ELECTROLYTIC METHOD FOR EXTRACTING THE CHROMIUM VALUES FROM CHROMIUM OXIDE BEARING ORES

Deibert C. Fieck, Reno, and Morton M. Wong, Boulder City, Nev., assignors to the United States of America as represented by the Secretary of the Interior
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The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of royalties thereon or therefor.

The present invention relates to electrowinning of ferrochrome from chromium ores.

Chromium is one of the most important alloying elements in modern metallurgy, alloys with iron, nickel, cobalt, tungsten and molybdenum being particularly outstanding. Ferrochrome, an alloy of iron and chromium, is the primary material from which most chromium alloys are made; a particularly important use is in preparation of a wide variety of chrome steels by addition of the ferrochrome to molten steel.

Ferrochrome is produced by reduction of chrome, FeO·CrO, with either coke or silicon to produce the high or low-carbon alloy, respectively. However, utilization of low grade (low chromium to iron ratio) chromite ore in these processes has not proved satisfactory or economical. Previous methods of utilizing low grade ores have included a costly preliminary chemical concentration step. One such procedure involves the following steps: The ore is mixed with coal and roasted at 1400°C. in a reducing atmosphere. This product is cooled and leached in 18 percent H₂SO₄ for 6/4 hours at 90°C. After a drying procedure, the residue is smelted in an arc furnace by conventional means to produce ferrochrome.

It has been proposed to recover chromium metal from certain of its compounds, such as chromium nitrate and chromium carbide by electrolysis in a molten salt bath of halide salts such as sodium chloride, potassium chloride or calcium chloride or mixtures thereof. However, such procedures are not effective when applied to chromite ores, such as chromite, since in the ore the ionic bonding between the iron and chromium is strong and, therefore, ionization necessary for electrodeposition is not easily attained.

It is, therefore, the object of this invention to provide a simple, rapid and economical method for electrowinning ferrochrome from a chromite ore.

It has now been found that this may be accomplished by electro-deposition of ferrochrome from a molten salt bath comprising the ore and either of two electrolyte compositions. The first electrolyte comprises a mixture of sodium pyrophosphate, sodium metaphosphate and sodium chloride; the second a mixture of sodium carbonate and sodium tetraborate. The invention is further characterized by the use of a graphite crucible or liner as both the container for the fused ore-electrolyte mixture and the anode in the electrolytic cell.

The accompanying drawing is a sectional view of the electrolytic cell employed in the invention.

The cell comprises a 3-inch mild steel container 1 having a hollow flange 2 through which cooling water is pumped by means of connections 15 and 16. Cover 3, also of mild steel is secured to container 1 by means of O-clamps 4 and 5 and neoprene gasket 6. The cover contains an opening 7 through which cathode lead 8 passes. Rubber seal 9 serves to prevent contact with the atmosphere. Cathode 10 is attached to the cathode lead and extends into ore-electrolyte mixture 11 which is contained in graphite liner 12. The cover additionally incorporates line 13 for introduction of helium and line 14 which connects to an oil bubbler (not shown in drawing).

The purpose of the oil bubbler is to exhaust the helium and CO₂ gases from the cell without obtaining a back diffusion of atmospheric gases. This oil bubbler consists of two rubber stoppered glass flasks, fastened together with glass tubing. The gas flows in and out of the first flask, which is empty, and then flows into the second flask, which is partially filled with a light-weight oil. The gas then bubbles through the oil and into the atmosphere. The one empty flask is needed to prevent siphoning the oil back into the cell if a vacuum accidentally develops in the cell.

It will be understood that the apparatus details are conventional and do not form a part of the essential inventive concept of this invention. The details of the apparatus may, accordingly, be varied widely without departing from the essential spirit and scope of the invention.

The graphite liner containing the electrolyte serves as the anode. The cathode may be of any suitable cathode material such as iron, molybdenum, chromium, tungsten or tantalum. Iron is generally used since it is the least expensive and most readily available.

The electrolyte composition and chromium ore are thoroughly mixed and heated to 750°—950°C. by means of an electrically heated furnace to produce a molten fused salt bath. A direct current is then applied between cathode and anode resulting in formation of a metallic deposit of ferrochrome at the cathode.

An inert atmosphere, such as helium, is employed to prevent oxidation of the cathode deposit at operating temperature.

Applicants have further found that the electrowinning of ferrochrome according to the process of the invention is substantially improved by subjecting the fused mixture of ore and electrolyte composition to a “soaking” period at the elevated temperature (750°—950°C.). Though the period employed may vary widely, a period of about 24 hours has been found to give very satisfactory results. The exact explanation of the advantageous results using the soaking period is not known but is believed due to a dissolving action on the metallic oxides in the ore, thus enabling the metals to be more effectively electrowon from the ore.

The current is supplied by a direct current rectifier connected to the cathode lead and to the mild steel container which serves as the anode lead. During a run the voltage is usually found to rise at first and then drop to or slightly below the starting voltage.

At the conclusion of a run the cathode lead is elevated to remove the cathode and metallic deposit from the molten electrolyte mixture, allowing part of the adhering molten salt to drain from the deposit. The cell is then cooled to room temperature, the lid removed, and the cathode and deposit removed from the cathode lead.

The metallic deposit is leached in a warm solution of hydrochloric acid with agitation to remove the remaining adhering salt. The deposits generally appear as small crystals or dendritic needles.

The following examples will serve to more specifically illustrate the invention.

**Example 1**

An electrolyte composed of 244 grams of Na₂P₂O₇, 116 grams NaCl and 40 grams NaPO₃ was mixed with 16 grams of chromite ore by rolling. This mixture was placed inside the graphite liner, the cell lid attached and the cell purged with helium and heated to 920°C. by means of a resistance furnace. The chromite employed
The cell was held at approximately 920° C. for 24 hours; the positive lead of a selenium rectifier was then connected to the cell bottom and the negative lead to the cathode. A series of runs were made (with no additional materials added) using a voltage of 1.8 volts to give a current of 4 amperes and an average cathode current density of 171 amperes per square foot on a 5%-inch iron cathode immersed 2 inches in the electrolyte. Each run in this series amounted to approximately 30 amperes hours, i.e., an average current of 4 amperes for a period of 7.5 hours.

The cathode and deposit were removed from the electrolyte, cooled and the deposit leached in a dilute HCl solution and dried. The following analyses were those of metals produced in the series of four runs:

<table>
<thead>
<tr>
<th>Run</th>
<th>Fe per cent</th>
<th>Cr per cent</th>
<th>C per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.7</td>
<td>20.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>26.3</td>
<td>24.2</td>
<td>0.34</td>
</tr>
<tr>
<td>3</td>
<td>18.4</td>
<td>48.2</td>
<td>1.08</td>
</tr>
<tr>
<td>4</td>
<td>12.1</td>
<td>80.7</td>
<td></td>
</tr>
</tbody>
</table>

1 Carbon analysis not made on runs 1 and 4.

It will be noted that the initial run gave the lowest Cr/Fe ratio with the ratio increasing rapidly with subsequent runs.

**Example II**

This example employed an electrolyte consisting of 360 grams of Na₂B₄O₇ and 40 grams of Na₂CO₃ to which 16 grams of the same chromite as Example I was added. The experimental conditions were the same as Example I. Analysis of the product was as follows:

<table>
<thead>
<tr>
<th>Fe per cent</th>
<th>Cr per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.4</td>
<td>14.03</td>
</tr>
</tbody>
</table>

The values of voltage, current and current density are not critical and may vary widely depending on such factors as nature of the ore, type of electrolyte, type of electrolytic cell employed, etc. Values of 1.7 to 1.9 for voltage, 3 to 5 for amperage and 129 to 216 amperes per square foot for current density have been found to be most effective though values of voltage from 0.6 to 2.4 with current densities from 182 to 366 amperes per square foot have been used successfully.

Since the electrolytes employed in the invention are highly corrosive, the anode must be a material which is highly corrosion-resistant. Graphite has been found to be very satisfactory in this respect while at the same time providing carbon to react with oxygen to form CO₂ gas.

Other inert gases such as argon could be used in place of helium; however, helium is preferred since it is much less expensive. Salt sublimation is also less when helium is used; this may be explained by the greater specific heat of helium.

Proportions of the ingredients of the electrolyte compositions is not critical and may be altered by several mole percent without adversely affecting the results. The following proportions have been found to be most satisfactory: For the first electrolyte, 26 to 30 mole percent Na₂B₄O₇, 10 to 14 percent NaPO₄ and 58 to 62 mole percent NaCl; for the second electrolyte, 15 to 19 mole percent Na₂CO₃ and 81 to 84 mole percent Na₂B₄O₇.

The invention is obviously capable of various modifications and changes without departing from the essential spirit and scope thereof.

What is claimed is:

1. A method for electrowinning ferrochrome from chromium ores comprising fusing in a graphite container a mixture of (1) the chromium ore and (2) an electrolyte composition from the group consisting of (a) a mixture of sodium pyrophosphate, sodium metaphosphate and sodium chloride, and (b) a mixture of sodium carbonate and sodium tetraborate, allowing the fused mixture to stand for a period of time sufficient to dissolve out at least a portion of the metallic oxides from the ore, and subsequently electrolysing the molten electrolyte-ore mixture, with the graphite container as anode, to deposit ferrochrome at the cathode.

2. Method of claim 1 in which the electrolyte composition comprises a mixture of sodium pyrophosphate, sodium metaphosphate and sodium chloride.

3. Method of claim 1 in which the electrolyte composition comprises a mixture of sodium carbonate and sodium tetraborate.

4. Method of claim 1 in which the chromium ore is chromite.

5. Method of claim 1 in which an inert atmosphere is maintained.

6. The method of claim 1 in which the fused ore-electrolyte mixture is maintained at a temperature of 750°-950° C. during the standing period and the electrolysis.

7. The method of claim 1 in which the fused ore-electrolyte mixture is allowed to stand at elevated temperature for a period of about 24 hours prior to electrolysis.

References Cited in the file of this patent

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