ELECTROLYTIC REDUCTION OF METAL OXIDES

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ABSTRACT
A method of electrolytically reducing a metal oxide (such as aluminium and magnesium oxides) to produce a metal in an electrolytic cell is disclosed. The method includes electrolytically reducing the metal oxide in an electrolytic cell that includes a pool of molten metal, the metal being the metal of the metal oxide to be reduced, and the molten metal pool forming a cathode of the cell. The electrolytic cell also includes a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides. The electrolytic cell also includes an anode extending into the electrolyte and a body of metal oxide to reduced in contact with the molten metal and the electrolyte.
ELECTROLYTIC REDUCTION OF METAL OXIDES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of application Ser. No. 10/474,746 filed Apr. 21, 2004, now abandoned, which claims the benefit of and priority to International Application No. PCT/0402/00456, filed Apr. 10, 2002, all of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to electrolytic reduction of metal oxides to produce substantially pure metals.

[0003] In particular, the present invention relates to electrolytic reduction of aluminum and magnesium oxides using a CaCl₂ electrolyte.

BACKGROUND ART

[0004] The present invention was made during the course of an ongoing research project on the electrolytic reduction of metal oxides using CaCl₂-based electrolyte being carried out by the applicant.

[0005] The research project investigated electrolytic reduction of a range of metal oxides in electrolyte cells based on the use of using CaCl₂ electrolyte.

[0006] The CaCl₂ electrolyte was a commercially available source of CaCl₂, namely calcium chloride dihydrate, that decomposed on heating and produced a very small amount of CaO.

[0007] The applicant operated the electrolytic cells at a potential above the decomposition potential of CaO and below the decomposition potential of CaCl₂.

[0008] The applicant found that the cells could electrolytically reduce a range of metal oxides to metals with very low concentrations of oxygen.

SUMMARY OF THE INVENTION

[0009] The present invention provides, in broad terms, a method of electrolytically reducing a metal oxide to produce a metal in an electrolytic cell, which method includes electrolytically reducing the metal oxide in an electrolytic cell that includes (a) a pool of molten metal, the metal being the metal of the metal oxide to be reduced, the molten metal pool forming a cathode of the cell, (b) a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides, (c) an anode extending into the electrolyte, and (d) a body of metal oxide to reduced in contact with the molten metal and the electrolyte.

[0010] In the above method electrolytic reduction of metal oxide takes place where there is contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte.

[0011] Preferably the metal oxide body has a geometric shape that maximizes contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte.

[0012] Preferably the method includes feeding the metal oxide body into the electrolytic cell to maintain contact of the metal oxide and the molten metal.

[0013] The metal oxide body may be in many forms, including rods, plates, blocks and the like, which can be readily immersed into the electrolyte and brought into contact with the molten metal.

[0014] Preferably the method includes maintaining the cell temperature above the melting points of the electrolyte and the metal of the metal oxide to be reduced.

[0015] Preferably the method includes operating the cell at a potential that is above a decomposition potential of at least one constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

[0016] Preferably the metal oxide is an aluminum oxide or a magnesium oxide.

[0017] In a situation in which the metal oxide is a aluminum oxide or magnesium oxide it is preferred that the electrolyte be a CaCl₂-based electrolyte that includes CaO as one of the constituents.

[0018] In such a situation it is preferred that the cell potential be above the decomposition potential for CaO.

[0019] It is also preferred that the cell potential be below the decomposition potential for CaCl₂.

[0020] It is preferred that the cell potential be less than 3.0 V.

[0021] It is preferred particularly that the cell potential be below 2.5 V.

[0022] It is preferred more particularly that the cell potential be below 2.0 V.

[0023] It is preferred that the cell potential be at least 1.5 V.

[0024] The CaCl₂-based electrolyte may be a commercially available source of CaCl₂, such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO.

[0025] Alternatively, or in addition, the CaCl₂-based electrolyte may include CaCl₂ and CaO that are added separately or pre-mixed to form the electrolyte.

[0026] At this stage, the applicant does not have a clear understanding of the electrolytic cell mechanism when the cell is operated at a potential at which CaCl₂-based electrolyte partially decomposes. Nevertheless, whilst not wishing to be bound by the comments in this paragraph, the applicant offers the following comments by way of an outline of a possible cell mechanism. The applicant believes that operating the electrolytic cell above a potential at which CaCl₂-based electrolyte partially decomposes produces Ca⁺⁺⁺⁺ cations that migrate to the vicinity of the metal oxide in contact with the molten metal cathode and provide a driving force that facilitates extraction of O⁻⁻⁻⁻ anions produced by electrolytic reduction to metal of metal oxide in contact with the molten metal cathode. The applicant also believes that the O⁻⁻⁻⁻ anions, once extracted from the metal oxide, migrate to the anode and react with anode carbon and produce CO and release electrons that facilitate electrolytic reduction of metal oxide to metal. The experimental work carried out by the applicant produced evidence of Ca metal in the electrolyte. The applicant believes that the Ca metal was the result of electrodeposition of Ca⁺⁺⁺⁺ cations as Ca metal on electrically conductive sections of the cathode and that at least part of the Ca metal dissolved in the electrolyte and migrated to the vicinity of the metal oxide in the cathode and participated in chemical reduction of oxides.

[0027] It is preferred that the anode be graphite.

[0028] Preferably the cell includes a base and side walls extending upwardly from the base formed from graphite.

[0029] Preferably the cell includes at least one tap hole for molten metal in one of the side walls and the method includes removing molten metal continuously or periodically.
The above-described method may be started-up in a number of ways. One option is to introduce the (pure) metal and the electrolyte in solid state into the cell and subsequently heat the entire system to melt the metal and the electrolyte. Another option is to introduce molten metal and molten electrolyte separately into the cell.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic illustration of an electrolytic cell 5 that can be scaled-up in application of the present invention.

**DESCRIPTION OF EXEMPLARY EMBODIMENT**

The following example illustrates an application of the invention in the process of reducing aluminum oxide (alumina) into substantially pure aluminum using an electrolytic cell as illustrated in FIG. 1.

FIG. 1 is a schematic illustration of an electrolytic cell 5 that can be scaled-up in application of the present invention.

Whilst the example described below relates to the reduction of alumina, the basic principle is equally applicable to other metals, particularly low melting point metals, more particularly magnesium.

The electrolytic cell 5 of FIG. 1 includes a graphite crucible 10 that has a base 21, side walls 31, and a tapping/discharge opening indicated as 12 in one of the side walls 31.

The electrolytic cell 5 further includes a bath of molten CaCl₂ electrolyte 13 in the crucible and a graphite electrode 11 immersed in the molten electrolyte 13. The graphite electrode 11 forms the anode of the cell 5.

The electrolytic cell 5 further includes a pool 15 of molten aluminum in a lower section of the crucible 10. The molten aluminum pool 15 forms the cathode of the cell.

The electrolytic cell 5 further includes a body 14 that consists of or incorporates alumina (Al₂O₃) to be reduced and extends into the electrolyte 13 and contacts the molten aluminum cathode 15. The alumina is shaped as a rod, sheet or prismatic body. Alumina body 14 is held in an appropriate manner to allow controlled movement into and away from the crucible interior as indicated by the arrow 16.

The electrolytic cell 5 further includes a suitable power source 18 connected to the anode 11 and to the molten aluminum cathode 15.

The molten aluminum cathode 15 is required in order to initiate electrolytic reduction of the alumina in the alumina body 14 to aluminum. The electrolytic reduction process is carried out at an elevated temperature of around 950°C at which the CaCl₂ electrolyte is and remains molten. On immersion of the alumina body 14 into the electrolyte 13 and subsequent contact of the alumina body 14 with the molten aluminum cathode 15, reduction of the alumina takes place. Since the process temperatures are above the melting point of aluminum, the latter will melt into the bath 15 and the bath level within crucible 10 will tend to rise.

In order to maintain optimum reduction conditions, the alumina body 14 is moved at a rate commensurate with the melting-off rate of aluminum from the alumina body 14 and the build-up of aluminum so that immersion of the alumina body 14 in the molten aluminum is kept at a minimum.

The process may be operated in a continuous mode by removing molten aluminum through tap hole 12 and positioning additional alumina bodies 14 in the electrolyte 13 to replace bodies 14 that are consumed in the reduction process.

Many modifications may be made to the embodiment of the present invention described above without departing from the spirit and scope of the present invention.

1. A method of electrolytically reducing a metal oxide to produce a metal in an electrolytic cell, which method includes electrolytically reducing the metal oxide in an electrolytic cell that includes a pool of molten metal, the metal being the metal of the metal oxide to be reduced, the molten metal pool forming a cathode of the cell, a pool of molten electrolyte in contact with the molten metal, the electrolyte containing alkali and/or alkaline earth halides, an anode extending into the electrolyte, and a body of metal oxide to be reduced in contact with the molten metal and the electrolyte.

2. The method defined in claim 1 wherein the metal oxide body has a geometric shape that maximises contact between (i) the molten metal, (ii) the metal oxide, and (iii) the electrolyte.

3. The method defined in claim 1 including feeding the metal oxide body into the electrolytic cell to maintain contact of the metal oxide and the molten metal.

4. The method defined in claim 1 wherein the metal oxide body includes one or more of rods, plates and blocks that can be readily immersed into the electrolyte and brought into contact with the molten metal.

5. The method defined in claim 1 including maintaining the cell temperature above the melting points of the electrolyte and the metal of the metal oxide to be reduced.

6. The method defined in claim 1 including operating the cell at a potential that is above a decomposition potential of at least one constituent of the electrolyte so that there are cations of a metal other than that of the cathode metal oxide in the electrolyte.

7. The method defined in claim 1 wherein the metal oxide is an aluminum oxide or a magnesium oxide.

8. The method defined in claim 7 wherein the electrolyte is a CaCl₂-based electrolyte that includes CaO as one of the constituents.

9. The method defined in claim 8 including maintaining the cell potential above the decomposition potential for CaO.

10. The method defined in claim 8 including maintaining the cell potential below the decomposition potential for CaCl₂.

11. The method defined in claim 10 including maintaining the cell potential less than 3.0V.

12. The method defined in claim 10 including maintaining the cell potential less than 2.5V.

13. The method defined in claim 10 including maintaining the cell potential less than 2.0V.

14. The method defined in claim 8 including maintaining the cell potential to be at least 1.5V.

15. The method defined in claim 1 wherein the cell includes at least one tap hole for molten metal and the method includes removing molten metal continuously or periodically via the tap hole.

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