

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ³: C22B 5/10, 5/12; C01G 23/047</p>	<p>A1</p>	<p>(11) International Publication Number: WO 82/00663 (43) International Publication Date: 4 March 1982 (04.03.82)</p>
<p>(21) International Application Number: PCT/AU81/00117 (22) International Filing Date: 18 August 1981 (18.08.81) (31) Priority Application Number: PE 5119 (32) Priority Date: 19 August 1980 (19.08.80) (33) Priority Country: AU (71) Applicant (for all designated States except US): ICI AUSTRALIA LIMITED [AU/AU]; 1 Nicholson Street, Melbourne, Vic. 3001 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only): FENSOM, Donald, John [AU/AU]; 1/21 Tivoli Place, South Yarra, Vic. 3141 (AU). (74) Agent: FRECKLETON, Douglas, Arthur; 1 Nicholson Street, P.O. Box 4311, Melbourne, Vic. 3001 (AU).</p>		<p>(81) Designated States: AU, DE (European patent), FR (European patent), GB (European patent), US. Published <i>With international search report</i></p>
<p>(54) Title: REDUCTION OF FERROTITANIFEROUS MATERIALS (57) Abstract A reduction process for the metallization of the iron content of ferrotitaniferous materials comprising a first reduction step in the range of 600°C to 850°C in an atmosphere of hydrogen so that more than 5% and not more than 50% of the iron content of the ferrotitaniferous material is converted to the metallic state and a second reduction step of heating the product from the first reduction step to at least 950°C in the presence of solid carbonaceous material so that at least 90% of the iron content of the product from the second reduction step is in the metallic state. At least 90% of the iron content of the ferrotitaniferous material is in the trivalent state when it is submitted to the first reduction step.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	KP	Democratic People's Republic of Korea
AU	Australia	LI	Liechtenstein
BR	Brazil	LU	Luxembourg
CF	Central African Republic	MC	Monaco
CG	Congo	MG	Madagascar
CH	Switzerland	MW	Malawi
CM	Cameroon	NL	Netherlands
DE	Germany, Federal Republic of	NO	Norway
DK	Denmark	RO	Romania
FI	Finland	SE	Sweden
FR	France	SN	Senegal
GA	Gabon	SU	Soviet Union
GB	United Kingdom	TD	Chad
HU	Hungary	TG	Togo
JP	Japan	US	United States of America

- 1 -

REDUCTION OF FERROTITANIFEROUS MATERIALS

TECHNICAL FIELD

The present invention relates to the metallization of the iron content of ferrotitaniferous materials, particularly naturally occurring ilmenites.

It is desirable to remove from ferrotitaniferous materials their iron content in order to make them more suitable for conversion to titanium containing products, chiefly titanium dioxide pigments.

10

BACKGROUND ART

There are several known methods of removing the iron content from ferrotitaniferous material. Most of these involve a reduction step to convert the iron content to a state whereby it may be conveniently separated from the relict titanium oxide material. For example in Australian Patent Specification 247 110 there is disclosed a multistep process for the upgrading of ilmenite wherein the ilmenite is reduced so that its iron content is metallized; the thus formed metallic iron is leached away from the titanium oxide material by a 'rusting'

20



- 2 -

process using an aqueous reagent. In another process described in US Patent No 3 252 787 ilmenite is metallized and the iron content then removed by treatment with ferric chloride solution. In yet another process
5 described in Australian Patent Specification 515 061 metallized ilmenite particles are subjected to a segregation treatment whereby small iron metal particles dispersed throughout each particle of metallized ilmenite are translocated and agglomerated to form large particles
10 outside the relict particles.

For such processes which require removal of iron by means of reactions with liquids or gases it is desirable to have the metallic iron particles in a very fine state, homogeneously dispersed and accessible to the
15 reactants through pores from the outside of the particles of metallized ferrotitaniferous material.

Studies on the reduction of ilmenite reported by G Ostberg (Jernkont Ann 1960 144) (1) p.46-76) showed that iron precipitated in grains of ilmenite by reduction
20 occurred as discrete particles, the number of which per given volume was greater when hydrogen was used as the reductant than when carbon monoxide or solid carbon was used. The size of the particles was inversely proportional to the number. The number of particles could be in-
25 creased by lowering the temperature used. These observations would indicate that to obtain a homogeneous dispersion of fine particles of metallic iron, hydrogen reduction should be used at the lowest practicable temperature. Unfortunately because of unfavourable re-
30 action equilibria hydrogen reduction is considerably more costly to carry out than reduction with solid carbon.



DISCLOSURE OF INVENTION

However we have now discovered a process for the metallization of the iron content of ferrotitaniferous materials by which the metallic iron is formed as fine particles homogeneously dispersed within the grains of the material. This process involves partial metallization of the ferrotitaniferous material with hydrogen at a low temperature, followed by completion of the metallization process using a solid carbon reductant at a higher temperature.

Accordingly the present invention provides a process for the metallization of the iron content of ferrotitaniferous material, which process comprises in sequence, a first reduction step of heating the said ferrotitaniferous material to a temperature in the range of 600°C to 850°C in a reducing atmosphere comprising hydrogen gas so that more than 5% and not more than 50% of the iron content of the ferrotitaniferous material is converted to the metallic state, and a second reduction step of heating the product from the first reduction step containing residual oxidized iron to a temperature of at least 950°C in the presence of a solid carbonaceous material so that at least 90% of the iron content of the product from the second reduction step is in the metallic state.

It is essential in order to achieve the desired result from the process of the invention, namely the formation of fine particles of metallic iron, that at least 90%, and preferably at least 95%, of the iron content of the ferrotitaniferous material be in the trivalent state when it is submitted to the first reduction step. Some ferrotitaniferous materials will meet this requirement but in many cases it will be necessary to submit the ferrotitaniferous material to an oxidation step prior

to the first reduction step.

Accordingly, in a further embodiment of the process of our invention we provide a process for the metallization of the iron content of ferrotitaniferous material, which process comprises in sequence an oxidation step of heating the said ferrotitaniferous material in an oxidizing environment to ensure that at least 90% of the iron content of the said material is in a trivalent state, a first reduction step of heating the product from the oxidation step to a temperature in the range of 600°C to 850°C in a reducing atmosphere comprising hydrogen gas so that more than 5% and not more than 50% of the iron content of the product from the oxidation step is converted to the metallic state, and a second reduction step of heating the product from the first reduction step to a temperature of at least 950°C in the presence of a solid carbonaceous material so that at least 90% of the iron content of the product from the second reduction step is in the metallic state.

20 BEST MODE OF CARRYING OUT THE INVENTION

For convenience, it is preferable to mix the product from the oxidation step with the carbonaceous material destined to be the reductant in the second reduction step before it is subjected to the first reducing step. It is essential, in this instance, that the temperature in the first reduction step does not exceed 850°C otherwise significant amounts of carbon reduction can occur which, in turn, will cause the metallic iron to be formed as relatively large particles. Below 600°C no significant reduction with hydrogen will occur. Preferably the first reduction step is operated at between 700°C and 800°C.

The time during which the treatment of the first reduction step is applied depends on the total iron content and its rate of reduction. The conditions of this



first reduction step must prevail for long enough for at least 5% of the iron content to be converted to the metallic state. To proceed beyond 50% metallization would be wasteful as regards utilisation of hydrogen.

- 5 Preferably the degree of metallization achieved in this step is between 10% and 20%.

In order to achieve optimum utilization of the hydrogen in the first reduction step the solids are preferably contacted with the hydrogen in a counter-current
10 manner. If fluidized bed reactors are used this is conveniently achieved by using at least two reactors. In the first reactor the solid product from the oxidation step is contacted with, and partly reduced by partially oxidized gas from the second reactor. In the second
15 reactor the reduced product from the first reactor is partially metallized by hydrogen.

If the carbonaceous material has not been added to the ferrotitaniferous material prior to the first reduction step, the product from this reduction step is
20 mixed with carbonaceous material required as the reductant in the second reduction step and the mixture is then subjected to the second reduction step.

The proportion of carbonaceous material to ferrotitaniferous material in the second reduction step is not
25 critical but there must be sufficient carbon present to reduce all the un-metallized iron content in the product from the first reduction step. Preferably the ratio of solid carbonaceous material to ferrotitaniferous material on a w/w basis is in the range of 0.1:1 to 0.3:1.

30 Solid carbonaceous materials which are suitable for use in the process of this invention are coal, coke and char. Although no hydrogen gas has to be added in the second reduction step it is likely that residual amounts from the first reduction step will be present and

- 6 -

some could be generated by reaction of water with the carbonaceous material.

5 Provided the temperature is above 950°C in step 3 the remaining oxidized iron can be metallized by the carbonaceous reductant, however temperatures in excess of 1300°C are undesirable because the titanium oxide phase will start to sinter. Preferably the temperature used in the second reduction step is between 1000°C and 1200°C.

10

INDUSTRIAL APPLICABILITY

The process of the invention is useful for the metallization of many titanium-bearing materials. Such ferrotitaniferous materials include, for example, those derived from titanium-bearing ores generally called
15 "ilmenite" which term includes the mineral ilmenite, FeTiO_3 , and other minerals having the ilmenite structure such as $(\text{Fe}, \text{Mn}, \text{Mg})\text{TiO}_3$ as well as oxidized forms of ores containing iron in the ferric state and weathered forms of such ores. Other names given to these materials include
20 ulvospinel, arizonite, pseudobrookite, titanomagnetite and kalkowskyn for example. Other suitable titaniferous materials include any of the above which also contain iron oxide inclusions, as well as materials described as iron sands. The titanium-bearing ores
25 usually occur in beach sand or as rock deposits.

Generally, if the ferrotitaniferous material to be metallized is derived from beach sand, there is no need to reduce its particle size prior to carrying out the process of the invention on it, but if it is of
30 rock origin then it is necessary to grind it to reduce its particle size to that suitable for use in the process. Preferably the ferrotitaniferous material to be treated by the process of this invention should consist of particles in the size range of 50 microns to 400



- 7 -

microns.

The process of the invention has no substantial effect on the particle size of the ferrotitaniferous material. This is an advantage because, if the metallic
5 iron content is removed by one of the known processes which also have no effect on particle size, the relict titanium oxide particle will be of convenient size for the processes commonly used to convert the titanium oxide to a pigment product.

10 It is characteristic of the process of the invention that it produces particles of titanium oxide material in which the metallized iron content is dispersed as fine particles which are less than 3 microns in size. These particles are homogeneously distributed
15 throughout the titanium oxide particles.

It is this homogeneous distribution of fine metallic iron particles which provides the major advantage of the process of the invention. The same type of product can be made by reduction with hydrogen alone.
20 However the process of the invention has a significant economic advantage in that a major part of the reduction is achieved by use of a solid carbon reductant. Efficient utilization of hydrogen requires complex and costly recycle processes.

25 Metallized ilmenite having its metallic iron content in the form of fine particles, evenly distributed and accessible, such as produced by the process of this invention, has been shown to be a suitable starting material for the segregation process disclosed in
30 Australian Patent Specification 515 061.

- 8 -

The process of the invention is now illustrated by, but not limited to, the following example. In this example all parts and percentages are by weight unless otherwise stated.

5 Example 1

A sample of beach sand ilmenite from west coast area of Australia (containing 54.7% TiO_2 , 25.3% FeO , and 16.6% Fe_2O_3 ; size range -52, +200 BS Sieve mesh) was heated in a shallow tray to $1000^{\circ}C$ for five hours
10 in an oxidizing combustion gas atmosphere.

The oxidized product obtained contained 30.1% iron, 98.5% of which was in the ferric state. A 50 g sample of this oxidized product was mixed with 12.7 g of brown coal char (particle size range -52 + 200 BSS).

15 The mixture was heated to $760^{\circ}C$ in a vibrating bed reactor for approximately 5 minutes during which time 9.83 mole of hydrogen was passed through the bed. A parallel experiment using similar conditions showed that about 15% metallization of the iron would have
20 taken place.

The vibration of the bed was stopped and the temperature raised to $1100^{\circ}C$ over approximately 15 minutes. The static bed was maintained at a temperature between $1050^{\circ}C$ and $1100^{\circ}C$ for 2 hours.

25 At least 95% of the iron content of the product ferrotitaniferous particles had been metallized. The product particles were in the same size range as the original ilmenite. Microscopic examination of the product particles showed that the particle size and dis-
30 tribution of the metallic iron particles in them were similar to those obtained when only hydrogen at about $750^{\circ}C$ was used to metallize a similar sample. A portion of the product, which was magnetic, was leached with dilute hydrochloric acid, washed and dried. The leached
35 product was non-magnetic and microscopic examination of



it revealed that the metallic iron particles had been dissolved away.

The average size of the metallic iron particles in the product particles was about 2 microns.

5 By way of comparison another sample of similar beach sand ilmenite on reduction with carbon at a high temperature (1150-1200°C) gave a product consisting of titanium oxide particles with large metallic iron agglomerates varied greatly in shape and size but common-
10 ly appeared as particles having a largest dimension of 20 microns, some having a largest dimension of 100 microns.

- 10 -

CLAIMS

1. A process for the metallization of the iron content of ferrotitaniferous material, which process comprises in sequence, a first reduction step of heating the said ferrotitaniferous material to a temperature in the range of 600°C to 850°C in a reducing atmosphere comprising hydrogen gas so that more than 5% and not more than 50% of the iron content of the ferrotitaniferous material is converted to the metallic state, and a second reduction step of heating the product from the first reduction step containing residual oxidized iron to a temperature of at least 950°C in the presence of a solid carbonaceous material so that at least 90% of the iron content of the product from the second reduction step is in the metallic state.

2. A process according to claim 1 which process comprises in sequence an oxidation step of heating the said ferrotitaniferous material in an oxidizing environment to ensure that at least 90% of the iron content of the said material is in a trivalent state, a first reduction step of heating the product from the oxidation step to a temperature in the range of 600°C to 850°C in a reducing atmosphere comprising hydrogen gas so that more than 5% and not more than 50% of the iron content of the



- 11 -

product from the oxidation step is converted to the metallic state, and a second reduction step of heating the product from the first reduction step to a temperature of at least 950°C in the presence of a solid carbonaceous material so that at least 90% of the iron content of the product from the second reduction step is in the metallic state.

3. A process according to claim 2 wherein in the said oxidation step at least 95% of the iron content is converted to the trivalent state.

4. A process according to claim 1 or claim 2 wherein the said solid carbonaceous material is mixed with the ferrotitaniferous material prior to the first reduction step.

5. A process according to claim 1 or claim 2 wherein the temperature of the first reduction step is in the range from 700°C to 800°C.

6. A process according to claim 1 or claim 2 wherein in the first reduction step more than 10% w/w and less than 20% w/w of the iron content is converted to metallic iron.

7. A process according to claim 1 or claim 2 wherein in the first reduction step the ferrotitaniferous material is contacted with the hydrogen by counter-current means.

8. A process according to claim 1 or claim 2 wherein the said solid carboniferous material is selected from the group consisting of coal, coke, char and mixtures thereof.

9. A process according to claim 1 or claim 2 wherein the weight/weight ratio of the solid carbonaceous to the



- 12 -

ferrotitaniferous material is in the range of 0.1:1 to 0.3:1.

10. A process according to claim 1 or claim 2 wherein the temperature of the second reduction step is in the range from 950°C to 1130°C.

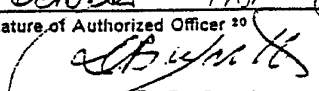
11. A process according to claim 1 or claim 2 wherein the temperature of the second reduction step is in the range from 1000°C to 1200°C.

12. A process according to claim 1 or claim 2 wherein the said titaniferous material is reduced by physical means to a particle size in the range of from 50 to 400 microns prior to treatment by the said process.



INTERNATIONAL SEARCH REPORT

International Application No **PCT/AU 81/00117**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³				
According to International Patent Classification (IPC) or to both National Classification and IPC				
Int.Cl. ³ C22B 5/10, 5/12, C01G 23/047				
II. FIELDS SEARCHED				
Minimum Documentation Searched ⁴				
Classification System	Classification Symbols			
IPC	C22B 5/10, 5/12, C01G 23/047			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶				
AU: IPC as above				
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴				
Category ⁵	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸		
A	AU, A, 37509/78 (ICI AUSTRALIA LTD.) 3 January 1980 (03.01.80) See page 2 lines 25-36	1-12		
A	AU, B, 56550/60(247110) (R.G. BECHER) 17 January 1963 (17.01.63) See page 1 lines 14-18	1-12		
A	AU, B, 17304/56(215666) (W.M.WEIL) 11 October 1956 (11.10.56) see page 1 line 8, page 2 line 7	1-12		
A	AU, B, 53537/73(473854) (I C I AUSTRALIA LTD.) 26 September 1974(26.09.74). See page 2 line 20, page 3 line 8.	1-12		
A	US, A, 2721793 (MAGRI AND SIEBER) 25 October 1955 (25.10.55) See page 2 lines 45-60	1-12		
<p>¹⁵ Special categories of cited documents:</p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </td> <td style="width: 50%; border: none;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </td> </tr> </table>			<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>
<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search ³	Date of Mailing of this International Search Report ³			
9 October 1981 (09.10.81)	15 October 1981 (15-10-81)			
International Searching Authority ¹	Signature of Authorized Officer ²⁰			
Australian Patent Office	 D. B. Cupitt			