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(54) Title: CATHODE FOR ELECTROLYTIC PRODUCTION OF TITANIUM AND OTHER METAL POWDERS

(57) Abstract: Disclosed herein are electrolytic cells comprising cathodes having a non-uniform current distribution and methods of use thereof.



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TITLE

CATHODE FOR ELECTROLYTIC PRODUCTION OF TITANIUM AND OTHER METAL POWDERS

5 CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/765,560, filed February 6, 2006 which is incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

10 Disclosed herein are electrolytic cells comprising cathodes having a non-uniform current distribution and methods of use thereof for the production of titanium and other multi-valence and high (2 or more) valence metals, in particular refractory metals such as, for example, chromium, hafnium, molybdenum, niobium, tantalum, tungsten, vanadium,
15 and zirconium.

BACKGROUND OF THE INVENTION

The simplest electrolytic cell for use in electrowinning metals consists of at least two electrodes and a molten electrolyte. The electrode at which the electron producing oxidation reaction occurs is the anode.
20 The electrode at which an electron consuming reduction reaction occurs is the cathode. The direction of the electron flow in the circuit is always from anode to cathode.

Metal particles are removed from solid cathodes by force of gravity or forced fluid flow across the face of the cathode. If the metal particles
25 grow too large or strongly stick to the surface of the cathode, the particles are difficult to dislodge and collect. Other levers that people have found to control particle size and morphology include: 1. feedstock concentration, 2. temperature, 3. electrolyte composition including special additives, and 4. current density.

30 Thus, there remains a need to control metal particle size via cathode design. It an objective herein to design electrolytic cells to produce powders fulfilling these needs through cathode design and fluid

flow which control the cross-sectional area and height of particles growing from the surface of the cathode.

SUMMARY OF THE INVENTION

One aspect is for electrolytic cell comprising a cathode having a
5 non-uniform current distribution.

A further aspect is for a method of controlling the morphology of a metal product in an electrolytic cell comprising the steps of (a) providing an electrolytic cell comprising a molten electrolyte, a cathode having a non-uniform current distribution in contact with the molten electrolyte, and an
10 anode in contact with the molten electrolyte; (b) providing a metal compound to the electrolyte; and (c) applying either a fixed voltage or a fixed current across the anode and the cathode thereby depositing metal on the cathode.

Other objects and advantages will become apparent to those skilled
15 in the art upon reference to the detailed description that hereinafter follows.

DETAILED DESCRIPTION OF THE INVENTION

Applicants specifically incorporate the entire content of all cited references in this disclosure. Further, when an amount, concentration, or
20 other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed.

25 Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

30 The disclosure herein, while relating in particular to the production of titanium from a titanium oxide, is also applicable to the production of titanium from other titanium compounds as well as for the production of other metal compounds such as, for example, chromium, hafnium,

molybdenum, niobium, tantalum, tungsten, vanadium, or zirconium from, for example, the respective oxides, halides, nitrides, or sulfides.

Cathode design is used to aid in controlling the cross-sectional area of electrodepositing metal particles by controlling the lines of constant
5 potential parallel to the face of the cathode surface. Isopotential lines will be parallel to the contour of the surface of the electrode and current distribution will be orthogonal or perpendicular to these lines and with metal deposition rates proportional to current density, the areas of highest current density will have the largest metal deposition rates. Furthermore,
10 current density is highest where the distance between cathode and anode is shortest so as particles grow from the cathode, current densities at the tip of the growing particles are highest.

One embodiment for producing this non-uniform current distribution relates to a cathode comprising a wire mesh screen. If a screen is used to
15 control particle cross-sectional area, particles can only grow where there is metal mesh, so, for example if the mesh is 100 microns across, the cross-sectional area of the particles formed will have an average cross-section of 100 microns. Similarly various other cathode sizes, shapes, and designs can be used to achieve the same non-uniform current distribution
20 effect. For example, additional useful cathode designs include, but are not limited to, bristles, cones, rods, combinations thereof, and combinations with mesh screens.

The height to which particles can grow from the cathode surface can be controlled by adjusting the electrolyte flowrate so the fluid would
25 shear particles as they form to the desired height. Alternatively, mechanical means can be used to dislodge the particles as they grow toward the anode, for example, vibration. Gas blowers can also be used to dislodge the particles.

There are preferred particle size ranges, particle aspect ratio
30 ranges and particle morphologies preferred for each powder metallurgical processing method used to make various forms of metal parts. For example, in metal injection molding using small parts, symmetric spherical powders with particles less than 45 microns are preferred. In press and

sintering, 45 to 150 micron asymmetric powder particles with aspect ratios of >1.5 are preferred. Those who desire to make thin sheet from powder prefer asymmetric particles with large aspect ratios and can tolerate wide size distributions above 45 microns.

5 Anodes useful in standard electrolytic cells can be utilized in an electrolytic cell containing a cathode having a non-uniform current distribution. For example, carbon anodes, inert dimensionally stable anodes, or a gas diffusion anodes fed with a combustible gas are all useful in electrolytic cells containing a cathode having a non-uniform current
10 distribution. Other useful anodes include consumable anodes containing a compound of the metal, such as titanium, to be deposited at the cathode. Consumable anodes are known in the art and an example of a suitable consumable anode is described in U.S. Patent No. 2,722,509 which is incorporated herein by reference. One anode or multiple anodes can be
15 employed. In one embodiment, the anode can be a molten metal anode as disclosed in U.S. Patent Publication No. 2005/0121333, incorporated herein by reference.

 Typically, the metal compound to be electrowon is a metal oxide, for example titanium oxide or titanium dioxide. It is also possible,
20 however, to electrowin a metal from other metal compounds that are not oxides. These compounds include, for example, halides such as, e.g., TiCl_3 , nitrides such as, e.g., titanium nitride, and carbides such as, e.g., titanium carbide. The metal compound may be in the form of a rod, sheet or other artifact. If the metal compound is in the form of swarf or
25 particulate matter, it may be held in a mesh basket. In another embodiment, the metal compound can also be solubilized in the electrolyte, optionally with the assistance of standard solubilizers.

 By using more than one metal compound, it is possible to produce an alloy. The metal compounds for alloy production may be incorporated
30 into the molten electrolyte simultaneously, added stepwise, or in any other manner as is necessary to produce the desired alloy. For example, an alloy of Ti--Al--V can be produced by mixing aluminum oxide, vanadium oxide, and TiO_2 in the electrolyte thereby to produce an alloy of Ti--Al--V in

the molten zinc cathode. The E_0 and current density should be adjusted to deposit precise composition alloy particles.

The electrolyte consists of salts which are preferably more stable than the equivalent salts of the metal which is being deposited. Using
5 salts with a low melting point, it is possible to use mixtures if a fused salt melting at a lower temperature is required, e.g. by utilizing a eutectic or near-eutectic mixture. It is also advantageous to have, as an electrolyte, a salt with as wide a difference between the melting and boiling points, since this gives a wide operating temperature without excessive vaporization.
10 Exemplary electrolytes include, but are not limited to, metal fluorides, metal chlorides, and mixtures thereof.

In one embodiment, the level of metal compound provided to the molten electrolyte is continuously adjusted in order to insure continuous operating electrolysis.

15 All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the
20 compositions and methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit, and scope of the invention. More specifically, it will be apparent that certain agents which are chemically related may be substituted for the agents described herein while the same or similar results would be
25 achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope, and concept of the invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A method of controlling the morphology of a titanium-containing product in an electrolytic cell comprising the steps of:
 - 5 (a) providing an electrolytic cell comprising a molten electrolyte, a cathode having a non-uniform current distribution in contact with the molten electrolyte, and an anode in contact with the molten electrolyte;
 - (b) providing a titanium-containing compound to the molten electrolyte; and
 - 10 (c) applying either a fixed voltage or a fixed current across the anode and the cathode thereby depositing a metal comprising titanium on the cathode.
2. The method of claim 1, comprising during or after step (c) the further step of removing the titanium from the cathode when the metal attains a morphology suitable for powder metallurgical applications.
3. The method of claim 2, wherein the removing step is accomplished by fluid flow, vibration, or blown gas.
4. The method of claim 2, wherein the metal is a low aspect ratio powder with a particle size of less than 45 microns.
5. The method of claim 2, wherein the metal is asymmetric powder particle with a particle size in a range of from 45 to 150 micron.
6. The method of claim 5, wherein the asymmetric powder particle has an aspect ratio of greater than 1.5.
7. The method of claim 1, wherein the cathode is wire mesh, bristles, rods, or combinations thereof.
8. The method of claim 1, wherein the metal is titanium.
9. The method of claim 1, wherein step (b) is accomplished by adding the titanium-containing compound to the molten electrolyte.
- 30 10. The method of claim 1, wherein the titanium-containing compound is titanium monoxide or titanium dioxide.

11. The method of claim 1, wherein the anode is a consumable anode and the titanium-containing compound is a component of the consumable anode which is provided to the molten electrolyte