(54) Titre: VALORISATION D’UN MATERIAU TITANIFERE
(54) Title: UPGRADING OF TITANIFEROUS MATERIAL

(57) Abrégé/Abstract:
A method of upgrading a titaniferous material includes nitriding and reducing a titaniferous material which includes TiO₂ and Fe oxides in the presence of nitrogen and carbon to convert the TiO₂ to TiN and to reduce most of the Fe oxides to Fe. The Fe is oxidised in preference to the TiN to form Fe²⁺ ions, whereafter the Fe²⁺ ions are removed to produce an upgraded low-Fe TiN bearing material.
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UPGRADING OF TITANIFEROUS MATERIAL

This disclosure relates to the upgrading of titaniferous material. In particular, the disclosure relates to a method of upgrading a titaniferous material.

Conventional processes, and in particular conventional commercial processes, to produce TiCl₄ use titaniferous raw materials with a high content of TiO₂. The TiO₂ is reacted with chlorine in a high temperature chlorinator (about 900°C) to produce TiCl₄, which is used commercially on large-scale to produce TiO₂ pigment or titanium metal. Unfortunately, chlorine reacts unselectively at high temperatures, with chlorine thus being consumed by other constituents of the titaniferous raw materials.

Various embodiments of the claimed invention pertain to a method of upgrading a titaniferous material, the method comprising nitriding and reducing a titaniferous material which comprises TiO₂ and Fe oxides in the presence of nitrogen and carbon to convert the TiO₂ to TiN and to reduce the Fe oxides to Fe, the TiN and Fe obtained from the nitriding and reduction of the titaniferous material being in the form of a carbo-nitrided intermediate which comprises TiN and Fe; oxidising the Fe in preference to the TiN to form Fe²⁺ ions, the oxidation of the Fe in preference to the TiN comprising reacting the carbo-nitrided intermediate which comprises TiN and Fe with a FeCl₃ solution in accordance with reaction (4):

\[ \text{Fe} + \text{TiN} + 2\text{FeCl}_3(\text{aq}) = 3\text{FeCl}_2(\text{aq}) + \text{TiN} \]

(4)

and removing the Fe²⁺ ions to produce an upgraded low-Fe TiN bearing material.

A method of upgrading titaniferous materials, such as ilmenite, to a form which consumes less chlorine or produce less chloride wastes from impurities in the titaniferous feed material and which can produce TiCl₄ in a process step conducted at a lower temperature
would be desirable. It would also be advantageous if such a method is more economical and can upgrade low-grade titaniferous materials, such as low-grade titanium-bearing slag.

According to the invention, there is provided a method of upgrading a titaniferous material, the method including

nitriding and reducing a titaniferous material which includes TiO<sub>2</sub> and Fe oxides in the presence of nitrogen and carbon to convert the TiO<sub>2</sub> to TiN and to reduce most of the Fe oxides to Fe;

oxidising the Fe in preference to the TiN to form Fe<sup>2+</sup> ions; and

removing the Fe<sup>2+</sup> ions to produce an upgraded low-Fe TiN bearing material.

Typically, the upgraded low-Fe TiN bearing material is an admixture of TiO, TiN and TiC.
A plurality of Fe oxides, e.g. Fe$^{2+}$ and Fe$^{3+}$ will thus be present in the titaniferous material. The Fe oxides in the titaniferous material are thus carbothermically reduced to Fe while the TiO$_2$ in the titaniferous material is nitrided to TiN. Advantageously, the TiN is more reactive than TiO$_2$, and chlorine, other than with Fe, reacts selectively with TiN at much lower temperatures than with TiO$_2$, e.g. about 170°C - 250°C, to form TiCl$_4$ with virtually no waste chlorides, except FeCl$_2$ and/or FeCl$_3$, being formed.

The method may thus include chlorinating the upgraded low-Fe TiN bearing material thereby converting the TiN therein to TiCl$_4$. The chemical reaction involved is in accordance with reaction (1):

$$\text{TiN} + 2\text{Cl}_2 = \text{TiCl}_4 + \frac{1}{2}\text{N}_2 \quad (1)$$

As most, if not substantially all of the Fe, as Fe$^{2+}$ ions, has been removed to provide the low-Fe TiN bearing material, chlorinating the TiN will lead to little chlorine being consumed by iron, thus advantageously improving the economics of the method of the invention.

The chlorination of TiN is selective regarding the bulk of impurities that may be found in the low-Fe TiN bearing material, such as SiO$_2$, CaO, Al$_2$O$_3$ and MgO. These compounds do not react with chlorine at the low temperatures, i.e. about 170°C - 250°C, where TiN reacts with chlorine (Cl$_2$).

Nitriding and reducing a titaniferous material which includes TiO$_2$ and Fe oxides in the presence of carbon and nitrogen to convert the TiO$_2$ to TiN and to reduce the Fe oxides to Fe may be effected by any method known to those skilled in the art, such as the method described in US 6,629,838. Typically, a large nitriding kiln is used to effect the nitriding and reduction, producing a carbo-nitrided intermediate which includes TiN and Fe. As will be appreciated, a source of nitrogen is required for this method step. Advantageously, if an air separation plant or facility is present to produce oxygen for downstream processing, nitrogen from the air separation plant may be used for nitriding purposes. The chemical reaction for the nitriding of TiO$_2$ is as follows, i.e. reaction (2):
TiO₂ + 2C + \frac{1}{2}N₂ = TiN + 2CO \quad (2)

When the TiO₂ is however mostly present as FeO·TiO₂, as in the case of ilmenite, which is the most abundant commercial mineral currently used for the extraction of titanium values, the FeO·TiO₂ may thus be nitrided carbothermically to provide TiN and metallic Fe and one or more carbon oxides (i.e. CO and/or CO₂). The nitriding and reducing reaction for the FeO·TiO₂ can in simplified form be described as follows, i.e. reaction (3):

\[
FeO\cdot TiO₂ + 3C + \frac{1}{2}N₂ = Fe + TiN + 3CO. \quad (3)
\]

In a more complex form, the nitriding and reducing reaction for the FeO·TiO₂ can for example be described by way of exemplary reaction (3a):

\[
FeO\cdot TiO₂ + 2.8C + \frac{1}{2}N₂ = Fe + TiN + 2.6CO + 0.2CO₂. \quad (3a)
\]

Oxidising the Fe in preference to the TiN to form Fe²⁺ ions may thus include reacting a carbo-nitried intermediate which includes TiN and Fe with an oxidising anion to convert the Fe to Fe²⁺. Typically, the oxidising anion is in the form of an aqueous salt solution.

The aqueous salt solution may be a chloride solution, preferably a FeCl₃ solution. Advantageously, both FeCl₃ and FeCl₂ have a high solubility in water. It is however to be appreciated that there are other salts, e.g. nitrates, that are also suitable for use in the method of the invention. For an efficient and economic process, the ferric ions must be in the form of a water-soluble salt and the corresponding ferrous salt must also be water-soluble, allowing water leaching of the ferrous salt from the carbo-nitried intermediate.

When FeCl₃ is used as the aqueous salt solution, the following reaction, i.e. reaction (4), describes the oxidation of the Fe in preference to TiN to form Fe²⁺ ions:

\[
Fe + TiN + 2FeCl₃(aq) = 3FeCl₂(aq) + TiN \quad (4)
\]
This reaction may conveniently be carried out at ambient temperature, but higher temperatures up to the boiling point of the ferric chloride solution enhance the rate of reaction between the Fe$^{3+}$ ions and the Fe and also increase the solubility of both ferric chloride and ferrous chloride.

Preferably, during nitriding and reducing of the titaniferous material, substantially all of the Fe oxides are reduced to metallic iron and not only to the divalent form. This is typically the case in any event at the highly reducing conditions at about 1300°C used to nitride the TiO$_2$ to produce TiN. Typically, the iron is in the form of small particles that are intimately mixed with small TiN particles that are sintered together with a remainder of the titaniferous material, i.e. a carbo-nitried intermediate which includes TiN and Fe. This advantageously allows extraction of the iron as Fe$^{2+}$ using FeCl$_3$ (ferric chloride) in accordance with reaction (4) above, instead of using hydrochloric acid. No hydrogen is thus formed, unlike the case with extraction by hydrochloric acid in accordance with reaction (5):

$$\text{Fe} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2 \quad (5)$$

thereby avoiding the dangers of hydrogen formation and problems caused by foaming. Furthermore, the reaction of FeCl$_3$ is rapid compared to processes where FeO is leached with HCl, making it possible to use shorter residence times and smaller reactors. In addition, the oxidation of aqueous ferrous chloride by oxygen, i.e. air, to regenerate FeCl$_3$ requires much less energy. Advantageously, the ferrous chloride (FeCl$_2$) can be oxidised (for purposes of recycling Fe$^{3+}$ and for purposes of removing an iron oxide by-product) in a separate reactor to a reactor in which the Fe is oxidised to form Fe$^{2+}$ ions, providing better separation of iron from TiN and providing the opportunity to select operating conditions to stimulate the growth of large iron oxide crystals, which is advantageous for the subsequent use or disposal of the iron oxides.

As will also be appreciated, where HCl is used to leach iron species from TiN, provision has to be made to contain and scrub HCl vapours. In contrast, the vapour pressure of HCl over ferric chloride solutions (FeCl$_3$ solutions) is orders of magnitude less than over HCl solutions, thus allowing a much simplified mechanical construction of a plant to employ the method of the invention.
Surprisingly, TiN is remarkably resistant against attack by FeCl₃. The inventors have surprisingly found that, even though there is a large change in Gibbs free energy for the reaction, i.e. reaction (6):

$$8\text{FeCl}_3 + 2\text{TiN} + 4\text{H}_2\text{O} = 8\text{FeCl}_2 + 2\text{TiO}_2 + 8\text{HCl} + \text{N}_2 \quad \Delta G_{25^\circ C} = -722 \text{ kJ} \quad (6)$$

and even though one would expect the very fine TiN particles formed by carbo-nitriding of titaniferous material such as ilmenite to be highly reactive as a result of their high surface to volume ratio, the oxidation of fine iron particles in nitrided ilmenite by aqueous ferric ions (Fe³⁺) according to reaction (4) above is much faster than the oxidation of TiN particles by the Fe³⁺ ions according to reaction (6) above. Advantageously, metallic iron in nitrided titaniferous material, such as ilmenite, can thus be converted to Fe²⁺ ions and leached from TiN, with an aqueous solution of a suitable Fe³⁺ containing salt.

Removing the Fe²⁺ ions to produce an upgraded low-Fe TiN bearing material typically includes separation of Fe²⁺ solution from the unreacted carbo-nitrided intermediate to produce the low-Fe TiN bearing material and a Fe²⁺ solution. The separation may be effected by a physical separation step, e.g. filtration, settling or centrifuging. If required or desirable, the method may include washing the low-Fe TiN bearing material with an aqueous fluid. Preferably, the low-Fe TiN bearing material is dried before it is chlorinated.

As intimated hereinbefore, the method of the invention may include the step of regenerating Fe³⁺ ions from the FeCl₂(aq) obtained by the leaching of the carbo-nitrided intermediate with FeCl₃(aq).

Typically, only a portion (e.g. about two-thirds) of the FeCl₂ is converted to Fe³⁺ ions, the balance being in the form of a by-product of the method of the invention containing iron in a non-chloride form. The regenerated Fe²⁺ ions may be recycled to oxidise the Fe in preference to the TiN to form Fe²⁺ ions.
Regeneration of the Fe$^{3+}$ ions may include oxidation of the FeCl$_2$ with oxygen (typically air at about 1 to 2 bar(g) and 90°C), e.g. according to reactions (7) and (8):

\[
\begin{align*}
6\text{FeCl}_2(\text{aq}) + 1\frac{1}{2}\text{O}_2 & = 4\text{FeCl}_3(\text{aq}) + \text{Fe}_2\text{O}_3 & (7) \\
6\text{FeCl}_2(\text{aq}) + 1\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} & = 2\text{FeO.OH} + 4\text{FeCl}_3(\text{aq}) & (8)
\end{align*}
\]

Depending on reaction conditions, Fe$_3$O$_4$ can also precipitate.

Instead, regeneration of the Fe$^{3+}$ ions may include the electrochemical oxidation of the FeCl$_2$ in a cell to produce FeCl$_3$ at an anode of the cell and electrolytic iron at a cathode of the cell. The electrochemical reactions to regenerate ferric chloride and to electrowin iron are as follows, i.e. reactions (9), (10) and (11):

\[
\begin{align*}
\text{cathode reaction} & : \text{Fe}^{2+} + 2\text{e}^- & = \text{Fe} & (9) \\
\text{anode reaction} & : 2\text{Fe}^{2+} = 2\text{Fe}^{3+} + 2\text{e}^- & (10) \\
\text{overall electrochemical reaction} & : 3\text{Fe}^{2+} = \text{Fe} + 2\text{Fe}^{3+} & (11)
\end{align*}
\]

The titaniferous material may be ilmenite, as hereinbefore indicated.

Instead, it may be a low-grade slag, e.g. a low-grade slag such as that produced by Highveld Steel and Vanadium Corporation in South Africa or by New Zealand Steel in New Zealand, containing about 30% TiO$_2$ and 5% Fe. The titaniferous material may also be a sulphate grade slag for example as produced by Exxaro Limited and Richards Bay Minerals, both of South Africa, which contains about 80% TiO$_2$ and 10% FeO.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings in which

Figure 1 shows a flowsheet of one embodiment of a method in accordance with the invention of upgrading a titaniferous material; and

Figure 2 shows a flowsheet of another embodiment of a method in accordance with the invention of upgrading a titaniferous material.

Referring to Figure 1 of the drawings, reference numeral 10 generally indicates a method of upgrading a titaniferous material. The method 10 includes a
nitriding step 12, an iron oxidation step 14, an Fe\textsuperscript{2+} ions removal step 16, an Fe\textsuperscript{2+} oxidation step 18 and an Fe\textsubscript{2}O\textsubscript{3} filtration step 20.

The method 10 is used to treat ilmenite, with a theoretic composition of FeO.TiO\textsubscript{2}, to provide a low-Fe TiN product. Ilmenite, nitrogen and a carbon-containing material, e.g. coal, are fed to the nitriding step 12 where the FeO is reduced to iron metal and the TiO\textsubscript{2} is nitrided to TiN. This is typically effected in a large refractory-lined kiln operated at a temperature of about 1300\textdegree C. The kiln produces a carbo-nitrided intermediate which includes TiN and Fe which is fed to the iron oxidation step 14. Carbon monoxide as an off-gas is produced by the nitriding step 12, in accordance with reaction (3)

\[
\text{FeO.TiO}_2 + 3\text{C} + \frac{1}{2}\text{N}_2 = \text{Fe} + \text{TiN} + 3\text{CO}. \quad (3)
\]

In the iron oxidation step 14, the carbo-nitrided intermediate comprising TiN and Fe is leached with an aqueous solution of FeCl\textsubscript{3} as lixiviant. Substantially all of the iron is converted to ferrous chloride (FeCl\textsubscript{2}) in accordance with reaction (4)

\[
\text{Fe} + \text{TiN} + 2\text{FeCl}_3(\text{aq}) = 3\text{FeCl}_2(\text{aq}) + \text{TiN} \quad (4)
\]

The ferric chloride solution may be at a temperature of about 80\textdegree C. Surprisingly, substantially none of the TiN is oxidised by the ferric chloride but substantially all of the iron present is converted to ferrous ions. In order for the method of the invention to work efficiently, the ferric ions must be in the form of a water-soluble salt and the corresponding ferrous salt must also be water-soluble. Chlorides are the preferred salts because of the high solubility of both FeCl\textsubscript{3} and FeCl\textsubscript{2} in water, but there are also other salts, e.g. nitrates that are suitable. Sulphates are preferably not used because of the low solubility of ferric sulphate in water.

The next step of the method 10 requires removal of Fe\textsuperscript{2+} ions from the carbo-nitrided intermediate subjected to ferric chloride leaching. This is typically effected by filtering a suspension comprising the leached carbo-nitrided intermediate and the aqueous ferrous chloride solution, producing a low-Fe TiN product and a ferrous chloride solution stream. Typically, the low-Fe TiN product is dried. If it is
desired to convert the TiN to TiCl₂, the TiN is chlorinated with chlorine in a chlorinator at a temperature of between about 170°C and 250°C, e.g. about 200°C. This step is not shown in the drawings, but may for example be effected in accordance with the teachings of US 6,423,291.

In order to regenerate Fe^{3+} ions for use in the iron oxidation step 14, the ferrous chloride solution is oxidised in the Fe^{2+} oxidation step 18, using air at about 1 to 2 bar(g) and 90°C. Depending on the temperature and oxidation potential at which this reaction is undertaken, it is possible to form different iron oxides such as FeO.OH, Fe(OH)₃ or Fe₂O₃. The chemistry of the formation of different iron oxides from ferrous chlorides is well documented and known to those skilled in the art and will not be discussed in any further detail.

In the embodiment of the method shown in Figure 1, it is assumed that the Fe^{2+} oxidation step 18 produces Fe₂O₃ in accordance with reaction (7)

\[
6\text{FeCl}_2 + 1\frac{1}{2}\text{O}_2 = 4\text{FeCl}_3 + \text{Fe}_2\text{O}_3 \quad (7)
\]

The Fe₂O₃ is present in the form of a Fe₂O₃ suspension and the Fe₂O₃ is thus separated from the suspension to provide an Fe₂O₃ by-product and a ferric chloride solution, with the ferric chloride solution being recycled to the iron oxidation step 14. Typically, about 2/3 of the ferrous chloride entering the Fe^{2+} oxidation step 18 is converted to ferric chloride and the balance forms part of the Fe₂O₃ by-product.

Referring to Figure 2 of the drawings, another embodiment of a method in accordance with the invention to upgrade a titaniferous material is shown and indicated generally by reference numeral 100. The method 100 is similar to the method 10 and unless otherwise indicated, the same process steps or features are indicated by the same reference numerals.

As will be noted, instead of having a Fe^{2+} oxidation step 18 and an Fe₂O₃ filtration step 20, the method 100 includes an Fe electrowinning step 102. The Fe electrowinning step 102 comprises an electrolytic cell in which the ferrous chloride
solution from the Fe^{2+} ions removal step 16 is electrolytically converted to a ferric chloride solution and iron, using reaction (11)

\[
3\text{Fe}^{2+} = \text{Fe} + 2\text{Fe}^{3+} \quad (11)
\]

The method of the invention, as illustrated, shows a number of advantages compared to conventional processes of which the applicant is aware in which TiO_2, instead of TiN, is produced for subsequent chlorination to TiCl_4. TiO_2 is stable and the titanium cannot be oxidised any further. In contrast, TiN is in a reduced form and can readily be oxidised to titanium in the quaternary valence state. This is an important aspect in the selective chlorination of TiN versus the unselective carbono-chlorination of TiO_2. The method of the invention enables lower capital costs for chlorination reactors for the chlorination of TiN as compared to the chlorination reactors required for the chlorination of TiO_2. The method of the invention, as illustrated, provides lower consumption of chlorine and does not use relatively expensive petroleum coke, in contrast to conventional processes of which the applicant is aware that use petroleum coke as reactant. The method of the invention, as illustrated, also does not require roasting of ilmenite followed by magnetic separation of small amounts of low-grade impurities, as the method of the invention can accommodate these impurities.

Furthermore, the method of the invention, as illustrated, allows lower grade titaniferous materials to be upgraded. In addition, any treatment of chlorinator off-gas when using the method of the invention, as illustrated, is simpler because the gas volume and gas temperature are significantly lower than for TiO_2 chlorinators, and the gas does not contain sublimed chlorides, such as FeCl_3. It is also expected that the method of the invention will provide lower TiCl_3 losses in off-gas from the chlorinators.
CLAIMS:

1. A method of upgrading a titaniferous material, the method comprising nitriding and reducing a titaniferous material which comprises TiO_2 and Fe oxides in the presence of nitrogen and carbon to convert the TiO_2 to TiN and to reduce the Fe oxides to Fe, the TiN and Fe obtained from the nitriding and reduction of the titaniferous material being in the form of a carbo-nitrided intermediate which comprises TiN and Fe; oxidising the Fe in preference to the TiN to form Fe^{2+} ions, the oxidation of the Fe in preference to the TiN comprising reacting the carbo-nitrided intermediate which comprises TiN and Fe with a FeCl_3 solution in accordance with reaction (4):

\[
\text{Fe} + \text{TiN} + 2\text{FeCl}_3(\text{aq}) = 3\text{FeCl}_2(\text{aq}) + \text{TiN} \quad (4)
\]

and removing the Fe\(^{2+}\) ions to produce an upgraded low-Fe TiN bearing material.

2. The method of claim 1, which comprises chlorinating the upgraded low-Fe TiN bearing material thereby converting the TiN therein to TiCl_4 in accordance with reaction (1):

\[
\text{TiN} + 2\text{Cl}_2 = \text{TiCl}_4 + \frac{3}{2}\text{N}_2 \quad (1)
\]

3. The method of claim 1 or 2, wherein the titaniferous material is ilmenite in which the TiO_2 is present as FeO•TiO_2, with the FeO•TiO_2 being nitrided carbothermically to provide TiN and metallic Fe and one or more carbon oxides.

4. The method of claim 1, 2 or 3, wherein reaction (4) is carried out at an elevated temperature between ambient temperature and the boiling point of the ferric chloride solution (FeCl_3(aq)), to enhance the rate of reaction between the Fe\(^{3+}\) ions and the Fe and to increase the solubility of both ferric chloride and ferrous chloride.
5. The method of any one of claims 1 to 4, wherein during the nitriding and reducing of the titaniferous material, all of the Fe oxide is reduced to metallic iron, with the iron being in the form of small particles that are intimately mixed with small TiN particles that are sintered together in the carbo-nitrided intermediate which comprises TiN and Fe, thereby allowing extraction of the iron from the carbo-nitrided intermediate as $\text{Fe}^{2+}$ using $\text{FeCl}_3$ in accordance with reaction (4) above.

6. The method of claim 5, which comprises the step of regenerating $\text{Fe}^{3+}$ ions from the ferrous chloride solution ($\text{FeCl}_2(\text{aq})$) obtained by the reaction of the carbo-nitrided intermediate with the ferric chloride solution ($\text{FeCl}_3(\text{aq})$).

7. The method of claim 6, in which only a portion of the ferrous chloride is converted to $\text{Fe}^{3+}$ ions, the balance being in the form of a by-product containing iron in a non-chloride form.

8. The method of claim 7, wherein the regenerated $\text{Fe}^{3+}$ ions are recycled for reuse to oxidise the Fe in preference to the TiN to form $\text{Fe}^{3+}$ ions.

9. The method of claim 6, 7 or 8, wherein regeneration of the $\text{Fe}^{3+}$ ions comprises oxidation of the ferrous chloride with oxygen according to reactions (7) and (8):

$$6\text{FeCl}_2(\text{aq}) + \frac{1}{2}\text{O}_2 = 4\text{FeCl}_3(\text{aq}) + \text{Fe}_2\text{O}_3$$  \hspace{1cm} (7)

$$6\text{FeCl}_2(\text{aq}) + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = 2\text{FeO}•\text{OH} + 4\text{FeCl}_3(\text{aq})$$ \hspace{1cm} (8).

10. The method of claim 6, 7 or 8, wherein regeneration of the $\text{Fe}^{3+}$ ions comprises the electrochemical oxidation of the ferrous chloride in a cell to produce ferric chloride at an anode of the cell and electrolytic iron at a cathode of the cell, with the electrochemical reactions to regenerate ferric chloride and to electrowin iron being in accordance with reactions (9), (10) and (11):
11. The method of any one of claims 1 to 10, wherein removal of the Fe\(^{2+}\) ions to produce the upgraded low-Fe TiN bearing material comprises separation of Fe\(^{2+}\) solution from any unreacted carbo-nitrided intermediate to produce the upgraded low-Fe TiN bearing material and a Fe\(^{2+}\) solution.

12. The method of claim 11, wherein the separation comprises a physical separation step, followed by washing the low-Fe TiN bearing material with an aqueous fluid.

13. The method of claim 12, which comprises drying the upgraded low-Fe TiN bearing material.
10

Ilmenite → N₂ → Carbon/coal →

12

\[ \text{FeO} \cdot \text{TiO}_2 + 3\text{C} + \frac{1}{2} \text{N}_2 = \text{Fe} + \text{TiN} + 3\text{CO} \]

Nitrided ilmenite

14

\[ \text{Fe} + \text{TiN} + 2\text{FeCl}_3 \text{(aq)} = 3\text{FeCl}_2 \text{(aq)} + \text{TiN} \]

TiN suspension

16

\[ 6\text{FeCl}_2 \text{(aq)} + 1\frac{1}{2} \text{O}_2 = 4\text{FeCl}_3 + \text{Fe}_2 \text{O}_3 \]

Low-Fe TiN

18

FeCl₃ solution → FeCl₂ solution →

20

Fe₂O₃ suspension → Fe₂O₃

FIG 1
Limenite → N₂ → Carbon/coal → 100

Fe₂O₃·TiO₂ + 3C + ½N₂ → Fe + TiN + 3CO

Nitrided ilmenite → 12

Fe + TiN + 2FeCl₃ (aq) → 3FeCl₂ (aq) + TiN

TiN suspension → 14

FeCl₃ solution → 16

FeCl₂ solution → 102

3FeCl₂ (aq) = 2FeCl₃ (aq) + Fe

Low-Fe TiN → 16

Fe → 102

FIG 2
FeO \cdot TiO_2 + 3C + \%N_2 = Fe + TiN + 3CO

Fe + TiN + 2FeCl_3(aq) \rightarrow 3FeCl_2(aq) + TiN

6FeCl_2(aq) + 1/2O_2 = 4FeCl_3 + Fe_2O_3