a method for reducing metalliferous material to a reduction product. The invention also relates to an apparatus for reducing metalliferous material to a reduction product.

Reduction of metalliferous material, such as metal-oxygen compounds, metal-oxides, such as for instance iron oxides, has been performed in large-scale reduction furnaces. For the reduction of iron-oxygen compounds, the blast furnace has been the workhorse for the production of pig iron from metalliferous material such as iron-oxygen compounds or iron ore for over a century. The primary reductant and source of chemical energy in these blast furnaces has been coke.

Coke is produced by baking coal in the absence of oxygen in order to remove volatile hydrocarbons and to give the coke the critical properties for stable blast furnace operation. Coke making is problematic from an environmental perspective as many of the volatile hydrocarbons are hazardous. Also not all types of coal are suitable for coke making. Moreover, demand has decreased for the by-products of coke making. Therefore, decreasing the coke consumption and the over-all fuel consumption of the blast furnace has been a major focus of recent developments. Coal injection directly into the blast furnace is one of these developments. Also new technologies to circumvent the blast furnace process, such as direct reduction of iron ore, have been developed.

Direct reduction involves the production of iron by reduction of iron ore with a reducing agent, which can be a solid reducing agent or a gaseous reducing agent, at temperatures below the melting point of iron. The solid reducing agents may be coal of any size, instead of coke. Examples of gaseous reducing agents are natural gas, hydrogen and carbon monoxide (CO).

Direct reduction of iron ore may produce a final reduction product in the form of solid direct-reduced iron or, in combination with a smelting device, a liquid product. The final reduction product of a direct reduction process may be discharged into a second reactor for melting and optional further refining, or cooled and stored for later use.

At present, dust and sludge from an integrated steelworks is recycled as raw material in the ore preparation stage. These waste materials, often referred to as 'fines', may contain iron-containing compounds such as iron oxides. However, due to the content of metals such as zinc or zinc-compounds in these fines, the accumulation of such elements, and the limitations of the amount of these metals for charging into a blast furnace, these waste materials have often to be recycled in another way or disposed of, resulting in additional costs or burdening of the environment.
From WO2005/116273 a process is known for reduction of iron ore based on supplying a solid carbonaceous material such as coal and an oxygen-containing gas in a fluidized bed in a first vessel and generating heat, converting coal into char, and discharging a hot off-gas stream containing CO formed by partly oxidising the char. The CO, char and the inevitable remaining solid particles (such as ash) are then brought into a second vessel where metalliferous material is at least partly reduced. The solid reduction product containing at least partially reduced iron ore fines can be processed further as required, for instance in a fluidized bed for a second reduction stage to achieve a higher degree of reduction. As a result of the high process temperatures of at least 900°C the iron ore fines have a tendency to form accretions and agglomerates. This sticking behaviour is controlled by forming excess amounts of char in the first vessel. A further disadvantage is the development of large volumes of complex and hazardous hydrocarbons. Condensation of these hydrocarbons must be avoided which requires removal or post-combustion of the off-gases while re-oxidation of the metal must be prevented. Also, because of the high operating temperatures and consequent heat losses, the energy efficiency of the direct reduction processes is generally poor resulting in a high carbon consumption rate. The high operating temperatures also result in the formation of significant amounts of harmful nitrogen-oxygen compounds (NOx-gases) or, in a reducing atmosphere, ammonia-type compounds. Furthermore, direct reduction technologies based on the direct use of coal have to deal with higher levels of sulphur because of the presence of sulphur in the coal.

US 3,788,835 discloses an iron ore reduction process where the major portion of the reduction is effected with a gaseous reductant, for instance methane which dissociates into hydrogen and CO at high temperature. Reduction of the iron ore by the gaseous reductant is carried out until a metallization of about 85 to 90% is achieved. In the zone where the major portion of the metallization is achieved, carbon is deposited on the ore while the ore is being reduced. After having reached the degree of metallization of about 85 to 90%, the deposited carbon is subsequently allowed to interact with any remaining oxides in a separate inert stage resulting in an increase of metallization of between 0.5 and 2.5%.

EP 1 568 793 discloses a method for reducing metal-oxygen compounds in a reduction reaction in which carbon is used for reducing the metal-oxygen compounds wherein a metal acts as a catalyst for the reduction reaction. EP 1 568 793 discloses reactor types to perform the method involving extruder type screws as transportation means for the solid reactants.

It is an object of the invention to provide a method and an apparatus for direct reduction of metalliferous material using solid carbon as a reductant.

It is also an object of the invention to provide a method and an apparatus for reducing metal-oxygen compounds which can operate at relatively low temperatures for
increasing energy efficiency and/or for producing lower volumes of hazardous off-gases such as for example hydrocarbons and/or NOx-gases.

It is also an object of the invention to provide a method and an apparatus for reducing metal-oxygen compounds, which can result in an increased carbon efficiency per unit of weight of reduced metal.

To achieve one or more of these objects there is provided a method of reducing metalliferous material to a reduction product, the method comprising the steps of:

- providing a gaseous phase comprising gaseous CO by gasifying a carbon-containing compound using an oxygen containing gas flow;
- providing the metalliferous material in a reaction chamber of a fluidized bed reactor;
- providing said gaseous CO in the reaction chamber of the fluidized bed reactor and converting the gaseous CO into solid carbon and gaseous carbon dioxide, making the solid carbon precipitate onto the metalliferous material and/or onto the reduction product;
- reducing at least partly the metalliferous material by the solid carbon to the reduction product thereby using the metalliferous material and/or the reduction product as promoter of the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide;
- discharging a final reduction product from the reaction chamber,

wherein the final reduction product is further reduced in an end stage reactor to a higher degree of metallisation by a substantially solid-solid reaction between the solid carbon and the incompletely reduced portion of the reduction product.

The solid carbon is referred to as Boudouard-carbon and typically has the crystalline structure of graphite with a very high surface-to-volume ratio. For the sake of clarity it is noted that any other form of carbonaceous compound, such as coal or charcoal, is not considered to be solid carbon in the context of this description, even though the carbon content of these solid compounds is very high. The CO may be substantially pure CO, but it may also be part of a gaseous mixture comprising CO. The solid carbon is generated by dissociation of carbon-monoxide by the Boudouard reaction:

\[ 2 \text{ CO} \rightarrow \text{ C} + \text{ CO}_2 \]

This reaction, which is an equilibrium reaction, is shifted to the right side under the right conditions such as temperature and pressure, so that the carbon is formed. Moreover, it was found that the metalliferous material or the reduction product also promotes the formation of the solid carbon by the Boudouard reaction. It is emphasised that the reduction product in the context of this invention is not a product with a defined degree of
reduction, but it is used to express any state of reduction between the state of reduction of the metalliferous material, which has a degree of reduction of zero, and the final reduction product, which has a desired degree of reduction. This means that during the process according to the invention reduction products of different degree of reduction will coexist.

The degree of reduction of the final reduction product is therefore the average degree of reduction of the various fractions of reduction product making up the final reduction product. The degree of metallisation of a reduction product in the case of reducing iron ore (as a non-limiting example) as metalliferous starting material is defined as the ratio between the number of iron atoms in iron-carbide and metallic iron over the total number of iron atoms in the reduction product. The ratio between metallic iron and iron carbide depends on the process conditions in the reaction chamber.

It is believed that the reduction of the metalliferous material may involve the existence of a meta-stable carbide. The solid carbon or the Boudouard-carbon may react with the metalliferous material resulting in a meta-stable carbide which carbide ultimately disintegrates into the metal of the metalliferous material and carbon dioxide. So in the context of this invention solid carbon includes Boudouard carbon and meta-stable metal-carbide. This process is schematically represented and simplified by the following reactions:

\[
\begin{align*}
\text{MeO} + 2\text{CO} & \rightarrow \text{MeC} + \text{CO}_2 \\
\text{MeC} & \rightarrow \text{Me} + \text{C}
\end{align*}
\]

As far as the selection of the appropriate conditions in the reaction chamber is concerned, it is deemed within the capabilities of the skilled person to select these appropriate conditions. Small amounts of hydrogen are known to promote the formation of solid-carbon and carbon dioxide from CO by the Boudouard reaction. In case of using pure CO, small amounts of hydrogen may thus be added to the CO. In the invention typically more than 50%, preferably more than 70%, more preferably more than 80%, even more preferably more than 90% of the oxygen of the metal-oxygen compounds is bound to the deposited solid carbon after the final reduction in the end-stage reactor. If the gaseous mixture comprising CO is produced for instance by gasifying coal, the gaseous mixture may also comprise hydrogen.

Preferably, the amount of hydrogen is below 40 vol.%, preferably below 30 vol.%, in case technically pure oxygen is used as the oxygen containing gas flow in the gasifier, and preferably below 8 vol.%, more preferably below 6 vol.% in case air is used as the oxygen containing gas flow in the gasifier. The hydrogen does not play a significant role in the reduction of the metal-oxygen compounds due to the chosen operating conditions.
Preferably, the entire process of gasifying, reduction and final reduction is performed at a super-atmospheric pressure. The inventors found that an overpressure of at least 3 bar(g), and preferably of about 5 bar(g) is desirable. Due to loss of pressure over the process, the gasifier may be operated at a pressure of 8 bar(g) to ensure a 5 bar(g) overpressure in the FB's. This enables smaller reactor vessels to be used, and it may have a beneficial effect on the process conditions in the vessels. It is noted that it is also possible to operate only the gasifying and reduction at a super-atmospheric pressure and the final reduction at a much lower pressure, preferably sub-atmospheric pressure, but this results in a significantly larger end stage redactor, and thus higher capital and operational costs.

It should be noted that in the method according to the invention it is essential that the carbon, which is formed from the gaseous CO in the reaction chamber, is brought into the reaction chamber in gaseous form and converted to solid carbon in the reaction chamber by the Boudouard-reaction. The invention could therefore be characterised by the absence of any addition of carbon in solid form to the reaction chamber unless the solid carbon has passed through the gaseous state as a carbon oxide, and precipitated in the reaction chamber, preferably onto the metalliferous material or the reduction product formed by the reduction of the metalliferous material, optionally through a form of carbide of the metal of the metalliferous material, or onto already precipitated carbon, by the Boudouard-reaction. It is noted that during the start-up of the reaction, there may not yet be any reduction product present. This will only be present after some reduction of the metalliferous material has taken place. Pre-reduced reduction product may also be added to stimulate a faster start-up of the process.

The formation of solid carbon from carbon-monoxide is an exothermic reaction under the conditions in the reaction chamber. The energy which is released by this exothermic reaction can be advantageously applied in the reduction reaction in the reaction chamber of the metalliferous material by the solid carbon for producing a reduction product.

The use of a fluidized bed is crucial because of the high heat and mass transfer coefficients that can be obtained therein, due to the high surface area-to-volume ratio of the particles. Since in the method according to the invention the reactants are brought very close together, and are very reactive, and the formation of one of the reactants, i.e. the solid carbon, is exothermic, the conditions in the fluidized bed are optimal for the reduction of the metalliferous material particle. It is clear that the metalliferous material must also be of a certain morphology to enable fluidisation. The maximum particle size of the metalliferous material which can still be accommodated depends on the design and operational parameters of the fluidized bed.
The method according to the invention has the advantage that the solid carbon needed for the reduction of the metalliferous material is formed in situ, in a very reactive form, and by an exothermic reaction. This prevents the introduction of solid carbon containing material of a less reactive nature, or even a disturbing nature, into the reaction chamber, or of material which does not contribute to the reduction at all, such as ash. This disturbing nature may manifest itself in pollution of the reduction product, e.g. by sulphur, in a disturbance of the reduction reaction of the metalliferous material by the solid carbon or possibly in a disturbance of the formation of the solid carbon. Since the metalliferous material are provided in a reaction chamber of a fluidized bed, and the solid carbon precipitates from gaseous carbon-monoxide in the reaction chamber, preferably directly onto the metalliferous material or the reduction product, there is no danger of forming accretions and agglomerates.

In an embodiment of the invention the final reduction product after discharging from the reaction chamber of the fluidized bed reactor has a degree of reduction of at least 50%. This amount provides a good starting point for the reduction in the end-stage reactor.

In an embodiment the reduction in the end stage reactor takes place in a non-inert atmosphere. The non-inert atmosphere is important to create the proper reactive conditions for the final reduction product to be further reduced in the end stage reactor to the desired degree of reduction or metallisation at the end of the process. In an embodiment a hot gas flow comprising gaseous CO is fed into the end stage reactor. It was found that the introduction of a hot gas flow comprising gaseous CO, for instance originating from the gasifier, or recycled process gas, resulted in the proper reactive conditions in the end stage reactor. In an embodiment a CO/CO₂ and/or oxygen containing gas is provided into the end stage reactor, preferably wherein the CO/CO₂ containing gas is fresh syngas and/or recycled process gas and/or wherein the oxygen containing gas is air or technically pure oxygen. The end-stage reactor is fed with the reduction product from the last CFB along with fresh syngas or recycled process gas comprising CO and technically pure oxygen or air which is injected into the end-stage reactor. The reaction in the end-stage reactor is endothermic, and the released heat as a result of the oxygen injection, preferably by bottom-injection in the end-stage reactor, facilitates the conditions to enable to reach to the desired degree of reduction or metallisation at the end of the process.

In an embodiment of the invention, the fluidized bed is of the fast fluidization or pneumatic conveying or toroidal fluidized bed reactor type. These types of fluidized bed reactor allow the formation of a fast fluidized bed providing a high reaction rate for gasification and enough residence time of solids to complete the reactions.
In an embodiment of the invention the method is performed as a continuous process wherein the metalliferous material and gaseous CO are provided continuously or batchwise to the reaction chamber of the fluidized bed reactor so as to continuously produce the reduction product and wherein the final reduction product can be discharged continuously or batchwise from said reaction chamber. In this embodiment the exothermic nature of the formation of the solid carbon can be optimally used, and the process can be conducted in the most economical way. The capacity of the reactor in terms of unit mass per unit time of reduction product is one of the parameters with which the optimum process efficiency and thereby process economy can be reached. The final reduction product which is discharged from the reaction chamber is in solid form and has a degree of reduction which is, as a matter-of-course, higher than that of the metalliferous material which was provided in the reaction chamber as feed material. It should be noted that the final reduction product may be used as metalliferous material in a following process to be reduced to an even higher degree of reduction. In the latter case, degree of reduction has to be determined in respect to the degree of reduction of the metalliferous material prior to the first reduction process, which is generally assumed to be 0. A degree of reduction of 50% of the reduction product indicates that 50% of the oxygen of the metalliferous material has been removed from the metalliferous material. 50% of metallisation means that 50% of the metal atoms originally present in the metalliferous material is in metallic form and/or as metal-carbide. The other 50% is still in a more or less oxidised state. For the sake of clarity, a degree of reduction of 50% may mean that the degree of metallisation is still 0 if (for example) all MeO₂ has been reduced to MeO. It should be noted that the advantages of the invention are fully exploited when the metalliferous starting material has a degree of reduction of 0%, but it will be clear that when the degree of reduction of the metalliferous starting material is already higher, for instance because of a preliminary reduction operation, that the starting degree of reduction may be higher than 0. In case of iron ore 100% Fe₂O₃ would have a degree of reduction of 0%. Preferably this starting degree of reduction of the metalliferous material is below 25%, preferably below 15, more preferably below 5% and most preferably 0%.

In a preferred embodiment the final reduction product after discharging from the reaction chamber of the fluidized bed reactor has a degree of reduction of at least 50%, preferably at least 60%, more preferably at least 70%. Although the optimum degree of reduction would be towards complete reduction, i.e. at least a degree of reduction of 90 or 95%, or even higher, and substantially full reduction or full metallization would be technically achievable in a fluidized bed reactor, it is likely to be not the most economical process to do so. Moreover, the tendency for the reduced particles to stick increases with increasing degree of metallisation. It was found to be preferable to aim for a somewhat
lower degree of reduction of the final reduction product of at least 50%, preferably at least 60%, more preferably at least 70% and perform the final step towards a substantially complete degree of at least 90 or 95% of reduction in a dedicated process step in an end stage reactor.

In a preferred embodiment of the invention, the metalliferous material is an iron-compound, preferably iron ore. The inventors found that the process according to the invention could be performed advantageously by using an iron-compound, preferably iron ore as metalliferous material, because the advantageous temperature range of the formation of solid carbon from gaseous CO and the advantageous temperature range for the reduction of the iron-compound, preferably iron ore into metallic iron at least partly coincide. This results in a very economic process for the production of a final reduction product with a high degree of reduction or metallization, or even of substantially metallic iron.

In an embodiment of the invention the maximum temperature in the reaction chamber, particularly when using an iron-compound as a metalliferous material, is 875°C, preferably 845°C, more preferably 825°C and even more preferably 800°C or 790°C. It was found that even at these low temperatures in the reaction chamber the reduction of the metalliferous material by the solid carbon for producing a reduction product could be performed. The exothermic reaction of the formation of the solid carbon is able to sustain the reaction to a large extent, and the low temperature has as beneficial consequences that the energy loss due to high process temperatures is limited and that the formation of harmful nitrogen-oxygen compounds (NOx-gases) is prevented. Another advantage of the low operating temperatures is that the solubility of various elements in a metal decreases with temperature, thereby obtaining a metal with a higher purity. It was found that at temperatures in the reaction chambers below 400°C no significant reduction could be observed. At about 450°C and higher, for instance 500°C, the reduction rate increases significantly. A suitable minimum temperature for the reaction chamber was found to be 640 °C, preferably 690°C. However, although no significant reduction could be observed at temperatures below 500°C, the carbon deposition occurs very readily at a temperature of between 400 and 500°C because the presence of the metalliferous material or the reduction product formed by the reduction of the metalliferous material promotes the precipitation of solid carbon from the gaseous CO, optionally through a form of carbide of the metal of the metalliferous material, or onto already precipitated carbon, by the Boudouard-reaction. The equilibrium of the Boudouard-reaction will shift towards the left (CO-side) at higher temperature and this shift becomes notable above 600°C. It was found that at these temperatures and higher carbon is only deposited when there is already solid carbon present.
In an embodiment of the invention the promoter of the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide also acts as promoter of the reduction of the metalliferous material. This promoter has the function of causing the formation of solid carbon from gaseous carbon-monoxide and/or the reduction of the metalliferous material to take place more quickly, more completely or at lower temperature (or combinations of these), either by catalysis or by another reaction mechanism.

It is noted that the process according to the invention is suited for a process wherein the metalliferous material is a nickel-compound, preferably a nickel-ore, a cobalt-compound, preferably a cobalt-ore, or mixtures thereof resulting in an economical way of producing metallic cobalt, nickel or alloys thereof.

In an embodiment of the invention, the metalliferous material or, more particularly, the iron-compound or iron ore is provided in the form of a fine compound or ore, preferably wherein the grain size of the compound or ore is between 0.1 and 5000 μm. A suitable maximum grain size is 200 μm, preferably 100 μm. Preferably the grain size is at least 5 μm and preferably at most 50 μm, and more preferably between 5 and 50 μm. The use of these types of ores is particularly attractive from an economical point of view, as fine ores are generally cheaper than lumpy iron, and also because these fine ores are suitable for processing in fluidised beds.

Since the solubility of various elements, for instance carbon, in the ferritic morphology of iron decreases strongly with the temperature, and for carbon is about 0.02% at 720°C, the resulting final reduction product in the form of iron contains very small amounts of possibly undesirable elements.

According to an embodiment of the invention the metalliferous material is a mixture of at least two compounds of the group of compounds comprising a nickel-compound such as a nickel-ore, a cobalt-compound such as a cobalt-ore, iron-compound such as an iron ore. By using such a mixture of compounds the resulting (final) reduction product after full reduction of the metalliferous material is a mixture of the respective metals, and therefore an economical and simple way to produce alloys is provided.

In an embodiment of the invention the solid carbon is precipitated onto the metalliferous material and/or onto the reduction product in the form of carbon nano-tubes. The inventors surprisingly found that the solid carbon which is formed from the gaseous CO has the morphology of carbon nano-tubes. By appropriately designing the reaction chamber and appropriately selecting the process parameters, the process according to the invention can, as an alternative to producing a metal as the reduction product by reducing the metalliferous material particles, also be used to produce solid carbon in the form of carbon nano-tubes by persisting in the formation of the solid carbon from the gaseous CO and using the metalliferous material and/or the reduction product as a substrate for and/or
promoter of the formation of the carbon. In a subsequent process the solid carbon can be separated from the substrate. The substrate can then be re-used in the process and the nano-tubes can be used for various purposes.

In an embodiment of the invention, the gaseous CO which is provided in the reaction chamber of the fluidized bed reactor is prepared by gasifying a carbon-containing compound using an oxygen containing gas flow, preferably wherein said gas flow is a hot gas flow. Preferably the oxygen containing gas flow is technically pure oxygen, for instance having an oxygen content of at least 85%, preferably at least 90%, more preferably at least 95%. The advantage of using oxygen over air is that the reactors can be made smaller and that the process is more energy efficient, because air contains 80% inert nitrogen which has to be heated and cooled. By using a separate gasifying step the gaseous CO which is supplied to the reaction chamber can be stripped of undesirable components such as volatile hydrocarbons or sulphur compounds which are present in the carbon-containing compound or are formed by gasifying the carbon-containing compound. The gasifying step may be performed in a standard gasifier, but it is preferable to use an entrained flow gasifier because the major part of the ash is removed as a slag because the operating temperature of an entrained flow gasifier is well above the ash fusion temperature. It will be clear that it depends on how the gasifier is operated what the amount of gaseous CO in the gas leaving the gasifier (i.e. the gasifier off-gas or 'syngas') actually is. Syngas may for instance comprise varying concentrations of CO, CO₂, H₂, H₂O and N₂. The amount of gaseous CO in the gasifier off-gas also depends on the nature of the gas which is fed into the gasifier for gasification of the coal. If pure oxygen is used, the level of CO in the off-gas is higher than when air is used. Preferably the amount of gaseous CO in the gasifier off-gas is at least 10% (vol%). The equilibrium CO/CO₂ in the gasifier off-gas is at least 2, preferably at least 5, more preferably at least 10. The CO/H₂ should be at least 1, preferably above 3. The carbon-containing compound may be cokes, coal, charcoal, oil, polymers, natural gas, paper, biomass, tar sands or strongly polluted carbon-containing energy sources. This way the process according to the invention may contribute to efficient use of waste materials or otherwise uneconomical carbon-sources. It should be noted that the temperature of the gasifier off-gas may be very high, such as between 1300 and 1600°C, or about 1500°C. To be suitable for introduction into the fluidized bed reactor for reducing the metalliferous starting material, the gasifier off-gas must be cooled. The gasifier off-gas is cooled preferably by mixing it with cooler recycled process gas or cooled fresh syngas, or by cooling it in a heat exchanging unit. The resulting gaseous phase has a temperature of about 800°C and is fed to the FB where the gaseous phase enters the reduction process. It will be clear that the composition of the gaseous phase may have changed as a result of the mixing with the recycled gas because the recycled process gas
is the gaseous phase which may have been cleaned and CO₂-scrubbed after exiting the FB after having interacted with the metalliferous starting material in the FB.

In an embodiment of the invention off-gas is discharged from the reaction chamber wherein at least part of the remaining gaseous CO and/or the CO₂ is separated from the off-gas for reintroduction of said remaining gaseous CO and/or CO₂ into the gasifier reaction chamber. The CO₂ can be used as a source for providing CO by the reverse Boudouard reaction by reacting with the carbon of the carbon-containing compound in the gasifier. It is also possible only to reuse the CO-compound from the off-gas. This implies that the CO has to be separated from the off-gas, for instance using separation means such as a scrubber. The recycled CO-gas may be reintroduced into the reaction chamber of the fluidized bed, either directly, or after passing through the gasifier or a heat exchanging unit.

Instead of recycling the carbon in the off-gas, it is also possible to recycle any remaining chemical and/or thermal energy still present in the off-gas by burning the off-gas and/or using the thermal energy for instance for reheating the oxygen containing gas flow entering the gasifier for instance by feeding the hot off-gas exiting the reaction chamber through a heat exchanging unit for reheating the oxygen containing gas flow prior to entering the gasifier.

In a preferred embodiment, the reduction of the metalliferous material by the solid carbon takes place in a circulating fluidized bed (CFB) reactor, said reactor comprising a riser part and a return leg, wherein the metalliferous material and the gaseous CO are provided into the riser part of the CFB, and wherein a gas stream comprising the gaseous CO moves the metalliferous material in a substantially upward direction through the riser part of the CFB, and wherein the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide takes place at least partly during the substantially upward movement of the metalliferous material and the gaseous CO.

By using a CFB the reactants circulate through the reaction chamber, the reaction chamber comprising the riser part and the return leg of the CFB, and it is believed that the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide takes place, at least partly, during the substantially upward movement of the metalliferous material and the gaseous CO and that the reduction of the metalliferous material takes place substantially during the more or less stagnant phase in the return leg prior to being reintroduced into the riser part. Consequently, in an embodiment of the invention the metalliferous material and the reduction product resulting from the reduction of the metalliferous material and the solid carbon are discharged into the return leg of the CFB and the metalliferous material and the reduction product and the solid carbon move in a substantially downward direction through the return leg of the CFB and wherein reduction
of the metalliferous material and the reduction product by the solid carbon takes place at least partly, and preferably substantially, in the return leg of the CFB. Since the reduction of the metalliferous material by solid carbon is a solid-solid reaction, the reaction rates are lower than those of the gas-solid reaction of the formation of the solid carbon from the gaseous CO. The difference in residence times in the riser part and the return leg account for these different reaction rates.

The residence time of the metalliferous particle in the CFB is chosen such that a large number of circulations are made, depending on the desired degree of reduction or metallization. The CFB may be provided with separation means, such as a cyclone, to separate the solid parts such as the metalliferous material, the reduction product resulting from the reduction of the metalliferous material, and the solid carbon from the upward moving gas stream, the gas stream comprising gaseous CO and gaseous carbon dioxide. This separation is preferably performed near the upper part of the riser part of the CFB, preferably by one or more cyclones.

The process according to the invention may be performed as a batch process in that when the reduction product has reached the desired degree of reduction or metallization it is discharged from the reaction chamber as a final reduction product. This final reduction product may be provided to a following process step for further reduction or metallization.

In an embodiment of the invention the reduction of the metalliferous material takes place in a plurality of fluidized bed reactors (i.e. 2 or more) wherein the final reduction product of a preceding fluidized bed reactor (i) is discharged and passed to a subsequent (i+1)-th fluidized bed reactor for further reducing to a still higher degree of reduction or metallization. The temperature in the (i+1)-th fluidized bed reactor is preferably higher than in the i-th fluidized bed reactor. In this embodiment, the process conditions and FB-design may be optimized to achieve the respective degree of reduction or metallisation of the final reduction product. It may also be designed in such a way that the preceding fluidized bed reactor or reactors may be optimized for solid carbon production and that the subsequent reactor or reactors may be optimized for achieving a desired degree of reduction or metallization of the metalliferous material.

In a preferred embodiment the gaseous phases discharged from a subsequent fluidized bed are discharged into a preceding fluidized bed reactor for further processing. This way a counterflow-process is achieved for the gaseous phases, thus achieving the most economic use of the heat present in the gas, and of the CO-gas in the gaseous phases. The gaseous phases having the highest concentration of CO is therefore introduced in the fluidized bed reactor containing the reduction product with the highest degree of reduction or metallisation. This embodiment is therefore characterised by an overall counter flow of gaseous phases and metalliferous particles, even though in a
fluidized bed reactor the gaseous phases and metalliferous particles are not in counter flow, but flow in the same direction.

In an embodiment of the invention the final reduction product is further reduced to a still higher degree of reduction or metallization of at least 90%, preferably at least 95%, more preferably at least 98%, in an end stage reactor to a final reduction product by a substantially solid-solid reaction between remaining solid carbon and the incompletely reduced portion of the reduction product, wherein the end stage reactor preferably is a rotary kiln, a rotary hearth furnace or a fluidized bed reactor. It was found that a process involving 4, preferably 3, subsequent fluidised beds, preferably CFB's, is sufficient to reduce a metalliferous starting material having a starting degree of reduction of below 25%, preferably below 15, more preferably below 5% and most preferably 0% in an economical way to a degree of reduction or metallization and an amount of deposited solid carbon suitable to achieve the final reduction in an end-stage reactor to directly reduced metal, such as DRI.

In this embodiment the metalliferous material is nearly completely reduced to the respective metal. It was found that it is beneficial to perform the final reduction in an end-stage reactor reduced to a still higher degree of reduction or metallization of at least 90%, preferably at least 95%, more preferably at least 98%. Ideally, the degree of metallization would be still higher, i.e. above 99% or even above 99.5%. A further reduction in a rotary kiln, rotary hearth furnace or another fluidized bed reactor has proven to be advantageous. It is also possible to achieve a higher degree of metallisation by subjecting the reduction product to a smelting operation.

The final reduction product as provided by the process according to the invention has a large surface area as a direct consequence of the process. When using iron-oxygen compounds or iron ore as metalliferous material, the intermediary and/or the final reduction product will comprise metallic iron or strongly reduced iron-oxygen compounds. In the process according to the invention, iron with very few contaminants and with a very large specific area is obtained. This makes the reduction product extremely suitable for the Sponge Iron Process (SIP) for the production of hydrogen. The Sponge Iron Process is a well-known technology for the production of hydrogen. It comprises a step wherein iron or reduced iron-oxide is re-oxidised with steam to form magnetite and hydrogen. The produced hydrogen has a high purity grade, compliant with the requirements of fuel cell noble metal catalysts. The process is therefore very interesting for production and purification of hydrogen for use in high and low temperature fuel cells. Of course the hydrogen can also be used for other purposes.

The final reduction product in the form of iron, or in the form of strongly reduced iron-oxygen compounds, with a very large specific surface area as provided by the process
according to the invention is used as a fuel in a vehicle wherein the reduction product is
oxidised by steam to form hydrogen which can, for instance, be used to power a fuel cell
and propel the vehicle, or drive an engine or device. The hydrogen which can be produced
using final reduction product in the form of iron or strongly reduced iron-oxygen
compounds produced by the process according to the invention is more economical than
that produced from, for instance, natural gas and produces less carbon dioxide as well.
The final reduction product may be subjected to a separation treatment to separate
the metallic part from a non-metallic part such as gangue or slag. This separation
treatment may comprise techniques such as gravimetric treatments, particle size
treatments or a magnetic treatment.
The final reduction product may be further processed by compacting the product into
a compacted product, preferably by briquetting or by rolling into a rolled product. This
briquetted or rolled product may be used in a smelting operation. The rolled product may
be used as feed material in a further rolling operation, or it may even be used for direct
application provided the rolled product has the desired properties for such a direct
application.

According to a second aspect of the invention there is provided an apparatus for
reducing metalliferous material to a reduction product according to the method of the
invention comprising:

- at least one fluidized bed reactor comprising a reaction chamber;
- a gasifier for producing a gaseous phase comprising gaseous CO by gasifying a
carbon-containing compound using an oxygen containing gas flow comprising an
inlet for providing said oxygen containing gas, an inlet for providing the carbon-
containing compound, an outlet for the gaseous phase comprising gaseous CO, and
an optional outlet for solid waste materials such as slag,
- a first inlet to the reaction chamber for introducing the metalliferous material;
- a second inlet for introducing the gaseous CO into the reaction chamber;
- means for generating a fluidized bed comprising the metalliferous material and the
gaseous CO in the reaction chamber;
- means for obtaining a suitable temperature in the reaction chamber for enabling
conversion of the gaseous CO into solid carbon and gaseous carbon dioxide, and
precipitation of the solid carbon onto the metalliferous material and/or onto the
reduction product, and for reducing the metalliferous material by the solid carbon for
producing a reduction product;
- means for directing at least a part of the constituents of the fluidized bed towards
separation means for separating the reduction product from the fluidized bed and
optionally means for directing the off-gas from the fluidized bed to recycling means;
- a return part for returning at least part of the reduction product separated from the gas stream to the reaction chamber and an outlet for discharging the remaining reduction product from the reaction chamber as final reduction product.

The fluidized bed reactor provides a very efficient device for allowing the metalliferous material to function as locations where the solid carbon can precipitate because of the high heat and mass transfer coefficients, due to the high surface area-to-volume ratio of the particles. Since the reactants are brought very close together, and are very reactive, and the formation of one of the reactants, i.e. the solid carbon, is exothermic, the conditions in the fluidized bed are optimal for the reduction of the metalliferous material particle. It is clear that the metalliferous material particle must also be of a certain size to enable fluidisation. The maximum particle size which can still be accommodated depends on the design and operational parameters of the fluidized bed. In addition, since the solid carbon precipitates from gaseous carbon-monooxide in the reaction chamber in the fluidized bed, preferably directly onto the metalliferous material or the at least partly reduced metalliferous material, there is no danger of forming accretions and agglomerates. The inlet for providing the oxygen containing gas, and the inlet for providing the carbon-containing compound into the gasifier may be combined into one inlet.

In a preferred embodiment the fluidized bed reactor is a circulating fluidised bed (CFB) comprising:

- a riser part for accommodating a substantially upward movement of the fluidized bed, the fluidized bed comprising the metalliferous material and the gaseous CO;
- means for directing the constituents of the fluidized bed towards separation means upon reaching the top part of the riser part for separating the reduction product from the fluidized bed and means for directing the gaseous phases from the fluidized bed to recycling means and means for directing the reduction product to the return leg;
- a return leg for accommodating a substantially downward movement of the reduction product;
- means for discharging the off-gas from the fluidized bed for further processing;
- means for returning at least part of the reduction product from the return leg to the reaction chamber, said means also comprising an outlet for discharging the remaining reduction product as the final reduction product from the reaction chamber.

The residence time of the metalliferous particle in the CFB is such that a large number of circulations are made, depending on the desired degree of metallization of the reduction product. The CFB may be provided with separation means, such as one or more cyclones, to separate the solid parts such as the metalliferous material, the reduction product, and the solid carbon are separated from the upward moving gas stream, the gas
stream comprising gaseous CO and gaseous carbon dioxide. This separation is preferably performed near the upper part of the riser part of the CFB, preferably by one or more cyclones.

In an embodiment of the invention the means for returning at least part of the reduction product from the return leg to the reaction chamber is a loop seal or loop seal valve. The advantage of a loop seal is that it can be used to selectively allow portions of the reduction process into the reaction chamber. By using a multiple loop seal, portions of the reduction product can also be allowed to be discharged as final reduction product.

In an embodiment the apparatus according to the invention comprises a plurality of connected fluidized bed reactors wherein means are provided for transporting the final reduction product from a preceding fluidized bed to the reaction chamber of a subsequent fluidized bed reactor for further reduction of to a higher degree of reduction. In the context of this description a plurality is understood to mean: two or more. So two, three, four or more connected fluidized bed reactors may be used. Means may also be provided for providing the gaseous phases discharged from a subsequent fluidized bed for further processing into a preceding fluidized bed reactor and thereby allowing the creation of an overall countercflow gas stream. In an embodiment means are provided for operating a subsequent fluidized bed reactor at a higher temperature than a preceding fluidized bed reactor, preferably wherein any subsequent reactor operates at a higher temperature than any preceding fluidized bed reactor.

In an embodiment the apparatus is provided with recycling means for separating at least part of the remaining gaseous CO and/or CO₂ from the off-gas for instance for reintroduction thereof into the reaction chamber of the fluidized bed reactor or into the reaction chamber of one or more of the fluidized bed reactors or into the gasifier or into a heat exchanging unit to recover at least part of the thermal or chemical energy still present in the off-gas, for instance by burning the combustible components and use the heat to preheat a gaseous phase entering the apparatus or by reintroducing the CO and/or CO₂ into the gasifier to use it as a carbon source.

In an embodiment the apparatus is provided with an end stage reactor for reducing the final reduction product to a still higher degree of reduction or metallization by a substantially solid-solid reaction of the solid carbon with the incompletely reduced portion of the reduction product, preferably wherein the end stage reactor is a rotary kiln, rotary hearth furnace or fluidized bed reactor. The solid carbon is preferably passed from the fluidized bed reactors where it was formed with the reduction product into the end stage reactor, although solid carbon could also be added to the reduction product prior to introduction of the reduction product into the end stage reactor in the event the amount of solid carbon transferred from the fluidised bed would be insufficient to achieve the desired
degree of reduction or metallization of the final reduction product after leaving the end stage reactor. In an embodiment the apparatus according to the invention comprises means for separating the metallic part of the final reduction product from the remaining part, for instance by gravimetric, magnetic or particle size means.

In a preferable embodiment, the apparatus for performing the process according to the invention comprises a gasifier, preferably of the entrained flow type, three consecutive CFB-reactors, and an end-stage reactor of the rotating kiln type or of the FB-type, preferably of the bubbling FB-type. The embodiment is described for the reduction of iron ore, but the description is equally valid for the reduction of other metalliferous materials requiring only minor amendments of the process parameters. The gasifier is provided with technically pure oxygen and coal powder. In the entrained flow gasifier the dry pulverized coal is gasified with technical oxygen in co-current flow. The gasification reactions take place in a dense cloud of fine particles. The high temperatures and pressures mean that a higher throughput can be achieved and that tar and volatile hydrocarbons such as methane are not present in the gasifier off-gas. An entrained flow gasifier removes the major part of the ash as a slag as the operating temperature is well above the ash fusion temperature. A smaller fraction of the ash is produced as a very fine dry fly ash which is transported with the gaseous CO towards the last CFB. The gasifier off-gas comprising the CO has a very high temperature at the outlet of the gasifier of about 1300 to 1600°C, preferably about 1400 to 1500°C. Optionally, cold CO₂ containing gas may be provided as a moderator for controlling the temperature in the gasifier. The conventionally used steam is not preferred as a moderator, because this will adversely affect the CO/H₂ ratio. The gasifier off-gas is cooled, preferably by mixing it with recycled cooler process gas or cooled syngas, or in a heat exchanging unit. The resulting cooled gasifier off-gas has a temperature of about 800°C and is fed to the last CFB where the gasifier off-gas (the syngas) enters the reduction process. Prior to introduction into the last CFB, the gasifier off-gas may have been treated to remove sulfur from the gas, for instance by a calcium treatment to form CaS.

The iron-compound or iron ore is provided in the form of a fine compound or ore, preferably having a grain size between 5 and 200 μm. This material is provided to the CFB's in counterflow to the gasifier off-gas, and therefore enters the apparatus in the first CFB. The temperature in this first CFB is the lowest, and optimised for the purpose of deposition of solid carbon onto the compound or ore. The temperature in the first CFB is controlled to be between 350 and 600°C, preferably between 400 and 500°C so as to form solid carbon (i.e. Boudouard carbon and/or iron-carbide). The reduction of the iron ore, particularly the reduction of hematite to magnetite already starts at these low temperatures and iron-carbide (Fe₃C) starts to be formed. The iron compound, and/or the products of the
reduction thereof act as a catalyst for the formation of solid carbon at these low temperatures. The conditions in the return leg of the CFB are such that the following reaction is made possible:

\[
\text{FeO} + \text{Fe}_2\text{C} \rightarrow (1+x) \text{Fe} + \text{CO}
\]

When leaving the last CFB (which because of the counterflow principle is the first one for the solid phases and the last one for the gaseous phase), the reduction product has reached the desired degree of reduction of at least 50%, preferably of at least 60%, more preferably at least 70%, and/or is loaded with enough solid carbon to enable the final reduction to DRI in the end-stage reactor to a degree of reduction or metallization of at least 90%, preferably at least 95%, more preferably at least 98%. So the process parameters can be so chosen that the iron ore has not reached the desired degree of 50% reduction when leaving the last CFB, but instead is loaded with enough solid carbon to enable the final reduction to DRI to the said degree of reduction or metallization of at least 90%. In this case the CFB-reactors are used to produce the solid carbon needed to reduce the iron ore, rather than to reduce the iron ore and the reduction of the iron ore consequently takes place in the end stage reactor.

The end-stage reactor is fed with the reduction product from the last CFB along with fresh syngas or recycled process gas comprising CO and technically pure oxygen or air which is injected into the end-stage reactor. The reaction in the end-stage reactor is endothermic, and the released heat as a result of the oxygen injection, preferably by bottom-injection in the end-stage reactor, facilitates the conditions to enable the abovementioned final reduction. As the end-stage reactor is a fluidised bed, the occurrence of local hot spots is prevented, and the risks of clogging the process by coagulation of the fine particles in the reactor is minimised. The risk of clogging can be further reduced, if necessary, by the addition of additives to the fluidised bed as described in US 3,615,352. The temperature in the end-stage reactor is preferably between 680 and 850°C, for instance about 750°C ± 20°. The majority of the reduction reactions in the end-stage reactor are believed to be net solid-solid reactions, and not gas-solid reactions. The gases present merely help creating the conditions to enable the solid-solid reactions to take place by manipulating the CO-\(\text{CO}_2\)-T stability diagram for iron and its oxides. The inventors found that the post combustion ratio of the gaseous phase entering the end-stage reactor is substantially the same as the post combustion ratio

\[
(\text{PCR} = \frac{\text{CO}_2 + \text{H}_2\text{O}}{\text{CO}_2 + \text{CO} + \text{H}_2\text{O} + \text{H}_2})
\]

result of the generation of CO during the final reduction. It is noted that, although the embodiment is described with 3 CFB's, that the use of 2, 4, 5 or more CFB's is also
possible. The inventors found that the use of 3 or 4 CFB's provides a good combination of a low temperature CFB for depositing carbon onto the metalliferous starting material, a medium temperature CFB for further depositing carbon, and a final 'high' temperature CFB for completing the reduction of the metalliferous starting material to the desired degree of reduction or metallization and amount of deposited solid carbon to provide a good reduction product for introduction into the end-stage reactor.

The final reduction product exiting the end-stage reactor may also comprise gangue, slag, CaS or other undesirable substances, and these may be separated from the metallic phase in a magnetic separation operation.

The final off-gas of the process, which can no longer be introduced into the process, may still retain some chemical or thermal energy which may be used, for instance by combusting it and/or using the heat.

In an embodiment the apparatus comprises a recycling unit for recycling Zn and/or Pb and/or Cd from Zn and/or Pb and/or Cd containing metalliferous material, the unit comprising means for enabling reduction of the Zn-, Pb- and/or Cd-containing compounds by the solid carbon to metallic Zn, Pb and/or Cd and to evaporate the Zn, Pb and/or Cd to produce gaseous Zn, Pb and/or Cd.

In an embodiment the apparatus comprises
- condensation means for condensing and/or solidify the gaseous Zn, Pb and/or Cd into liquid and/or solid Zn, Pb and/or Cd, or
- oxidation means for oxidizing the gaseous Zn, Pb and/or Cd to zinc-oxygen compounds, lead-oxygen compounds and/or cadmium-oxygen compounds.

This embodiment allows for the processing of, for example, iron-rich waste material from the steel industry. These materials, such as iron rich dust from the steel production, can be used as metalliferous material in the process and apparatus according to the invention. Beside iron-oxygen compounds, these materials may also comprise zinc-oxygen compounds, lead-oxygen compounds or cadmium-oxygen compounds. These compounds are recycled from the metalliferous material by reducing the iron-oxygen compounds to iron compounds. The Zn, Cd or Pb is also reduced in the course of the process and brought in a gaseous state. The reduction of zinc-oxygen compounds, lead-oxygen compounds or cadmium-oxygen compounds may take place by the solid carbon or by direct reaction with gaseous CO or H₂. Thereafter, the Zn, Cd or Pb metals can be condensed from the gaseous states, or oxidised and collected as zinc-oxygen compounds, lead-oxygen compounds and/or cadmium-oxygen. In a preferable embodiment the apparatus comprises a de-zincing unit, the de-zincing unit comprising heating means for heating the metalliferous material or the reduction product or the final reduction product for reducing the Zn-containing compounds to metallic Zn and to evaporate the Zn to produce...
gaseous Zn or to oxidize the Zn to produce a zinc-oxygen compound such as ZnO or Zn(OH)$_2$. This embodiment is particularly advantageous for processing Zn-rich waste material of which the Zn-content is too high to be used in for example conventional iron and steel production. The process can also be adapted to extract the Zn-, Cd and/or Pb from the fines and using the fines in a conventional iron production route involving a blast furnace.

In an embodiment the apparatus comprises condensation means for condensing and/or solidify the gaseous Zn into liquid and/or solid Zn.

The invention will now be further explained by means of the following, non-limiting figures. In figure 1, the basic layout of the fluidized bed reactor is shown. In figure 2, the basic layout of the complete apparatus for carrying out the method of the invention is shown. In figure 3, the basic layout of the apparatus for carrying out the method of the invention comprising at least two circulating fluidized bed reactors and an end stage reactor is shown. In figure 4, the basic layout of the apparatus according to figure 2 comprising a recycling unit for recycling Zn from Zn containing metalliferous material is shown. Figure 5 and 6 show alternative embodiments of figure 2 and 3 respectively.

In figure 1, the fluidized bed reactor, in this example a circulating fluidized bed, 1 is provided with metalliferous material 2, and a gas flow comprising gaseous CO 3. After the upward movement through the riser part of the circulating fluidized bed 1 of the metalliferous material 2, and a gas flow comprising gaseous CO, the material is led towards means 5 for separating gas and solid particles. The off-gas is led away from the means 5, which is indicated by the arrow pointing upward from means 5.

The solid parts comprising the solid carbon which is formed from the gaseous CO and the metalliferous material react so as to reduce the metalliferous material to a reduction product. This reduction product descends through the return leg to means 7, such as a loop-seal, for returning at least part of the reduction product to the reaction chamber of the circulating fluidized bed for one or more additional cycles. Alternatively, at least part of the reduction product may be discharged as a final reduction product, which is indicated by the arrow pointing right from means 7.

In figure 2, the part of the reduction product which may be discharged from the means 7 is provided into means 4. This means 4 may be an end stage reactor, such as a rotary kiln, rotary hearth furnace or fluidized bed reactor. Alternatively, means 4 may be one or more additional cycles comprising parts 1, 5, 6 and 7, wherein 6 is the schematical representation of the return leg of the circulating fluidized bed reactor, 1 is the riser part and 5 is the separation means, such as a cyclone. This situation is schematically indicated in figure 3. Means 4 may also represent one or more circulating fluidized bed reactors and an end stage reactor. In figure 2 and 3 the gas flows are schematically indicated with the
dotted or dashed arrows ('g') and non-gas-flows are indicated with the full arrows ('s').

Gaseous products separated by means 5 may be led towards a gas cleaning unit 11 and
led away, or it may be led from the gas cleaning unit 11 towards the gas source 12, such
as a gasifier, for re-use of the gas and/or for preheating purposes. In figure 2, the gas
comprising the gaseous CO is produced in gas source 12, for instance by gasifying coal,
and the hot gas flow 8 comprising the gaseous CO is fed through means 4 in general or
overall countercurrent to the metalliferous material and/or the reduction product. This
is indicated by gas flow 3. Within the riser part of the circulating fluidized bed the flow of the
metalliferous material and/or the intermediary reduction product is concurrently with the
gas flow, as indicated by the fat arrow in the riser part 1 and 1a.

In figure 4, the apparatus of figure 2 is combined with a unit for recycling Zn and/or
Pb and/or Cd from Zn and/or Pb and/or Cd containing metalliferous material. The final
reduction product 9 still comprising the Zn and/or Pb and/or Cd containing metalliferous
material is brought into means 13 together with a hot gas flow 8 comprising gaseous CO,
which is used to reduce the zinc-oxygen compounds or lead-oxygen compounds or
cadmium-oxygen compounds to metallic lead, zinc or cadmium. This metallic lead, zinc or
cadmium may then be brought in a gaseous state and provided into means 15. In means
15, the metals can be condensed from the gaseous states, or oxidised and collected as
zinc-oxygen compounds, lead-oxygen compounds and/or cadmium-oxygen.

In figure 5 an alternative embodiment to the one in figure 2 is presented wherein the
syngas from the gasifier, after being cooled to about 800°C, is introduced into the CFB.
The syngas is separated from the solid particles in means 5 and the recycled gas is
cleaned in gas cleaning unit 11. After the gas cleaning unit the recycled process gas may
be led to the end stage reactor 4, or to the gasifier 12. The recycled gas may be led
directly into the gasifier, or it may be used to cool the fresh syngas produced by the gasifier
to about 800°C. Means 4 may have the same alternative meanings as presented for figure
2. The alternative gas flow as presented in figure 5 may also be applied to the embodiment
of figure 3 (see figure 6) and figure 4.
CLAIMS

1. Method of reducing metalliferous material to a reduction product, the method comprising the steps of:
   - providing a gaseous phase comprising gaseous CO by gasifying a carbon-containing compound using an oxygen containing gas flow;
   - providing the metalliferous material in a reaction chamber of a fluidized bed reactor;
   - providing said gaseous CO in the reaction chamber of the fluidized bed reactor and converting the gaseous CO into solid carbon and gaseous carbon dioxide, making the solid carbon precipitate onto the metalliferous material and/or onto the reduction product;
   - reducing at least partly the metalliferous material by the solid carbon to the reduction product thereby using the metalliferous material and/or the reduction product as promoter of the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide;
   - discharging a final reduction product from the reaction chamber, wherein the final reduction product is further reduced in an end stage reactor to a higher degree of reduction or metallization by a substantially solid-solid reaction between the solid carbon and the incompletely reduced portion of the reduction product.

2. Method according to claim 1 wherein the final reduction product after discharging from the reaction chamber of the fluidized bed reactor has a degree of reduction of at least 50%.

3. Method according to claim 1 or 2 wherein the reduction in the end stage reactor takes place in a non-inert atmosphere.

4. Method according to claim 1, 2 or 3 wherein a hot gas flow comprising gaseous CO is fed into the end stage reactor.

5. Method according to any one of the preceding claims wherein a CO/CO\(_2\) and/or oxygen containing gas is provided into the end stage reactor, preferably wherein the CO/CO\(_2\) containing gas is fresh syngas and/or recycled process gas and/or wherein the oxygen containing gas is air or technically pure oxygen.
6. Method according to any one of preceding claims wherein the method is performed as a continuous process wherein the metalliferous material and gaseous CO are provided continuously or batchwise to the reaction chamber so as to continuously produce the reduction product, and wherein the final reduction product is discharged continuously or batchwise from said reaction chamber.

7. Method according to any one of preceding claims wherein the final reduction product has a degree of reduction of at least 50%, preferably at least 60%, more preferably at least 70%.

8. Method according to any one of preceding claims wherein the maximum temperature in the reaction chamber is 875°C, preferably 845°C, more preferably 825°C and even more preferably 800°C.

9. Method according to any one of preceding claims wherein the promoter of the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide also acts as promoter of the reduction of the metalliferous material.

10. Method according to any of the preceding claims wherein the metalliferous material is an iron compound, preferably iron ore.

11. Method according to claim 10 wherein the iron ore is provided in the form of a fine ore, preferably wherein the grain size of the ore is between 0.1 and 5000 μm and more preferably between 5 and 50 μm.

12. Method according to any one of claims 1 to 9 wherein the metalliferous material is a nickel-compound, preferably a nickel-ore, a cobalt-compound, preferably a cobalt-ore, or mixtures thereof.

13. Method according to any one of claims 1 to 9 wherein the metalliferous material is a mixture of at least two compounds of the group of compounds comprising a nickel-compound such as a nickel ore, a cobalt-compound such as a cobalt ore, an iron-compound such as an iron ore.

14. Method according to any one of the preceding claims wherein the gaseous CO is prepared by gasifying a carbon-containing compound using an oxygen containing gas flow, preferably wherein said gas flow is a hot gas flow.

15. Method according to any one of the preceding claims wherein off-gas is discharged from the reaction chamber, and wherein at least part of the remaining gaseous CO
and/or the CO\textsubscript{2} is separated from the off-gas for reintroduction of said remaining gaseous CO and/or CO\textsubscript{2} into the gasifier reaction chamber.

16. Method according to any one of the preceding claims wherein off-gas is discharged from the reaction chamber, and wherein at least part of the remaining gaseous CO and/or the CO\textsubscript{2} is separated from the off-gas for preheating the gas flow before entry into the gasifier.

17. Method according to any one of the preceding claims wherein the reduction of the metalliferous material by the solid carbon takes place in a circulating fluidized bed (CFB) reactor, said reactor comprising a riser part and a return leg, wherein the metalliferous material and the gaseous CO are provided into the riser part of the CFB, and wherein a gas stream comprising the gaseous CO moves the metalliferous material in a substantially upward direction through the riser part of the CFB, and wherein the conversion of the gaseous CO into solid carbon and gaseous carbon dioxide takes place at least partly during the substantially upward movement of the metalliferous material and the gaseous CO.

18. Method according to claim 17 wherein the metalliferous material and the reduction product resulting from the reduction of the metalliferous material and the solid carbon are discharged into the return leg of the CFB and the metalliferous material and the reduction product and the solid carbon move in a substantially downward direction through the return leg of the CFB and wherein reduction of the metalliferous material and the reduction product by the solid carbon takes place at least partly, and preferably substantially, in the return leg of the CFB.

19. Method according to any one of the preceding claims wherein reduced metalliferous material having reached the desired degree of reduction is discharged from the reaction chamber as the final reduction product.

20. Method according to any one of the preceding claims wherein the reduction of the metalliferous material takes place in a plurality of fluidized bed reactors wherein the final reduction product of a preceding fluidized bed reactor is discharged and passed to a subsequent fluidized bed reactor for further reducing to a still higher degree of reduction.

21. Method according to claim 20 wherein the gaseous phases discharged from a subsequent fluidized bed is discharged into a preceding fluidized bed reactor for further processing.
22. Method according to any one of the preceding claims, wherein the fluidized bed is of the fast fluidization or pneumatic conveying type.

23. Method according to any one of the preceding claims wherein the final reduction product is further reduced to a degree of metallization of at least 90%, preferably at least 95%, more preferably at least 98% in the end stage reactor by a substantially solid-solid reaction between the solid carbon and the incompletely reduced portion of the reduction product, wherein the end stage reactor preferably is a rotary kiln, a rotary hearth furnace or a fluidized bed reactor.

24. Method according to any one of the preceding claims wherein the final reduction product is treated to separate the metallic part from a non-metallic part such as gangue or slag.

25. Method according to any one of the preceding claims wherein the final reduction product is further processed by compacting the product into a compacted product, preferably by briquetting or by rolling into a rolled product.

26. Method according to any one of the preceding claims wherein the metalliferous material comprises iron-oxygen compounds and zinc-oxygen compounds, the method involving reduction of the iron-oxygen compounds according to any one of the preceding claims, involving reduction of the zinc-oxygen compound by solid carbon originating from the gaseous CO to zinc, vaporising the zinc, followed by a zinc recovery step optionally involving condensation of the zinc from the gaseous states or involving re-oxidation of the zinc and collection as zinc-oxygen compounds.

27. Apparatus for reducing metalliferous material to a reduction product according to the method of any of the preceding claims comprising:
   - at least one fluidized bed reactor comprising a reaction chamber;
   - a gasifier for producing a gaseous phase comprising gaseous CO by gasifying a carbon-containing compound using an oxygen containing gas flow comprising an inlet for providing said oxygen containing gas, an inlet for providing the carbon-containing compound, an outlet for the gaseous phase comprising gaseous CO, and an optional outlet for solid waste materials such as slag,
   - a first inlet to the reaction chamber for introducing the metalliferous material;
   - a second inlet for introducing the gaseous CO into the reaction chamber;
   - means for generating a fluidized bed comprising the metalliferous material and the gaseous CO in the reaction chamber;
means for obtaining a suitable temperature in the reaction chamber for enabling conversion of the gaseous CO into solid carbon and gaseous carbon dioxide, and precipitation of the solid carbon onto the metalliferous material and/or onto the reduction product, and for reducing the metalliferous material by the solid carbon for producing a reduction product;

- means for directing at least a part of the constituents of the fluidized bed towards separation means for separating the reduction product from the fluidized bed and optionally means for directing the off-gas from the fluidized bed to recycling means;

- a return part for returning at least part of the reduction product separated from the gas stream to the reaction chamber and an outlet for discharging the remaining reduction product from the reaction chamber as final reduction product.

- an optional end stage reactor for further reducing the reduction product to a higher degree of reduction by a substantially solid-solid reaction of the solid carbon with the reduction product, preferably wherein the optional end stage reactor is a rotary kiln, rotary hearth furnace or fluidized bed reactor.

28. Apparatus according to claim 27 wherein the fluidized bed reactor is a circulating fluidised bed comprising:

- a riser part for accommodating a substantially upward movement of the fluidized bed, the fluidized bed comprising the metalliferous material and the gaseous CO;

- means for directing the constituents of the fluidized bed towards separation means upon reaching the top part of the riser part for separating the reduction product from the fluidized bed and means for directing the gaseous phases from the fluidized bed to recycling means and means for directing the reduction product to the return leg;

- a return leg for accommodating a substantially downward movement of the reduction product;

- means for discharging the off-gas from the fluidized bed for further processing;

- means for returning at least part of the reduction product from the return leg to the reaction chamber, said means also comprising an outlet for discharging the final reduction product from the reaction chamber.

29. Apparatus according to claim 28 wherein the means for returning at least part of the reduction product from the return leg to the reaction chamber is a loop seal.
30. Apparatus according to any one of claims 27 to 29 comprising a plurality of connected fluidized bed reactors wherein means are provided for transporting the final reduction product from a preceding fluidized bed to the reaction chamber of a subsequent fluidized bed reactor for further reduction of the final reduction product to a higher degree of reduction and/or wherein means are provided for providing the gaseous phases discharged from a subsequent fluidized bed into a preceding fluidized bed reactor.

31. Apparatus according to claim 30 wherein means are provided for operating a subsequent fluidized bed reactor at a higher temperature than a preceding fluidized bed reactor, preferably wherein any subsequent reactor operates at a higher temperature than any preceding fluidized bed reactor.

32. Apparatus according to any one of the preceding claims wherein the apparatus is provided with a gasifier, preferably of the entrained flow type, for providing the gaseous CO, a plurality of connected circulating fluidized beds, preferably 3, each comprising a reaction chamber, for providing the reduction product, an end stage reactor of the bubbling fluidised bed type for further reducing the reduction product wherein there is a continuous link between the gasifier, the circulating fluidized beds and the end stage reactor, preferably wherein an overpressure of at least 2, preferably at least 4 bar exists in the apparatus.

33. Apparatus according to the preceding claims comprising a recycling unit for recycling Zn and/or Pb and/or Cd from Zn and/or Pb and/or Cd containing metalliferous material, the unit comprising heating means for enabling reduction of the Zn-, Pb- and/or Cd-containing compounds by the solid carbon to metallic Zn, Pb and/or Cd and to evaporate the Zn, Pb and/or Cd to produce gaseous Zn, Pb and/or Cd.

34. Apparatus according to claim 33 provided with
   - condensation means for condensing and/or solidify the gaseous Zn, Pb and/or Cd into liquid and/or solid Zn, Pb and/or Cd, or
   - oxidation means for oxidizing the gaseous Zn, Pb and/or Cd to zinc-oxygen compounds, lead-oxygen compounds and/or cadmium-oxygen compounds.

35. Use of the reduction product produced by the method of any one of claims 6 to 26 in a sponge iron process for the production of hydrogen.
Figure 1

Figure 2