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(54) **IMPROVED METHOD FOR BENEFICIATING TITANIUM-BEARING MATERIAL CONTAINING IRON**

VERFAHREN ZUR ANREICHERUNG VON TITANIN EISENENTHALTENDEN STOFFEN

PERFECTIONNEMENT DU PROCEDE DE REDUCTION DE MATIERE TITANIFERE CONTENANT DU FER

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• **PATENT ABSTRACTS OF JAPAN vol. 12, no. 219**
(C-506)22 June 1988 & JP,A,63 014 826
(MARUBENI KK) 22 January 1988 see abstract

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Description

This invention relates to an improved method for beneficiating titanium-bearing material containing iron.

High grade titanium-bearing material containing low amounts of iron is becoming increasingly scarce and expensive. While low grade titanium-bearing material containing significant amounts of iron can be used in the chloride process for making titanium dioxide pigment or titanium metal, significant amounts of iron chloride byproduct are produced. Some byproduct iron chloride can be used as a flocculant to remove sediment in the treatment process to produce potable water. Because, however, the amount of iron chloride required for this use is limited, the production of significant amounts of iron chloride can be a waste disposal problem.

A number of different processes have been proposed to beneficiate titanium-bearing material containing iron. These processes, however, appear to be deficient in one or more aspects, including, (a) being expensive or not feasible on an industrial scale or (b) producing iron chloride which has the aforementioned disposal problems, and producing low-grade iron.

The following information is to disclose which may be of interest in the examination of this application:

U.S. patent 3,929,463 discloses a continuous method of effecting an endothermic metallurgical reduction reaction in the reactor space of a rotatable mechanical kiln which functions as a reaction vessel. During the reaction, the charged kiln is rotated at a speed which is lower than the speed at which the charge closest to the kiln ceases to move relative to the wall. The charge is thereby disintegrated and heated to effect the reaction. The reaction carried out can be the reduction of iron, copper, nickel or zinc oxides or sulfides. It is also disclosed that the process can be used to reduce the iron content in titaniferous magnetite and ilmenite in the form of magnetic power which then can be separated magnetically.

British patent 1,397,200 discloses a process for producing metallic iron from materials containing iron oxides and a nonferrous metal oxide. In the process, the oxide containing material is heated in a furnace in the presence of hydrogen chloride, a flux, and a solid carbonaceous material, to a temperature below that at which a slag is formed.

UK published patent application 2,000,755 states that particles containing a mixture of iron and titanium oxide can be heated in a nonoxidizing environment with an iron salt or a precursor thereof to segregate the iron from the titanium bearing component. The process may be applied to beneficiation of ilmenite by first reducing the iron component thereof to metallic iron. The segregated iron can then be separated from the titanium bearing component by physical or chemical means.

An article entitled "Kinetics of Reduction of Ilmenite with Graphite at 1000 to 1100 degrees C." by S. K. Gupta, V. Rajukumar, and P. Grieveson, appears in the December 1987 issue of Metallurgical Transactions and discloses an experimental process for reducing ilmenite with graphite. It is stated by the authors that the rate is increased significantly by the addition of ferric chloride, which promotes the nucleation of iron.

An article entitled "Reduction of Ilmenite with Carbon", by D.K. Gupta, V. Rajakumar and P. Grieveson, appearing in the June 1988 issue of Metallurgical Transactions, discloses an experimental process for the reduction of ilmenite ore with coal in the presence of ferric chloride. According to the authors, the ferric chloride promoted the nucleation of iron and increased the rate of reduction.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a process for beneficiating particulate titanium-bearing material containing iron oxides comprising:

(a) subjecting said particulate titanium-bearing material to reducing conditions in the substantial absence of a flux in the presence of particulate carbonaceous reducing material to convert about 20-90 percent of the iron oxides to metallic iron,

(b) feeding to a separate mechanical reduction kiln, and contacting, in the substantial absence of a flux, the products resulting from step (a), particulate carbonaceous reducing material, and HCl or one or more materials which will produce HCl during step (b), or mixtures thereof,

said contacting taking place in the substantial absence of titanium chlorination and while (i) the mechanical reduction kiln turns and cascades the material therein, (ii) a temperature of about 900-1100 degrees C is maintained, and (iii) reducing conditions are maintained,

said particulate titanium-bearing material being ground during step (b), with the aid of grinding media, to have a mean diameter of less than about 40 micrometers,

said step (b) causing iron oxide to be converted to metallic iron and causing liberation of the metallic iron from the titanium bearing material,

said contacting and grinding, with the aid of grinding media, continuing until the metallic iron produced in step

(b) has a mean diameter of at least about 50 micrometers,

(c) removing the resulting products from step (b) from the kiln, and

(d) separating the metallic iron and titanium-bearing material from the resulting products from step (c).

There is also provided a preferred process for beneficiating particulate titanium-bearing material containing iron oxides comprising:

(a) subjecting said particulate titanium-bearing material to reducing conditions in the presence of particulate carbonaceous reducing material to convert about 50-70 percent of the iron oxides to metallic iron,

(b) feeding the products resulting from step (a) to a mechanical reduction kiln and contacting the products with one or more particulate carbonaceous reducing materials and solid hydrated ferrous chloride under reducing conditions which cause additional iron oxide to be converted to metallic iron and the solid hydrated ferrous chloride to vaporize, wherein (i) the weight ratio of solid hydrated ferrous chloride to non-reduced iron in the product being fed is about 0.01-0.5, (ii) the weight ratio of water to ferrous chloride in the solid hydrated ferrous chloride is about 0.03-1.0, (iii) the particulate titanium-bearing material being ground, with the aid of grinding media, has an average particle size of less than about 40 micrometers and (iv) the average particle size of the metallic iron so produced being at least about 50 micrometers, said step (b) taking place in the substantial absence of titanium chlorination,

(c) removing the products resulting from step (b) from the kiln,

(d) contacting the gaseous products from step (c) with water at a temperature of about 140-200 degrees C under conditions which form solid hydrated ferrous chloride, and recycling the solid hydrated ferrous chloride to the kiln, and

(e) separating the metallic iron and titanium-bearing material from the solid product of step (c).

It has been found that the process of this invention is advantageous because rather than producing iron chloride which can be a disposal problem, it produces high purity metallic iron which can be sold to make various iron products or steel. Also, compared to prior art processes, the process of this invention appears to be able to remove more iron oxides from the titanium-bearing materials.

Other advantages of the process of this invention include:

- There is minimal loss of TiO_2 ,
- The beneficiation reaction in the mechanical reduction kiln can take place at low temperatures which reduces energy requirements,
- Very fine particulate metallic iron and TiO_2 can be produced by the process,
- Prereduction reduces the overall time for carrying out the process and appears to enhance the amount of conversion to metallic iron, and
- The process can be successfully operated with titaniferous materials having a wide range of impurities.

DETAILED DESCRIPTION OF THE INVENTION:

Titanium Bearing Material:

Any suitable titanium-bearing material containing iron oxides can be used for the process of this invention. Examples include ilmenite, anatase, and titaniferous slags. By iron oxides is meant iron oxides per se, and iron oxides in association, compounds or complexes with other metals, such as FeTiO_3 .

Prereduction:

If this step is used in the process of this invention, particulate titanium-bearing material containing iron oxides is subjected to reducing conditions in the presence of particulate carbonaceous material to convert about 20-90 percent of the iron oxide to metallic iron.

Any suitable reducing conditions can be used. Generally, this will require heating the titanium-bearing material in the presence of a solid carbonaceous material until the desired reduction takes place.

The reduction can take place in a rotary kiln, a fixed kiln, a fluidized bed, or any suitable vessel. Preferably, a rotary kiln should be used.

The heating should be sufficient to carry out the desired reduction and will depend on the type of carbonaceous material and titanium-bearing material being used. Generally, the heating will be in the range of about 900 to 1100 degrees C. and more preferably about 950-1050°C. Also, generally, sufficient air or oxygen will be excluded to ensure

reducing conditions.

Suitable carbonaceous materials include coke, coal, charcoal, lignite, and lignite char. Preferred are lignite, lignite char, and coke. Especially preferred is lignite char. The carbonaceous materials should be in particulate form. Often, one carbonaceous material will have a particle size of greater than about 70 microns to minimize it being blown out of the kiln before it has been reacted.

Preferably, at least a stoichiometric amount of carbonaceous material will be used, although about a 5-30 percent excess can be used if desired to ensure optimum iron metalization.

Generally, the prereduction conditions will be sufficient to convert about 20-90 percent, preferably about 50-70 percent, and most preferably about 60-65 percent of the iron oxide to metallic iron.

For some ores, prereduction is preferred because it can reduce the total time to conduct the process and can enhance the amount of conversion to metallic iron.

Processing in Mechanical Reduction Kiln

This step of the process of this invention comprises

(a) contacting in a mechanical reduction kiln, particulate titanium-bearing material, particulate carbonaceous reducing material, and HCl or one or more materials which will produce HCl during step (a), or mixtures thereof,

said contacting taking place in the substantial absence of titanium chlorination and while (i) the mechanical reduction kiln turns and cascades the material therein, (ii) a temperature of about 900-1100 degrees C. is maintained, and (iii) reducing conditions are maintained,

said particulate titanium bearing material having a mean diameter of less than about 40 microns, which diameter exists in the ore which is introduced into the kiln or is ground in the kiln to have such diameter,

said step (a) causing iron oxide to be converted to metallic iron and causing liberation of the metallic iron from the titanium bearing material,

said contacting continuing until the metallic iron produced in step (b) has a mean diameter of at least about 50 microns,

In one preferred embodiment of this invention, this step comprises feeding prereduced titanium-bearing material to a mechanical reduction kiln and contacting the products with solid hydrated ferrous chloride under reducing conditions which cause additional iron oxide to be converted to metallic iron and the solid hydrated ferrous chloride to vaporize. Subsequently, if desired, the ferrous chloride can be recovered and recycled.

A suitable mechanical reduction kiln, and its method of operation, is described in U.S. Patent 3,929,463 which is hereby incorporated by reference. In principle, the mechanical kiln is a large media mill which is provided with a refractory lining. The mechanical work inside the kiln (e.g. grinding, attrition, friction, etc.) generates a controlled amount of inert heat for the reaction. The use of the mechanical kiln overcomes the problems involved in heat treating large amounts of ore and char or other carbonaceous material with FeCl_2 , or other source of HCl, without major dilution of the reducing and chlorinating gases.

Thus, in operation, heat is generated by the rotation of the vessel, while the charge is ground to a fine powder, which increases the rate of reaction. The temperature inside the kiln can be controlled by the rotation speed. Also, if desired, additional heat can be supplied from external sources.

Generally, the mechanical reduction kiln should operate at a speed lower than the critical speed. By critical speed is meant that speed above which the charge closest to the kiln wall ceases to move relative to the wall. At speeds lower than the critical speed, the charge will be agitated vigorously by the rotation of the kiln.

Grinding media will be used in the mechanical reduction kiln. The grinding media should be heavy material and resistant to the atmosphere in the kiln. Often best results will be obtained if the media occupies less than about fifty percent of the volume of the kiln. Preferably, the media will be generally spherically shaped. A preferred grinding media is alumina. The media can vary in size depending on the size of the kiln, speed of rotation of the kiln, hardness of the titanium-bearing material, heat required to be generated, etc. Often, the media will have a diameter of about 5-300 millimeters, preferably about 10-200 millimeters, and most preferably about 20-100 millimeters.

The temperature in this step of the invention should be high enough to vaporize the ferrous chloride (if it is used as the source of HCl) but not high enough to cause substantial sintering of the titanium dioxide. Generally, the temperature utilized in this step of the process of this invention will be about 900-1100 degrees C., more preferably about 950-1050 degrees C., and most preferably about 1000 degrees C.

In this step of the process of this invention, there is used HCl, one or more materials which will produce HCl during the processing in the mechanical reduction kiln, or mixtures thereof. Examples of materials which will form HCl include hydrated ferrous chloride, hydrated ferric chloride, chlorinated hydrocarbons, ferric chloride and water, ferrous chloride

and water, mixed iron chlorides which are a byproduct from the chloride process to make TiO_2 and water, and mixtures thereof. Preferred sources of HCl include HCl, hydrated ferrous chloride, and mixed iron chlorides which are a by-product from the chloride process to produce TiO_2 .

The amount of HCl used should be sufficient to produce the desired degree of iron metalization and liberation under the conditions in the mechanical reduction kiln. Generally, the amount of HCl required can vary depending upon the temperature, iron content of the titanium containing material, and the rate of grinding in the mechanical reduction kiln. Often the HCl will be present in an amount sufficient to exert a partial pressure in the mechanical reduction mill, of about 0.05 to 0.9 atmospheres, preferably about 0.1-0.6 atmospheres, and preferably about 0.15-0.5 atmospheres.

This step of the process of this invention is conducted under reducing conditions, i.e., under conditions which will cause the iron oxide to be reduced to metallic iron. However, if desired, minor amounts of excess oxygen or air can be admitted to combust or partially combust some of the carbonaceous material. This can be desirable to generate additional heat for the reactions in the mechanical reduction kiln. If this is done, then sufficient oxygen or air will be admitted to provide the desired amount of heat while still maintaining the desired reducing conditions. If excess air or oxygen is used, it should be noted that use of lignite or lignite char can be especially advantageous because it appears to be very reactive and readily combusts with any oxygen present. The amount of excess air or oxygen admitted can vary greatly depending on the amount of grinding done in the kiln, (and thus the amount of heat generated by the grinding); the desired reaction temperature, the reactivity of the reactants, etc. Often, however, the excess air or oxygen will provide up to about 35 percent, and preferably up to about 20 percent, by volume, of the carbon monoxide exiting the mechanical reduction kiln. If excess air is used, this percentage can be conveniently monitored by analyzing for nitrogen in the gas exiting the mechanical reduction kiln. From the amount of nitrogen, the amount of oxygen can be readily determined from the ratio of nitrogen to oxygen in air.

In addition, this step of the process of this invention is carried out in the substantial absence of titanium chlorination, i.e., generally, less than 5 percent, preferably less than 3 percent, and most preferably less than 1 percent titanium chlorination takes place.

If hydrated ferrous chloride is used as the source of HCl, the weight ratio of solid hydrated ferrous chloride to nonreduced iron in the titanium-bearing material being fed should be about 0.01-0.5, and more preferably about 0.01-0.3.

The weight ratio of water to ferrous chloride in the solid hydrated ferrous chloride should be about 0.03-1.0, more preferably about 0.1-0.6, and most preferably about 0.1-0.2.

The particulate titanium-bearing material will have a mean particle size of less than about 40 micrometers. If the material is reduced to this size prior to being fed to the mechanical reduction kiln, then the amount of grinding required by such kiln can be reduced. However, if desired, material of larger particle size can be fed to the kiln and the action of the kiln can reduce it to smaller particle size. It is important to note, however, that some grinding in the mechanical reduction kiln is important to aid (1) iron oxide being converted to metallic iron, (2) the metallic iron being liberated from the ore, and (3) producing metallic iron having a mean particle size of at least 50 micrometers.

The carbonaceous materials used in the mechanical reduction kiln can be the same as those specified above for the prereduction step preferred are lignite and lignite char. The carbonaceous material can be fed directly into the mechanical kiln or an excess can be used in the prereduction step, so that when the products of the prereduction step are fed to the mechanical reduction kiln, sufficient carbonaceous material exists for the processing in the mechanical reduction kiln. Preferably, the carbonaceous material will have an average particle size of less than 200 microns, preferably less than 100 microns, and most preferably less than 50 microns. The carbonaceous material can have this particle size when it is introduced into the mechanical reduction kiln or can be ground to this size in the mechanical reduction kiln.

Process optimization can be obtained if the hot products resulting from the prereduction step, if used, are promptly fed to the mechanical reduction kiln, i.e., before the products have cooled to ambient temperature. If this is done, then less mechanical heat will be required to be generated in the mechanical kiln.

Preferably, the iron particles produced in step (b) have a mean particle size of at least about 50 microns. Often the iron particles will have a mean size of about 50-200 microns, and preferably about 50-100 microns. It should be noted that the ability to produce iron of this particle size is an important advantage of this invention since it aids separation from the beneficiated titanium-bearing material resulting from the process, which generally will have a smaller particle size.

The iron produced by the process of this invention can have high purity, e.g., often at least 90-95 percent. Iron of such purity can have high value for producing iron and steel, as well as for powdered metallurgy.

Removing and Separating the Resulting Products from the Mechanical Reduction Kiln:

These steps of the process of this invention entail:

- o removing the resulting products from the mechanical reduction kiln, and
- o separating the metallic iron and the titanium-bearing material from the resulting products.

Any suitable means can be used for the separation, including magnetic separation, settling, flotation, classification, washing, hydrocloning, and combinations thereof.

Preferably, magnetic separation is used to separate the metallic iron from the products resulting from step (b). Then flotation can be used to separate the beneficiated titanium dioxide from the remaining reaction products such as char and ash. Another preferred process is hydrocloning.

The following description concerns the removing and separating steps when hydrated ferrous chloride is used in the mechanical reduction kiln and hydrated ferrous chloride is recycled. In such case, the products resulting from the mechanical reduction kiln are removed from the kiln, separated into gaseous and solid products, and further treated.

Specifically, such gaseous products are contacted with water under conditions which form solid hydrated ferrous chloride, and the solid hydrated ferrous chloride is recycled to the kiln. Generally, the temperature used in this step of the invention should be about 140-300 degrees C., and more preferably about 140-240 degrees C. Enough water should be added in this step to form the desired amount of solid, hydrated ferrous chloride. Generally, at least about a stoichiometric amount of water will be used, because if less water is used, some ferrous chloride would be lost. Often, a slight to a moderate amount of excess of water will be used (e.g. 10-30 percent) to aid desired process kinetics and to compensate for some loss of water in the process.

In regard to the solid products, the metallic iron and titanium bearing material are separated therefrom. Any suitable means can be used for the separation, including magnetic separation, settling, flotation, classification, washing, hydrocloning, cycloning, and combinations of the above. Preferably, magnetic separation is used to separate the metallic iron from the products resulting from step (c). Then flotation can be used to separate the beneficiated titanium dioxide from the remaining reaction products such as char and ash. Another preferred process is to use hydrocloning.

Other Process Aspects

The process of this invention can be carried out in a batch or continuous process. Preferred is a continuous process. If a continuous process is used, preferably the steps (a)-(c) (or steps (a)-(e) if hydrated ferrous chloride is used) are carried out simultaneously.

The following Example illustrates this invention. Unless otherwise indicated, all percentages and parts are by weight.

EXAMPLE

A refractory lined mechanical reduction kiln having a charge of 65 millimeter diameter Al_2O_3 grinding balls was used for this experiment. The mill had an inside diameter of 3500 millimeters and a length of 3800 millimeters. The refractory liner had a thickness of 500 millimeters. Approximately 40 percent of the volume of the kiln was occupied by the grinding balls. The mill had a drive motor power of 240-250 kilowatts.

The kiln was fed with ilmenite preheated to 550-600 degrees C., 100 kilograms of cold lignite char, and 25 kilograms cold HCl gas per hour. The mill temperature equilibrated at 920-940 degrees C. The mill was rotated at 13.2 revolutions per minute. The ore fed analyzed 63.6 weight percent TiO_2 , 20.6 weight percent iron, 4.7 weight percent miscellaneous oxides and 2.8 weight percent volatiles. The lignite char analyzed 86 weight percent fixed carbon, 7 weight percent volatiles as 7 weight percent ash.

The kiln discharge solids contained 75% of the iron as metal segregated to particles of 60 microns mean diameter. These were separated from the remaining ore by gravity (by use of a hydroclone) and by further magnetic separation-attrition grinding steps. A total of 99% of the metallic iron was recovered. The remainder (i.e., the 25 percent not recovered) was present in the ore as FeO or formed ferrous chloride. The discharge was:

Total discharge =	436 Kg/hr
Iron product =	63 Kg/hr as 98% Fe, 1% TiO_2 , 1% C
TiO_2 rich product =	295 Kg/hr as 87% TiO_2 and 6.6% FeO
Char =	58 Kg/hr
FeCl_2 =	20 Kg/hr

The TiO_2 recovery was greater than 95% and was in the form of particles averaging 10 microns diameter. The char was the same size.

The offgas from the kiln analyzed as follows:

H ₂ - 10	Volume percent
O ₂ - 0.5	Volume percent
N ₂ - 7.8	Volume percent
CO - 70.9	Volume percent
HCl - 6.0	Volume percent
CO ₂ - 4.8	Volume percent

Claims

1. Process for beneficiating particulate titanium-bearing material containing iron oxides comprising:

- (a) subjecting said particulate titanium-bearing material to reducing conditions in the substantial absence of a flux in the presence of particulate carbonaceous reducing material to convert about 20-90 percent of the iron oxides to metallic iron,
- (b) feeding to a separate mechanical reduction kiln, and contacting, in the substantial absence of a flux, the products resulting from step (a), particulate carbonaceous reducing material, and HCl or one or more materials which will produce HCl during step (b), or mixtures thereof,

said contacting taking place in the substantial absence of titanium chlorination and while (i) the mechanical reduction kiln turns and cascades the material therein, (ii) a temperature of about 900-1100 degrees C is maintained, and (iii) reducing conditions are maintained,

said particulate titanium-bearing material being ground during step (b), with the aid of grinding media, to have a mean diameter of less than about 40 micrometers,

said step (b) causing iron oxide to be converted to metallic iron and causing liberation of the metallic iron from the titanium bearing material,

said contacting and grinding, with the aid of grinding media, continuing until the metallic iron produced in step (b) has a mean diameter of at least about 50 micrometers,

(c) removing the resulting products from step (b) from the kiln, and

(d) separating the metallic iron and titanium-bearing material from the resulting products from step (c).

2. The process of claim 1 wherein the HCl is produced by one or more materials which will produce HCl during step (b), said materials being selected from the group consisting of hydrated ferrous chloride, hydrated ferric chloride, chlorinated hydrocarbons, ferric chloride and water, ferrous chloride and water, mixed iron chlorides from the chloride process to make TiO₂ mixtures thereof.

3. The process of claim 1 or 2 wherein the titanium-bearing material is ilmenite and the carbonaceous reducing material is lignite or lignite char.

4. The process of any one of the preceding claims wherein the HCl is present in an amount to have a partial pressure of about 0.0507-0.912 x 10⁵ pascals (0.05 to 0.9 atmospheres).

5. The process of any one of the preceding claims wherein air or oxygen provides up to about 35 percent by volume of the carbon monoxide exiting the mechanical reduction kiln.

6. Process for beneficiating particulate titanium-bearing material containing iron oxides comprising:

(a) subjecting said particulate titanium-bearing material to reducing conditions in the presence of particulate carbonaceous reducing material to convert about 50-70 percent of the iron oxides to metallic iron,

(b) feeding the products resulting from step (a) to a mechanical reduction kiln and contacting the products with one or more particulate carbonaceous reducing materials and solid hydrated ferrous chloride under reducing conditions which cause additional iron oxide to be converted to metallic iron and the solid hydrated ferrous chloride to vaporize, wherein (i) the weight ratio of solid hydrated ferrous chloride to non-reduced iron in the product being fed is about 0.01-0.5, (ii) the weight ratio of water to ferrous chloride in the solid hydrated ferrous chloride is about 0.03-1.0, (iii) the particulate titanium-bearing material being ground, with the aid of grinding

media, has an average particle size of less than about 40 micrometers and (iv) the average particle size of the metallic iron so produced being at least about 50 micrometers, said step (b) taking place in the substantial absence of titanium chlorination,

(c) removing the products resulting from step (b) from the kiln,

(d) contacting the gaseous products from step (c) with water at a temperature of about 140-200 degrees C under conditions which form solid hydrated ferrous chloride, and recycling the solid hydrated ferrous chloride to the kiln, and

(e) separating the metallic iron and titanium-bearing material from the solid product of step (c).

Patentansprüche

1. Verfahren zur Anreicherung von teilchenförmigem titanhaltigem Material, das Eisenoxide enthält, umfassend:

(a) Unterwerfen des teilchenförmigen titanhaltigen Materials unter Reduktionsbedingungen in der wesentlichen Abwesenheit eines Flusses in Gegenwart von teilchenförmigem kohlenstoffhaltigem Reduktionsmaterial, um etwa 20 bis 90 % der Eisenoxide zu metallischem Eisen umzuwandeln,

(b) Einspeisen in einen getrennten mechanischen Reduktionsbrennofen und Zusammenbringen, im wesentlichen in Abwesenheit eines Flußmittels, der Produkte, die sich aus der Stufe (a) ergeben, mit teilchenförmigem kohlenstoffhaltigem Reduktionsmaterial und HCl oder mit einem oder mehreren Materialien, die während der Stufe (b) HCl produzieren, oder von Gemischen davon, wobei das Zusammenbringen im wesentlichen in Abwesenheit einer Titanchlorierung erfolgt, und während (i) des Drehens des mechanischen Reduktionsbrennofens und des kaskadenartigen Herabstürzens der Materialien darin, (ii) eine Temperatur von etwa 900-1100 °C beibehalten wird, und (iii) die Reduktionsbedingungen beibehalten werden,

wobei das teilchenförmige titanhaltige Material während der Stufe (b) mit Hilfe von Mahlmedien gemahlen wird, so daß es einen mittleren Durchmesser von weniger als etwa 40 µm aufweist,

wobei die Stufe (b) dazu führt, daß das Eisenoxid in metallisches Eisen umgewandelt wird und es zu einer Freisetzung des metallischen Eisens aus dem titanhaltigen Material kommt,

wobei das Zusammenbringen und Mahlen mit Hilfe von Mahlmedien fortgesetzt wird, bis das metallische, in Stufe (b) erzeugte Eisen einen mittleren Durchmesser von wenigstens etwa 50 µm besitzt,

(c) Entfernen der resultierenden Produkte der Stufe (b) aus dem Brennofen, und

(d) Abtrennen des metallischen Eisens und des titanhaltigen Materials von den resultierenden Produkten der Stufe (c).

2. Verfahren nach Anspruch 1, bei dem die HCl durch ein oder mehrere Materialien produziert wird, die während der Stufe (b) HCl produzieren, wobei die Materialien ausgewählt werden aus der Gruppe, bestehend aus Eisen(II)-chloridhydrat, Eisen(III)-chloridhydrat, chlorierten Kohlenwasserstoffen, Eisen(III)-chlorid und Wasser, Eisen(II)-chlorid und Wasser, gemischten Eisenchloriden aus dem Chlorid-Verfahren, um TiO₂-Gemische daraus herzustellen.

3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem das titanhaltige Material Ilmenit ist und das kohlenstoffhaltige Reduktionsmaterial Braunkohle oder Braunkohlekoks ist.

4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die HCl in einer Menge vorhanden ist, so daß sie einen Partialdruck von etwa 0,0507-0,912 x 10⁵ Pascal (0,05 bis 0,9 Atmosphären) besitzt.

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem Luft oder Sauerstoff bis zu etwa 35 Vol.-% des Kohlen-monoxids liefert, das aus dem mechanischen Reduktionsbrennofen austritt.

6. Verfahren zur Anreicherung von teilchenförmigem titanhaltigem Material, das Eisenoxide enthält, umfassend:

(a) Unterwerfen des teilchenförmigen titanhaltigen Materials unter Reduktionsbedingungen in Gegenwart von teilchenförmigem kohlenstoffhaltigem Reduktionsmaterial, um etwa 50-70 Gew.-% der Eisenoxide in metallisches Eisen umzuwandeln,

(b) Einspeisen der aus Stufe (a) resultierenden Produkte in einen mechanischen Reduktionsbrennofen und Zusammenbringen der Produkte mit einem oder mehreren teilchenförmigen kohlenstoffhaltigen Reduktionsmaterialien und festem Eisen(II)-chloridhydrat unter Reduktionsbedingungen, die dazu führen, daß zusätzliches Eisenoxid in metallisches Eisen umgewandelt wird und festes Eisen(II)-chloridhydrat verdampft, worin

- (i) das Gewichtsverhältnis von festem Eisen(II)-chloridhydrat zu nicht reduziertem Eisen in dem Produkt, das eingespeist wird, etwa 0,01 bis 0,5 beträgt, (ii) das Gewichtsverhältnis von Wasser zu Eisen(II)-chlorid in dem festen Eisen(II)-chloridhydrat etwa 0,03 bis 0,1 beträgt, (iii) das teilchenförmige titanhaltige Material, das mit Hilfe von Mahlmedien gemahlen wird, eine durchschnittliche Teilchengröße von weniger als etwa 40 µm besitzt, und (iv) die durchschnittliche Teilchengröße des metallischen, so hergestellten Eisens wenigstens etwa 50 µm beträgt, wobei Stufe (b) im wesentlichen in Abwesenheit einer Titanchlorierung stattfindet,
- (c) Entfernen der aus Stufe (b) resultierenden Produkte aus dem Ofen,
- (d) Zusammenbringen der gasförmigen Produkte aus Stufe (c) mit Wasser bei einer Temperatur von etwa 140 bis 200 °C unter Bedingungen, die festes Eisen(II)-chloridhydrat bilden, und Recycling des festen Eisen(II)-chloridhydrates in den Brennofen, und
- (e) Abtrennen des metallischen Eisens und des titanhaltigen Materials von dem festen Produkt aus Stufe (c).

Revendications

1. Procédé d'enrichissement d'une matière titanifère particulaire renfermant des oxydes de fer, comprenant les opérations consistant :

- (a) à soumettre ladite matière titanifère particulaire à des conditions réductrices en l'absence sensiblement complète d'un fondant et en présence de matière réductrice carbonée particulaire pour convertir environ 20 à 90 pour cent des oxydes de fer en fer métallique,
- (b) à envoyer dans un four de réduction mécanique séparé et à mettre en contact, en l'absence sensiblement totale d'un fondant, les produits résultant de l'opération (a), de la matière réductrice carbonée particulaire et du HCl ou une ou plusieurs matières propres à produire du HCl pendant l'opération (b), ou des mélanges de ces matières,

ladite mise en contact ayant lieu en l'absence sensiblement totale de chloration de titane et pendant que (i) le four de réduction mécanique tourne et fait cascader la matière qu'il contient, (ii) une température d'environ 900 à 1000°C est maintenue, et (iii) des conditions réductrices sont maintenues,

ladite matière titanifère particulaire étant broyée pendant l'opération (b), avec l'aide d'éléments de broyage, pour avoir un diamètre moyen de moins d'environ 40 micromètres,

ladite opération (b) ayant pour effet de convertir de l'oxyde de fer en fer métallique et de provoquer la libération du fer métallique par la matière titanifère,

ladite mise en contact et ledit broyage, avec l'aide d'éléments broyeurs, étant poursuivis jusqu'à ce que le fer métallique produit dans l'opération (b) ait un diamètre moyen d'au moins environ 50 micromètres,

(c) à sortir du four les produits résultant de l'opération (b), et

(d) à séparer le fer métallique et la matière titanifère des produits résultant de l'opération (c).

2. Le procédé de la revendication 1 dans lequel l'acide chlorhydrique est produit par une ou plusieurs matières qui produiront du HCl pendant l'opération (b), lesdites matières étant choisies dans le groupe formé par le chlorure ferreux hydraté, le chlorure ferrique hydraté, les hydrocarbures chlorés, le chlorure ferrique et l'eau, le chlorure ferreux et l'eau, des chlorures de fer mixtes provenant du procédé au chlorure de préparation de TiO₂, et des mélanges de ces matières.

3. Le procédé de la revendication 1 ou 2 dans lequel la matière titanifère est de l'ilménite et la matière réductrice carbonée est du lignite ou du lignite carbonisé.

4. Le procédé de l'une quelconque des revendications précédentes dans lequel HCl est présent en une proportion propre à lui conférer une pression partielle d'environ 0,0507 à 0,912 Pa (0,05 à 0,9 atmosphère).

5. Le procédé de l'une quelconque des revendications précédentes dans lequel de l'air ou de l'oxygène représente jusqu'à environ 35 pour cent en volume du monoxyde de carbone quittant le four de réduction mécanique.

6. Procédé d'enrichissement d'une matière titanifère particulaire contenant des oxydes de fer, comprenant les opérations consistant :

(a) à soumettre ladite matière titanifère particulaire à des conditions réductrices en présence de matière réduc-

trice carbonée particulaire pour convertir environ 50 à 70 pour cent des oxydes de fer en fer métallique,
(b) à envoyer les produits résultant de l'opération (a) dans un four de réduction mécanique et à mettre en
contact les produits avec une ou plusieurs matières réductrices carbonées particulières et avec du chlorure
ferreux hydraté solide dans des conditions réductrices propres à donner lieu à la conversion d'un supplément
d'oxyde de fer en fer métallique et à la vaporisation du chlorure ferreux hydraté solide, (i) le rapport pondéral
du chlorure ferreux hydraté solide au fer non réduit dans le produit envoyé au four étant d'environ 0,01 à 0,5,
(ii) le rapport pondéral de l'eau au chlorure ferreux dans le chlorure ferreux hydraté solide étant d'environ 0,03
à 1,0, (iii) la matière titanifère particulaire broyée, à l'aide d'éléments broyeurs, ayant une grosseur moyenne
de particules de moins d'environ 40 micromètres et (iv) la grosseur moyenne des particules du fer métallique
ainsi produit étant d'au moins environ 50 micromètres, ladite opération (b) ayant lieu en l'absence pratiquement
complète de chloration de titane,
(c) à sortir du four les produits résultant de l'opération (b) , et
(d) à mettre en contact les produits gazeux issus de l'opération (c) avec de l'eau à une température d'environ
140 à 200°C dans des conditions propres à former du chlorure ferreux hydraté solide, et à recycler au four le
chlorure ferreux hydraté solide, et
(e) à séparer le fer métallique et la matière titanifère du produit solide de l'opération (c).