(54) Title: METHOD OF MANUFACTURE FOR FERRO-TITANIUM AND OTHER METAL ALLOYS ELECTROLYTIC REDUCTION

(57) Abstract: A method for the production of a master alloy including the steps of: introducing mixed ores comprising the metals of the alloy; introducing the mixed ores into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as M₂Y in which contaminants X contained in the mixed ores are soluble, and a relatively inert anode; conducting electrolysis under conditions favourable to the selective dissolution of contaminants contained in the mixed ores in preference to the deposition of the M₂ cation; and following electrolysis, reclaiming the purified mixed ore to form the cathode.
METHOD OF MANUFACTURE FOR FERRO-TITANIUM AND OTHER METAL ALLOYS ELECTROLYTIC REDUCTION

This invention relates to a method for the manufacture of alloys from metal ores. More particularly, the invention is directed to the reduction of metal ores to form alloys. Such alloys include but are not limited to Ferro-titanium alloys.

WO99/64638 and the Applicants co-pending applications British Patent applications nos. GB 0003971.9 and GB 0010873.8 the disclosures of which are incorporated herein by reference) describe methods for the electrolytic reduction of metal compounds.

Certain embodiments of these methods involve the electrolysis of metal oxides or other compounds (M₂X) in a cell containing a liquid (fused salt M₂Y) electrolyte and an anode, the metal oxide or other compound forming the cathode. Conditions are controlled so as to bring about the selective dissolution of the oxygen or other contaminant of the cathode in preference to deposition of the metal cation. Improved efficiency of this process can be achieved by various methods as described in GB 0003971.9 and GB 0010873.8 some of which are summarised below.

Production of powder by reduction of sintered metal oxide granules

Sintered granules or powders of metal oxide can be used as the feedstock for the electrolysis described in the above referenced method, as long as appropriate conditions are present. In one example, powdered titanium dioxide in the form of granules or a powder is used, the powdered particles preferably have a size in the region of 200μm.

Production of powder by deposition of M₁ onto the cathode

If a metal is deposited onto a cathode (based on the electrolytic process previously described) from a second source of the metal M₁ which is maintained at a more positive potential, the resulting metal deposited thereon is dendritic in structure.
This is particularly so where the metal is titanium. This form of titanium is easy to break up into a powder as the individual particles are connected together only by a small surface area. This method can be used to produce titanium powder from titania. In this method, a second cathode is provided which is maintained at a potential which is more negative than the first cathode. When the deposition of titanium on the first cathode has progressed sufficiently, the second electrode is switched on, leading to the dissolution of titanium from the first cathode and deposition onto the second cathode in dendritic form.

**Feedstock production by addition of binder to rutile and amorphous titania**

The manufacture of titanium dioxide from the raw ore (sand mined illemite) comprises a large number of steps in the production of titanium.

During one of these stages titanium dioxide in the form of an amorphous slurry undergoes calcining. The titanium dioxide slurry can be used as the principle feedstock in the above described electrolytic method. A small percentage of calcined material is mixed with amorphous material and a binder to obtain the most satisfactory results after sintering. The calcined material should constitute at least about 5% by weight of the mixture.

**Production of alloy metal matrix composites (MMC’s)**

Individual SiC fibres are coated with an oxide/binder slurry (or mixed oxide slurry for an alloy) of the appropriate thickness. Alternatively, the fibres may be combined with an oxide paste or slurry to produce a preformed sheet consisting of parallel fibres in a matrix of oxide powder and binder, or, a complex three dimensional shape containing the fibres in the correct positions could be cast or pressed from oxide slurry or paste. The coated fibres, preform sheet or three dimensional shape can then be made the anode of an electrochemical cell (with or without a pre-sinter step) and the oxide powder may be reduced by the previously described electrolytic process to a metal or alloy. The product may then be washed or vacuum annealed to remove salt.
and then hot isostatically pressed to give a 100% dense fibre reinforced composite.

In the proposed method, fine ceramic particles such as titanium diboride are blended with titania powder to give a uniform mixture prior to sintering and electrolytic reduction. After reduction the product is washed or vacuum annealed to remove salt, and then hot pressed to give a 100% dense composite material. Depending on the reaction chemistries, the ceramic particles may either remain unchanged by the electrolysis and hot pressing or may be converted to another ceramic material which would then be the reinforcing element of the MMC. For example, in the case of titanium diboride, the ceramic reacts with the titanium to form titanium monoboride. In a variation of this process, fine metal powder is mixed with the titania powder in place of a ceramic powder, with the intention of forming a fine distribution of a hard ceramic or intermetallic phase by reaction with titanium or another alloying element or elements. For example, boron powder can be added, and this reacts to form titanium monoboride particles in the alloy.

Use of continuous powder feed

Continuously feeding a fine powder of metal oxide into the electrochemical cell, allows for a constant current and a higher reaction rate. A carbon electrode is preferred for this method. This method permits the use of cheaper feedstock as a sintering and/or forming stage is no longer needed.

Production of metal foams

Metal foams, more typically titanium foams, are attractive for a number of applications such as filters, medical implants and structural fillers. The fabrication of a sponge-like sintered oxide pre-form from the starting material $M_1X$ can be converted into a solid metal/alloy foam via the electrolytic method previously described. Various established methods may be used to make the foam like material from the mixture of oxide powders. The foam preform desirably has open porosity that is, porosity which is interconnected and open to the exterior.
In a preferred embodiment of this method, a natural or synthetic polymeric foam is infiltrated with a metal (eg titanium) oxide slip, then dried and fired to remove the polymeric foam, leaving an open "foam" which is an inversion of the original polymeric foam. The sintered preform is then electrolytically reduced in accordance with the previously described method to convert it into a titanium/titanium alloy foam. The foam is then washed or vacuum distilled to remove the salt.

Alternatively, the metal oxide powder may be mixed with organic foaming agents. These materials are typically two liquids which when mixed, react to evolve a foaming gas, and then cure to give a solidified foam with either an open or closed structure. The metal powder is mixed with one or both of the precursor liquids prior to production of the foam. The foam is then fired to remove the organic material, leaving the ceramic foam which is then electrolytically reduced in accordance with the previously described method.

Production of metal or metal alloy components

A near net shape component may be made using the previously described electrolytic method by reducing a ceramic facsimile of the component made from a mixture of a metal oxide or mixture of metal oxide and the oxides of other alloying elements. Again this method is particularly suited to the manufacture of titanium metal and alloy components. The ceramic facsimile may be produced using any of a variety of well known production methods for ceramic articles which include; pressing, injection moulding, extrusion and slip casting, followed by firing (sintering). Full density of the metallic component can be achieved by sintering with or without the application of pressure, either in the electrochemical cell, or in a subsequent operation. Shrinkage of the component during the conversion to metal or alloy should be allowed for by making the ceramic facsimile proportionally larger than the desired component.

Electrolysis of a preformed sintered mass

The electrolysis is performed on a preformed sintered mass comprising a
mixture of metal oxide made up of a proportion of particles of size generally greater than 20 microns and a proportion of finer particles of less than 7 microns. Preferably the finer particles make up between 10 and 55% by weight of the sintered block.

High density granules of approximately the size required for the powder are manufactured and then are mixed with very fine unsintered metal oxide (e.g., titanium dioxide), binder and water in the appropriate ratios and formed into the required shape of feedstock. This feedstock is then sintered to achieve the required strength for the reduction process. The resulting feedstock, after sintering but before reduction, consists of high density granules in a lower density (porous) matrix.

The feedstock can be reduced in block form using the previously described electrolytic method and the result is a friable block which can easily be broken up into powder.

The calcine discharge used can be replaced by cheaper amorphous TiO\textsubscript{2}. The key requirement for this “matrix” material is that it sinters easily with significant shrinkage during the sintering process. Any oxide or mixture of oxides which fulfil these criteria would be usable. In the case of TiO\textsubscript{2} this means the particle size must be less than about 1 μm. It is estimated that at least 5% of the matrix material should be present in order to give any significant strength to the sintered product.

The starting granules for this method need not be rutile sand but could be manufactured by a sintering and crushing process, and in principle there is no reason to suppose that alloy powders could not be made by this route.

Electrolytic reduction using swarf or chips as starting materials

Manufacturing operations generate large quantities of swarf and chips, some of which can be processed and recycled. However, certain operations such as cutting create high temperatures in the swarf and chips and cause absorption of high quantities of oxygen into these pieces. The high surface area to volume ratio of such pieces may
result in penetration of oxygen through almost the entire body of the piece. Beyond an optimum, increasing quantities of oxygen in the metal have an increasingly detrimental effect on its mechanical properties.

Where the quantities of oxygen absorbed are low to moderate, it is known to mix these waste products with quantities of scrap having lower levels of oxygenation and/or with quantities of virgin metals to ensure that the end product of the mixture has below a certain desired maximum oxygen content. At higher levels of contamination, it becomes increasingly uneconomical to dilute the highly contaminated metal in this manner and consequently, much of this potentially useful material is abandoned as redundant.

A co-pending application made this same date by the Applicants proposes novel methods for the reclamation of metals from highly contaminated metal waste utilising some of the principles of the methods previously described, these methods prescribe reclaiming a metal \( M_1 \) from a source of highly contaminated scrap material \( M_1X \), including the steps of:

- introducing the highly contaminated scrap metal into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as \( M_2Y \) in which contaminant \( X \) is soluble, and a relatively inert anode;

- conducting electrolysis under conditions favourable to the selective dissolution of the contaminant \( X \) in preference to the deposition of the \( M_2 \) cation; and

- following electrolysis, reclaiming the decontaminated metal \( M_1 \) from the cathode.

In any of the aforementioned methods \( X \) may be a metalloid such as oxygen, sulphur, carbon or nitrogen, preferably, \( X \) is oxygen. \( M_1 \) may be a Group IVA
element such as Ti, Si, Ge, Zr, Hf, Sm, Nd, Mo, Cr, Nb or an alloy of any of the preceding metals, preferably, \( M_1 \) comprises titanium. A preferred electrolyte, \( M_2Y \), is calcium chloride (CaCl\(_2\)). Other suitable electrolytes include but are not limited to the molten chlorides of all common alkali and alkaline earth metals. Other preferred metals for \( M_2 \) are barium, caesium, lithium, strontium and yttrium. The anode of the cell is preferably of a relatively inert material. One suitable anode material is graphite.

Processing conditions suitable for the favourable dissolution of the contaminant X require that the potential of the cell preferably be maintained at a potential which is less than the decomposition potential of the molten electrolyte \( M_2Y \) during the process. Allowing for polarisation and resistive losses in the cell, it will be understood that the cell potential may be maintained at a level equal to, or marginally higher than, the decomposition potential of \( M_2Y \) and still achieve the desired result. Potentiostatic methods may be used to control the potential.

It is also preferred that the temperature of the cell is maintained at an elevated temperature which is significantly above the melting point of \( M_2Y \) but below the boiling point of \( M_2Y \). Where \( M_2Y \) is CaCl\(_2\), suitable processing parameters include a potential of up to about 3.3V and a processing temperature of between about 825 and 975 °C.

Optionally, this more recent method may include an additional step wherein the scrap metal may be processed before being introduced into the electrochemical cell, for example to form small granules, or a powder, or an amorphous slurry of the contaminated material. Alternatively or in addition to this additional processing step, the scrap metal may be fabricated into a sponge-like sintered oxide preform prior to electrolysis. Alternatively or in addition to the additional processing step, the scrap material may be sintered in a mixture containing particles of \( M_1X \) greater than 20 microns in size and finer particles of \( M_1X \) less than about 7 microns in size, binder and water to form a friable block. Preferably in this method, the finer particles are in a proportion of about 10 to about 55% by weight of the sintered block. Alternatively or in addition to the additional processing step, the scrap metal may be fabricated into a ceramic facsimile of a desired metal or metal alloy component before introduction into
the electrochemical cell. This fabrication may be achieved by various known methods including pressing, injection moulding, extrusion and slip casting followed by sintering.

The present application proposes a further novel application for these technologies.

The present invention provides a method for the production of a Ferro-titanium master alloy including the steps of:

introducing mixed ores comprising the metals of the alloy in suitable proportions to meet the desired proportions of the master alloy;

introducing the mixed ores into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as M₂Y in which contaminants contained in the mixed ores are soluble, and a relatively inert anode;

conducting electrolysis under conditions favourable to the selective dissolution of contaminants contained in the mixed ores in preference to the deposition of the M₂ cation; and

following electrolysis, reclaiming the purified alloy from the cathode.

The invention is particularly suited to the manufacture of Ferro-titanium alloys. Preferred ores include ilmenite and rutile, other suitable ores will no doubt occur to the skilled addressee. Preferably, the ores are mixed in proportions suitable to provide a eutectic Ferro-titanium alloy comprising about 70% Ti to about 30%Fe by weight.

The ores can be obtained already crushed into small pieces or powders or may be ground or crushed as a first step of the method. For good homogeneity in the end alloy, preferred sizes of the crushed pieces are in the order of 100 to 600 microns The ores are mixed in proportions suitable to provide the constituent alloy metals in correct
stoichiometric quantities to form the chosen alloy. The mixed particles of ore are sintered and may be used as a starting material in any of the variations of the electrochemical reduction processes previously described. In the particular case of Ferro-titanium for use in the steel making process, it is not necessary to reduce the contaminant level to the low levels actually obtainable by the reduction process. The process may therefore be applied for a shortened period to reduce the contamination to below a maximum acceptable level. Also, since homogeneity is not important for this application, crushed pieces of the order of a few millimetres in size are acceptable.

At present, around 50,000 tons/year of Ferro-titanium is used in the steel making industry as a deoxidant. Prior to the present invention, this Ferro-titanium has been manufactured by melting together iron and scrap titanium based materials. It is recognised by the inventors that naturally occurring ores may contain a range of metallic impurities which might not normally be found in Ferro-titanium alloys produced by the prior art methods, equally, it is appreciated that these impurities are unimportant where the Ferro-titanium is to be used as a deoxidant in steel making in accordance with usual practices. It is further appreciated by the inventors that the purification of the mixed ores provided by the electrolytic reduction method described herein, may not need to be completed, since the total elimination of contaminants such as oxygen is not essential for these purposes. For example, in Ferro-titanium, oxygen levels of up to 2% by weight are considered acceptable. Accordingly, the present invention maybe used to partially purify the mixed ores to a state where the contaminant levels are acceptable but not negligible. The time taken to reduce the level of contaminant oxygen to about 2% in Ferro-titanium made according to this method has been found to be only about 70% of the time taken to reduce the levels to about 0.1% by weight, the preferred level for other commercial applications of the alloy. Trials carried out by the inventors have also shown the process to have a current efficiency of around 70% in reducing the oxygen to about 2% as opposed to about 40% efficiency in reducing the oxygen levels to about 0.1%. Thus, the partial purification reduces the overall processing cost in manufacturing the Ferro-titanium alloy.

A preferred electrolyte, \( \text{M}_2\text{Y} \), is calcium chloride (\( \text{CaCl}_2 \)). Other suitable
electrolytes include but are not limited to the molten chlorides of all common alkali and alkaline earth metals. Other preferred metals for M₂ are barium, caesium, lithium, strontium and yttrium. The anode of the cell is preferably of a relatively inert material. One suitable anode material is graphite.

Processing conditions suitable for the favourable dissolution of the contaminants require that the potential of the cell preferably be maintained at a potential which is less than the decomposition potential of the molten electrolyte M₂Y during the process. Allowing for polarisation and resistive losses in the cell, it will be understood that the cell potential may be maintained at a level equal to, or marginally higher than, the decomposition potential of M₂Y and still achieve the desired result. Potentiostatic methods may be used to control the potential.

It is also preferred that the temperature of the cell is maintained at an elevated temperature which is significantly above the melting point of M₂Y but below the boiling point of M₂Y. Where M₂Y is CaCl₂ suitable processing parameters include a potential of up to about 3.3V and a processing temperature of between about 825 and 1050 °C.

By adapting the method in accordance with various embodiments previously described herein and in GB 00039719 and GB 0010873.8 from which this application claims priority, the Ferro-titanium alloy can be provided in various physical forms, eg, powdered, foamed, sintered plate or 3-dimensional shape as may be required in different applications.
CLAIMS

1. A method for the production of a master alloy including the steps of;

   introducing mixed ores comprising the metals of the alloy and contaminants X in suitable proportions to meet the desired proportions of the master alloy;

   introducing the mixed ores into an electrochemical cell, the cell containing a liquid electrolyte comprising a fused salt or mixture of salts generally designated as $M_2Y$ in which contaminants X contained in the mixed ores are soluble, and a relatively inert anode;

   conducting electrolysis under conditions favourable to the selective dissolution of contaminants contained in the mixed ores in preference to the deposition of the $M_2$ cation; and

   following electrolysis, reclaiming the purified mixed ore from the cathode.

2. A method as claimed in claim 1 wherein the ores are crushed, ground or powdered prior to mixing.

3. A method as claimed in claim 2 wherein the crushed, ground or powdered particles are preformed to a near net shaped of the end product prior to being introduced to the electrochemical cell.

4. A method as claimed in claim 2 wherein the crushed, ground or powdered particles are formed into a foam prior to being introduced to the electrochemical cell.
5. A method as claimed in any of claims 2 to 4 wherein the crushed, ground or powdered foam, or preform or foam, made therefrom is sintered prior to introduction into the electrochemical cell.

6. A method as claimed in any preceding claim wherein the ores comprise iron and titanium and are mixed in proportions suitable to provide a eutectic Ferrotitanium alloy comprising about 70\% Ti to about 30\% Fe by weight.

7. A method as claimed in any preceding claim wherein the selected ores include ilmenite and/or rutile.

8. A method as claimed in any preceding claim, wherein the electrochemical reduction is halted when the quantity of contaminant X has been reduced to a predetermined acceptable maximum level which is greater than the minimum level achievable if reduction is completed.

9. A method for the production of a master alloy substantially as described herein.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B34/12 C25F1/16 C25C3/28 C22B5/00 C22C33/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B C25F C25C C21C C22C

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

Electronic data base consulted during the international search (name of data base and where practical, search terms used)
WP Data, EPO-Internal, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 99 64638 A (FARTHING THOMAS WILLIAM; UNIV CAMBRIDGE TECH (GB); CHEN ZHENG (GB)) 16 December 1999 (1999-12-16) cited in the application claims 1,10,23,25; examples 10,12</td>
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X Further documents are listed in the continuation of box C.

X Patent family members are listed in annex.

* Special categories of cited documents:
'**' document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search
15 June 2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epos nl, Fax (+31-70) 340-3016

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