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(54) ELECTROCHEMICAL REDUCTION OF METAL OXIDES

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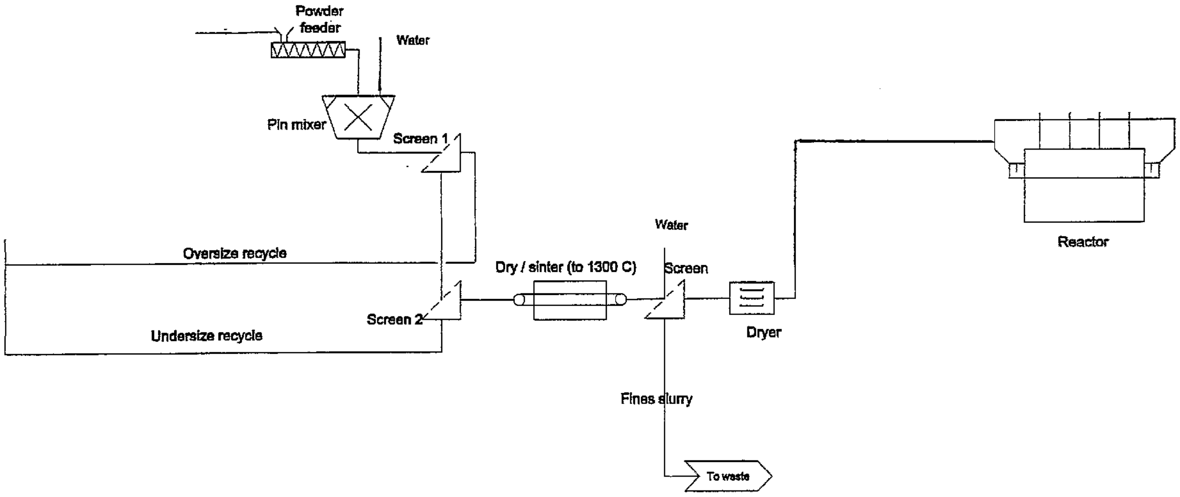
(57) ABSTRACT

A metal oxide feed material for an electrochemical reduction process is disclosed. The feed material is in the form of powders and/or pellets that have sufficient porosity, typically 35-60%, to enable penetration of molten electrolyte into the powders and/or pellets during the course of an electrochemical reduction process in an electrolytic cell and subsequent washing of electrolyte from the powders and/or pellets after the powders and/or pellets are discharged from the cell. A process for preparing the metal oxide feed material is also disclosed.



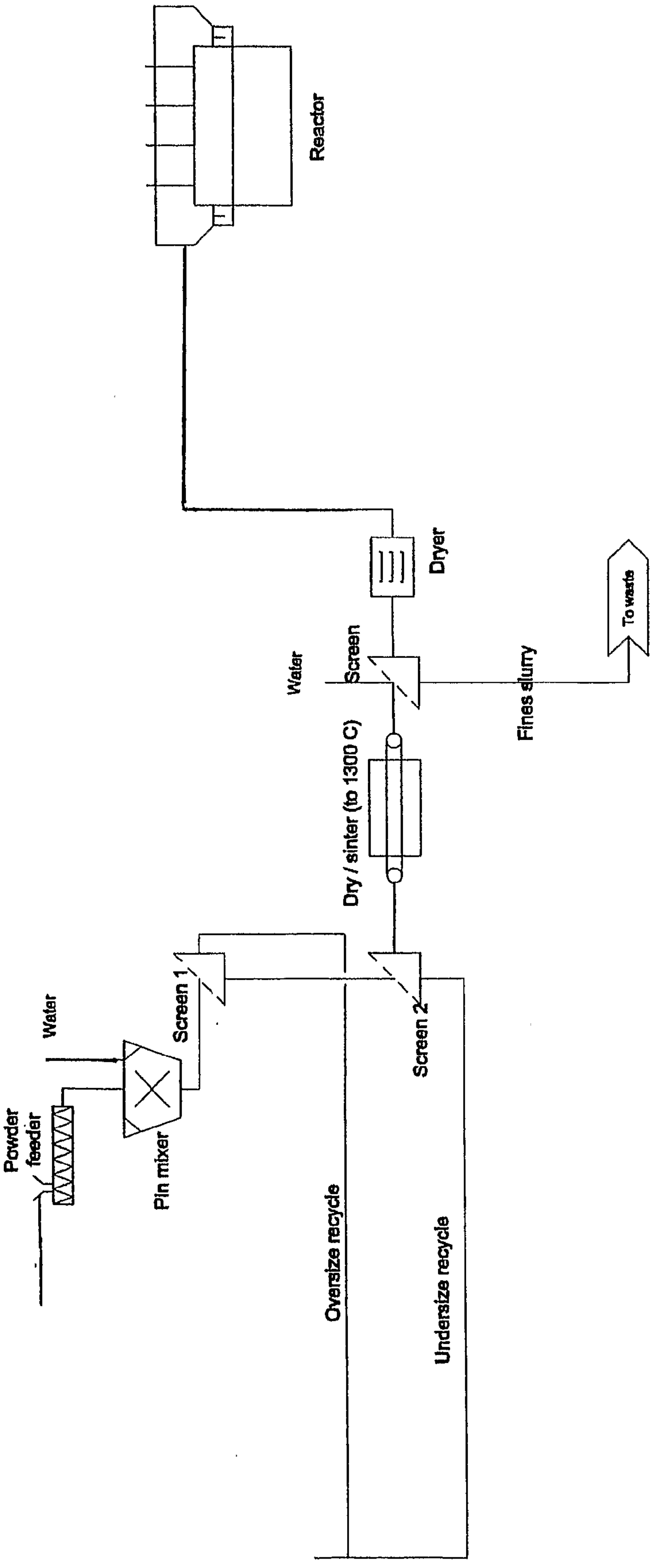

Reactor
Dryer
Water
Screen
Fines slurry
To waste
Dry / sinter (to 1300 C)
Water
Screen 1
Screen 2
Powder feeder
Pin mixer
Oversize recycle
Undersize recycle

FIGURE 1

ELECTROCHEMICAL REDUCTION OF METAL OXIDES

[0001] This application is a continuation-in-part of and claims priority to PCT application PCT/AU2005/000899 published in English on Dec. 29, 2005 as WO 2005/123986 and to Australian application no. 2004903409 filed Jun. 22, 2004, the entire contents of each are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to electrochemical reduction of metal oxides.

[0003] The present invention relates particularly to electrochemical reduction of metal oxides in the form of powders and/or pellets to produce metal having a low oxygen concentration, typically no more than 0.5% by weight.

[0004] The present invention is a metal oxide feed material for a process and an apparatus for electrochemically reducing metal oxide feed material in powder and/or pellet form on a continuous basis, or a semi-continuous basis or a batch basis.

[0005] The present invention is also a process for preparing a suitable metal oxide feed material for the process described in the preceding paragraph.

BACKGROUND OF THE INVENTION

[0006] The present invention was made during the course of an on-going research project on electrochemical reduction of metal oxides being carried out by the applicant. The research project has focussed on the reduction of titania (TiO_2).

[0007] During the course of the research project the applicant has carried out a series of experiments investigating the reduction of titania in electrolytic cells comprising a pool of molten $CaCl_2$-based electrolyte, an anode formed from graphite, and a range of cathodes.

[0008] The $CaCl_2$-based electrolyte used in the experiments was a commercially available source of $CaCl_2$, namely calcium chloride dihydrate, which decomposed on heating and produced a very small amount of CaO.

[0009] The applicant operated the electrolytic cells at a potential above the decomposition potential of CaO and below the decomposition potential of $CaCl_2$.

[0010] The applicant found that the cells electrochemically reduced titania to titanium with low concentrations of oxygen, i.e. concentrations less than 0.2 wt. %, at these potentials.

[0011] The applicant operated the cells under a wide range of different operating set-ups and conditions.

[0012] One of the inventions made by the applicant in the course of the research project is a process and an apparatus for electrochemically reducing metal oxides, such as titania, on a continuous or a semi-continuous basis.

[0013] This invention is described and claimed in International application PCT/AU03/001657 in the name of the applicant. The disclosure in the International application is incorporated herein by cross-reference.

[0014] The process described and claimed in the International application includes the steps of: applying a cell potential across an anode and a cathode of an electrolytic cell, continuously or semi-continuously feeding the metal oxide powders and/or pellets into the molten electrolyte bath, transporting the powders and/or pellets along a path within the molten electrolyte bath and reducing the metal oxide as the metal oxide powders and/or pellets move along the path, and continuously or semi-continuously removing reduced material from the molten electrolyte bath.

[0015] In the context of the International application, the term “powders and/or pellets” is understood to mean particles having a particle size of 3.5 mm or less. The upper end of this particle size range covers particles that are usually described as “pellets”. The remainder of the particle size range covers particles that are usually described as “powders”.

SUMMARY OF THE INVENTION

[0016] In the context of the present invention, it is necessary to expand on the definition of powders and/or pellets. Powders may be single particle powders. Powders may also be made from a plurality of smaller particles. Powders tend to be generally uniform in size, with no immediately apparent length and width dimensions for individual particles. Pellets tend to be shaped, for example by being slip cast in moulds. The shapes can be any suitable shapes. One example of a shape is a disc with a cylindrical side wall and flat top and bottom walls, and with the diameter of the cylinder being considerably greater that the thickness of the disc between the top and bottom walls. One example is a disc that is 20 mm in diameter and 2 mm thick.

[0017] In all cases herein, references to dimensions of powders and/or pellets are understood to mean the minimum dimensions of the powders and pellets. Thus, for example, the above-mentioned maximum size of 3.5 mm is the size of the minimum dimension of a powder and/or a pellet.

[0018] The term “semi-continuously” is understood in the International application and herein to mean that the process includes: (a) periods during which metal oxide powders and/or pellets are supplied to the cell and periods during which there is no such supply of metal oxide powders and/or pellets to the cell, and (b) periods during which reduced material is removed from the cell and periods during which there is no such removal of reduced material from the cell.

[0019] The overall intention of the use of the terms “continuously” and “semi-continuously” in the International application and herein is to describe cell operation other than on a batch basis.

[0020] In the context of the present invention, the term “batch” is understood to mean supplying a batch, i.e. a selected amount, of metal oxide powders and/or pellets to a cell, operating the process in the cell for a period of time and reducing the powders and/or pellets, and removing the reduced material from the cell, and repeating the procedure for a next batch of metal oxide powders and/or pellets.

[0021] The applicant has realised that the physical properties of the metal oxide feed material are extremely important to successful operation of the process on a continuous basis, a semi-continuous basis, and a batch basis. In particular, the applicant has realised that it is important that powders and/or pellets of metal oxide feed material have a particular combination of physical properties in order to achieve successful operation of the process.

[0022] In particular, the applicant has identified powder and pellet porosity as a key parameter. In general terms, the present invention is a metal oxide feed material in a form of powders and/or pellets that have sufficient porosity, typically 35-60%, to enable penetration of molten electrolyte into the powders and/or pellets during the course of an electrochemical reduction process in which metal oxide is at least partially reduced to metal in an electrolytic cell and subsequent washing of electrolyte from the powders and/or pellets after the powders and/or pellets are discharged from the cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Embodiments of the invention will be described, by way of example, with reference to the accompanying drawings.

[0024] FIG. **1** is a flowsheet of one embodiment of a process for electrochemically reducing titania in accordance with the present invention that includes one embodiment of a process for preparing titania for use as a feed material in the process in accordance with the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0025] According to the present invention there is provided a metal oxide feed material for electrochemically reducing metal oxides, such as titania, in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode, which metal oxide feed material is in a form of powders and/or pellets and includes a sufficient porosity to enable penetration of molten electrolyte into the powders and/or pellets during the course of an electrochemical reduction process that reduces metal oxide in the powders and/or pellets to metal and subsequent washing of electrolyte from powders and/or pellets after the powders and/or pellets are discharged from the cell.

[0026] Preferably the metal oxide feed material also includes any one or more than one of: (a) a density that is higher than the density of molten electrolyte so that the powders and/or pellets of metal oxide feed material do not float in the molten bath; (b) a size that is sufficiently large so that the powders and/or pellets can sink at a reasonable rate within the molten bath if supplied to the molten bath from above the surface of the molten bath; (c minimum fines that could restrict access of molten electrolyte to larger powders and/or pellets of metal oxide feed material and minimise reduction rates during the course of the process; and (d) sufficient strength so that there is minimal breakdown of the powders and/or pellets in the process, including handling the powders and/or pellets pre- and post-processing in the cell.

[0027] The term "density" is understood herein to include the density of the powders and/or pellets of the feed material in air and the density of the powders and/or pellets of the feed material in the electrolyte.

[0028] In situations in which the metal oxide feed material includes powders and/or pellets of a titanium oxide, such as titania, and the electrolyte is a $CaCl_2$-based electrolyte that contains CaO when in a molten state, preferably the powders and/or pellets have an open connected pore structure with a porosity in the range of 35-60% by volume.

[0029] The term "open connected pore structure" is understood herein to mean that the powders and/or pellets have a series of interconnected pores that are open to the outer surface of the powders and/or pellets that enable penetration of liquids, such as molten electrolyte and washing water into the powders and/or pellets.

[0030] It is preferred particularly that the porosity be at least 40 vol. %. It is also preferred particularly that the porosity be less that 55 vol. %. Typically, the porosity is in a range of 40-50 vol. %. Preferably at least 25 vol. % of the pores have a size of 0.005-10 microns measured by Mercury Intrusion porosimetry. Preferably the remainder of the pores have a size of less than 0.005 microns measured by gas absorption.

[0031] In addition, in situations in which the metal oxide feed material includes powders and/or pellets of a titanium oxide, such as titania, and the electrolyte is a $CaCl_2$-based electrolyte that contains CaO when in a molten state, preferably the powders and/or pellets also include any one or more than one of: (a) a density of 2.5-3.5 g/cc in air, (b) a size of 1-4 mm, (c) a minimum mechanical strength to minimise decrepitation of powders and/or pellets prior to, during, and after processing the powders and/or pellets in the cell; and (d) a minimum strength to withstand thermal shock associated with introducing powders and/or pellets into the cell.

[0032] It is preferred particularly that the powder/pellet size be 1-2.5 mm. It is noted that, in the context of the discussion above, the size of 1-2.5 mm is the size measured in the minimum dimensions of the powders and/or pellets. It is preferred more particularly that the powder/pellet size be 1.5-2 mm.

[0033] According to the present invention there is also provided a process for preparing a metal oxide feed material for electrochemically reducing metal oxides, such as titania, in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode, which process includes the steps of: (a) forming powders and/or pellets of metal oxide feed material having a required porosity; (b) sintering powders and/or pellets from step (a) to a required strength; and (c) washing the sintered powders and/or pellets to remove fines attached to the powders and/or pellets.

[0034] Preferably the process includes a further step of separating the powders and/or pellets formed in step (a) into at least two fractions on the basis of size. Preferably the process includes supplying a larger size fraction to step (b). Preferably the process includes returning a smaller size fraction to step (a).

[0035] Preferably the pore structure of the powders and/or pellets formed in step (a) is an open connected pore structure and the required porosity is 35-60 vol. %. Preferably step (a) includes forming powders and/or pellets of metal oxide feed material having a required size and/or a required density.

[0036] Preferably step (a) includes forming powders and/or pellets of metal oxide feed material by agglomerating particles of metal oxide material. Preferably the particles of metal oxide material for agglomeration are fully dense particles. Preferably the minimum dimensions of the particles of metal oxide material for agglomeration are less than 50 microns. More preferably the minimum dimensions of the particles of metal oxide material for agglomeration are less than 30 microns. Typically the minimum dimensions of the particles of metal oxide material for agglomeration range from nanometer size up to 15 microns.

[0037] More preferably step (a) includes forming powders and/or pellets of metal oxide feed material by agglomerating particles of metal oxide material with or without binders. Preferably step (a) includes forming powders and/or pellets of metal oxide feed material by agglomerating (i) particles of metal oxide material, (ii) fines washed from the sintered powders and/or pellets in step (c), and (iii) the smaller size fraction from the separation step, with or without binders.

[0038] Preferably step (a) includes agglomerating particles of metal oxide material in a mixer, such as a pin mixer, that is capable of high impact and high velocity mixing of metal oxide material. Preferably step (a) includes agglomerating particles of metal oxide material by supplying particles of metal oxide material and water to the mixer and operating the mixer and forming agglomerates of a required porosity.

[0039] Preferably the required strength for sintered powders and/or pellets in step (b) is a strength that is sufficient to withstand thermal shock associated with introducing powders and/or pellets into the cell.

[0040] In situations in which the metal oxide feed material is a titanium oxide, such as titania, preferably the required porosity of the powders and/or pellets formed in step (a) is an open pore structure with 35-60 vol. %, more preferably 40-50%, porosity. In addition, preferably the powders and/or pellets formed in step (a) have a size of 1-4 mm and a density of 2.5-3.5 g/cc.

[0041] In situations in which the metal oxide feed material is titania, preferably step (b) includes sintering the powders and/or pellets formed in step (a) at a temperature in the range of 850-1400° C. Preferably step (b) includes sintering the powders and/or pellets formed in step (a) in air.

[0042] According to the present invention there is also provided a process for electrochemically reducing metal oxides, such as titania, in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode using the above-described metal oxide feed material.

[0043] According to the present invention there is also provided a process for electrochemically reducing metal oxides, such as titania, in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode, which process includes the above-described feed preparation process.

[0044] The present invention is described further by way of example only with reference to the accompanying drawing which is a flowsheet of one embodiment of a process for electrochemically reducing titania in accordance with the present invention that includes one embodiment of a process for preparing titania for use as a feed material in the process in accordance with the present invention.

[0045] The process as shown in the flowsheet of FIG. **1** includes the following steps.

[0046] Pigment grade titania powders (i) that have a particle size of 100-200 nanometers and are fully dense and (ii) water are supplied to a pin mixer, with the amount of water being 15-20% by weight of the total weight of the titania and the water, and operating the pin mixer and agglomerating the powders and forming powders/pellets having a required agglomerate size, porosity, and density. The applicant has found that preferred agglomerates have a density of 2.5-3.5 g/cc in air, a size of 1-4 mm, and an open pore structure with a porosity of 40-50%. The agglomerates may be described as powders or pellets depending on the particle size.

[0047] Processing material, which is predominantly agglomerated powders/pellets, is discharged from the pin mixer in two successive screen assemblies. The retained material on screen **1** is an oversize fraction and is recycled to a mill. The material passing through the screen is transferred to screen **2**. The material passing through screen **2** is an undersize fraction and is recycled to the pin mixer. The retained material on screen **2**, which is entirely agglomerated powders/pellets, has the required particle size range for downstream electrochemical processing.

[0048] Drying and sintering the material retained on screen **2**, hereinafter referred to as "agglomerates" at a temperature of 850-1400° C. in air, for example in a multi-hearth furnace, and thereby increasing the mechanical strength of the agglomerates as required. Key considerations are that the mechanical strength be sufficient to withstand thermal shock when supplied to a molten electrolyte bath and be handled prior to being supplied to the bath and while in the bath without substantial break-down of the agglomerated powders/pellets. The sintering step does not increase the overall size of the agglomerates. However, inevitably, the sintering step increases the size of crystals in the agglomerated powders/pellets, typically to 2-10 microns, subject to the sintering temperature and time, and decreases slightly the porosity of the agglomerates, without affecting the open pore structure.

[0049] Washing the sintered agglomerated powders/pellets and removing piggy-back fines. Drying the washed sintered agglomerated powders/pellets in a dryer. Supplying the dried agglomerated powders/pellets to a reactor that includes an electrolytic cell and electrochemically reducing at least part of the titania to titanium in the cell. The cell includes a bath of molten electrolyte and an anode and a cathode. As described above, the process may be carried out on a continuous basis, a semi-continuous basis, or a batch basis. Washing agglomerated powders/pellets discharged from the cell to remove retained electrolyte and subsequently processing the titanium as required.

[0050] Many modifications may be made to the present invention described above without departing from the spirit and scope of the invention. By way of example, whilst step (a) of the above-described embodiment includes agglomerating pigment grade titania in a pin mixer, the present invention is not so limited and extends to any suitable means of forming powders and/or pellets of titania having a required porosity. By way of example, shaped pellets may be formed by slip casting.

[0051] Since modifications within the spirit and scope of the invention may readily be effected by persons skilled within the art, it is to be understood that this invention is not limited to the particular embodiment described by way of example hereinabove.

1. A metal oxide feed material for electrochemically reducing metal oxides in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode comprising one of a powder or pellet that includes a sufficient porosity to enable penetration of molten electrolyte into the one of a powder or pellet during the course of an electrochemical reduction process and subsequent washing of electrolyte from the one of a powder or pellet after the one of a powder or pellet is discharged from the cell.

2. The feed material defined in claim 1 wherein the one of a powder or pellet includes any one or more than one of:

a. a density that is higher than the density of the molten electrolyte so that the one of a powder or pellet of metal oxide feed material does not float in the bath;

b. a size that is sufficiently large so that the one of a powder or pellet can sink at a reasonable rate within the bath if supplied to the bath from above the surface of the bath;

c. minimum fines that could restrict access of molten electrolyte to the one of a powder or pellet of metal oxide feed material and minimise reduction rates during the course of the process; and

d. sufficient strength so that there is minimal breakdown of the one of a powder or pellet in the process, including handling the one of a powder or pellet pre- and post-processing in the cell.

3. The feed material defined in claim 1 wherein when the one of a powder or pellet is a titanium oxide material and the electrolyte is a $CaCl_2$-based electrolyte that contains CaO when in a molten state, the one of a powder or pellet has an open connected pore structure with a porosity in the range of about 35 to about 60% by volume.

4. The feed material defined in claim 3 wherein the porosity is at least about 40 vol. %.

5. The feed material defined in claim 3 wherein the porosity is at least about 55 vol. %.

6. The feed material defined in claim 3 wherein the porosity is in a range of about 40 to about 50 vol. %.

7. The feed material defined in claim 3 wherein at least about 25 vol. % of the pores have a size of about 0.005 microns to about 10 microns as measured by Mercury Intrusion porosimetry.

8. The feed material defined in claim 7 wherein the remainder of the pores have a size of less than about 0.005 microns measured by gas absorption.

9. The feed material defined in claim 3 wherein when the one of a powder or pellet is a titanium oxide material and the electrolyte is a $CaCl_2$-based electrolyte that contains CaO when in a molten state, the one of a powder or pellet includes any one or more than one of:

(i) a density of about 2.5 to about 3.5 g/cc in air,

(ii) a size of about 1 mm to 3 mm,

(iii) a minimum mechanical strength to minimise decrepitation of the one of a powder or pellet prior to, during, and after processing the one of a powder or pellet in the cell; and

(iv) a minimum strength to withstand thermal shock associated with introducing the one of a powder or pellet into the cell.

10. The feed material defined in claim 9 wherein the one of a powder or pellet has a size in the range of about 1 mm to about 2.5 mm.

11. The feed material defined in claim 9 wherein the one of a powder or pellet has size in the range of about 1.5 mm to about 2 mm.

12. A process for preparing a metal oxide feed material for electrochemically reducing metal oxides in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode, which process includes the steps of:

a. forming one of a powder or pellet of metal oxide feed material having a required porosity;

b. sintering the one of a powder or pellet from step (a) to a required strength; and

c. washing the sintered the one of a powder or pellet to remove fines attached to the one of a powder or pellet.

13. The process defined in claim 12 includes a further step of separating the one of a powder or pellet formed in step (a) into at least two fractions on the basis of size.

14. The process defined in claim 13 includes supplying a larger size fraction to step (b).

15. The process defined in claim 13 includes returning a smaller size fraction to step (a).

16. The process defined in claim 12 wherein step (a) includes forming the one of a powder or pellet of metal oxide feed material to have an open connected pore structure and a porosity of about 35 to about 60 vol. %.

17. The process defined in claim 12 wherein step (a) includes forming one of a powder or pellet of metal oxide feed material to have one or more of a required size or a required density.

18. The process defined in claim 12 wherein step (a) includes forming one of a powder or pellet of metal oxide feed material by agglomerating particles of metal oxide material.

19. The process defined in claim 18 wherein the particles of metal oxide material for agglomeration are fully dense particles.

20. The process defined in claim 18 wherein the minimum dimensions of the particles of metal oxide material for agglomeration are less than about 50 microns.

21. The process defined in claim 18 wherein the minimum dimensions of the particles of metal oxide material for agglomeration are less than about 30 microns.

22. The process defined in claim 18 wherein the minimum dimensions of the particles of metal oxide material for agglomeration range from nanometer size up to about 15 microns.

23. The process defined in claim 18 wherein step (a) includes forming the one of a powder or pellet of metal oxide feed material by agglomerating particles of metal oxide material with a binder.

24. The process defined in claim 18 wherein step (a) includes forming the one of a powder or pellet of metal oxide feed material by agglomerating one or more of

(i) particles of metal oxide material,

(ii) fines washed from the sintered one of a powder or pellet in step (c), and

(iii) the smaller size fraction from the separation step, wherein the agglomeration is optionally conducted with a binder.

25. The process defined in claim 18 wherein step (a) includes agglomerating particles of metal oxide material in a mixer that is capable of high impact and high velocity mixing of metal oxide material.

26. The process defined in claim 18 wherein step (a) includes agglomerating particles of metal oxide material by supplying particles of metal oxide feed material and water to the mixer and operating the mixer and forming agglomerates of a required porosity.

27. The process defined in claim 12 wherein when the metal oxide feed material is a titanium oxide, the required porosity of the one of a powder or pellet formed in step (a) is an open pore structure with about 35 to about 60% porosity.

28. The process defined in claim 27 wherein the one of a powder or pellet formed in step (a) has a size of about 1 mm to 4 mm and a density of about 2.5 to about 3.5 g/cc.

29. The process defined in claim 12 wherein, in situations in which the metal oxide feed material is titania, step (b) includes sintering the one of a powder or pellet formed in step (a) at a temperature in the range of about 850 to about 1400° C.

30. The process defined in claim 29 wherein step (b) includes sintering the one of a powder or pellet formed in step (a) in air.

31. A process for electrochemically reducing metal oxides in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode using the metal oxide feed material defined in claim 1.

32. A process for electrochemically reducing metal oxides in an apparatus that includes an electrolytic cell that includes a bath of molten electrolyte and an anode and a cathode, which process includes the feed preparation process defined in claim 12.

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