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International Classification - C 22 b 47/00

"Improved process for the production of manganese metal by electrolysis".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH,
Raja Marg, New Delhi-1, India, an Indian registered body
incorporated under the Registration of Societies Act
(Act XI of 1860).

The following specification describes the nature of this invention.

PENCE: TPCD KEROSE
This invention relates to improvements in the production of electrolytic manganese metal.

Hitherto manganese metal has been produced either by aluminothermic reduction of pure manganese oxides or by electrolysis of manganese chloride/manganese sulphate solutions.

The first procedure involves the production of aluminium metal by fused salt electrolysis and subsequently its use for the production of massive manganese metal. The electrolysis of manganese chloride/manganese...
Sulphate solutions have about 50 per cent current efficiency. The current densities employed are of the order of about 0.04-0.06 A/sq.cm of cathode area. Not only large sized cells are necessary but also the manganese metal obtained by aqueous electrolysis has to be melted carefully in order to obtain manganese metal in a compact form.

To obviate the difficulties or for effecting improvements in the said processes, the production of massive manganese metal in one stage directly by fused salt electrolysis has been successfully carried out.

Thus, the object of the invention is to have a compact one stage fused electrolysis process to obtain a stable and pure material for use in many applications.

The process, in brief, consists in the electrolysis of manganese oxides (manganese ore) in stable fused fluoride mixtures of alkali and alkaline earth fluorides along with manganese fluoride in ratio ranging from 1:1 upto 5:1 at 1200°C-1300°C employing graphite rod anode and mild steel cathode with caustic current density of 2 to 2.5 A/cm² for the production of manganese metal which settles at the bottom.
### Example 1

**Electrolyte:** Calcium fluoride and manganese fluoride in the ratio 7:1

**Feed material:** 0.75 kg of pure manganese dioxide obtained by the decomposition of pure manganese carbonate

**Temperature of electrolysis:** 1200°C - 1250°C

**Quantity of metal obtained:** 250 grams

**Composition of the metal obtained:**
- Manganese: 99.3%
- Silicon: rest

**Cell voltage and amp:** 5.2 V; 200 amp.

**Current efficiency:** 25%

### Example 2

**Electrolyte:** Calcium fluoride and manganese fluoride in the ratio 2:1

**Feed material:** 2 kg of -100 mesh manganese ore containing 48% manganese metal - as such (i.e. untreated ore)

**Temperature of electrolysis:** 1200°C - 1300°C

**Quantity of metal obtained:** 900 grams

**Composition of the metal obtained:**
- Manganese: 90%
- Iron: 17%

**Cell voltage and amp:** 5.5 to 6; 400-450 A

**Current efficiency:** 34%

### Example 3

**Electrolyte:** Calcium fluoride and manganese fluoride in the ratio 3:1

**Feed material:** 2.5 kg of -100 mesh manganese ore containing 48% manganese metal, partially reduced with charcoal.
Temperature of electrolysis: 1200-1300°C

Quantity of metal obtained: 1200 grams

Composition of the metal obtained:
- Manganese: 4.72%
- Iron: 7.6%

Cell voltage and amperage: 6.8V; 600 A.

Current efficiency: 52%

Advantages of this invention are:

1. By this process, the metal can be obtained in the molten form and it is very easy to handle the metal without oxidation since it is obtained in a massive form under the protective layer of the electrolyte.

2. This is an one stages process. This avoids beneficiation of the ore such as reduction, leaching of the ore etc and it is possible to produce manganese metal in massive form from manganese ore by directly feeding the said ore at ~ 100 mesh size onto the molten bath of fluorspar and manganese fluoride at any ratio between 1 fluorspar to 1 manganese fluoride to 1 manganese fluoride to 5 fluorspar.

3. This process avoids the intermediate steps of either production of aluminium metal as in the conventional alumino thermic process, or melting of electrolytic manganese metal obtained through intermediate production of very pure chloride/sulphate of manganese.

4. By this process, it is possible to operate the cell at higher cathodic current densities, say, the order of 2 to 2.5 A/cm² as opposed to 0.06 A/cm² in aqueous electrolysis.

Dated this 26th day of Dec. 1970.

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION
(Section—10)

"Improved process for the production of manganese metal by electrolysis".

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH, Safi Marg, New Delhi-110001, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed:—
This is an invention by KUPPUSWAMY VENUGOPALAN, Scientist, VHERARACHA ARAVAMUTHAN, Scientist, RAMDAY VENKATAKRISHNA UDUPA, Director, MOHAMED KAMALUDEEN, Senior Scientific Assistant, VENUGOPAL COPALAP RENJANATHAN, Junior Scientific Assistant, all of the Central Electrochemical Research Institute, Karaikudi-623006, Tamil Nadu, India, all Indian Nationals.
This invention is related to the production of massive manganese metal by electrolysis needed by iron and steel industries as well as the non-ferrous metallurgical industries.

Hitherto manganese metal has been produced either by alumino-thermic reduction of pure manganese oxides or by electrolysis of manganese chloride/manganese sulphate solutions.

The drawbacks of the hitherto known processes are:

(a) The manganese metal obtained by aqueous electrolysis will be in flaky form which is highly susceptible to oxidation.

(b) Further the aqueous process involves the pretreatment of ores like charcoal reduction at higher temperature, acid leaching etc.

(c) The operation of the aqueous electrolytic cell with a low cathodic current density of 0.04-0.06 A/cm² necessitates a large size cell.

(d) In the alumina-thermic process, an external reductant like aluminium (560 kg of aluminium for one ton of manganese-reported value) is required.

In aqueous electrolysis, not only large sized cells are necessary but also the manganese metal obtained has to be melted carefully in order to obtain manganese metal in a compact form.

In alumino-thermic process also, the manganese metal obtained is not completely free from aluminium. To obviate the difficulties, effecting improvements in the said process,
the production of massive manganese metal in one stage
directly by fused salt electrolysis has been carried out.

The main object of the invention is to develop a
process for the production of manganese metal in a massive
form by a single stage electrolytic process directly from
manganese ore/oxides.

It is made possible to produce manganese metal in
massive form by the electrolysis of manganese ore/oxide
using a molten bath containing mixture of fluorapar and
manganese fluoride in ratio ranging from 1:1 to 3:1.

The electrolysis of manganese ore/oxide in stable
fused fluoride mixture of alkaline earth fluoride (calcium
fluoride) along with manganese fluoride in the ratio ranging
from 1:1 to 3:1 at 1200°C employing graphite rod anode and
mild steel cathode with anodic and cathodic current density
of 9-10 and 2-2.5 A/cm² will result in the production of
massive manganese which settles at the bottom. Thus,
a high cathodic current density of 2-2.5 A/cm² can be
maintained in fused salt electrolysis as compared to
0.04 A/cm² in aqueous electrolysis.

The present invention accordingly provides an improved
process for the production of manganese metal by electrolysis
of manganese oxide in a stable molten bath comprising
alkaline earth fluoride in an electrolytic cell comprising
a refractory lined mild steel vessel fitted with a mild steel
plate cathode and a graphite rod anode, the interelectrode distance being maintained at 3.8 to 5 cm at a temperature range of 1200°C to 1250°C, the manganese metal being obtained in a massive form, i.e. compact form and not in flaky form at the bottom of the cell over the cathode.

The advantages of the process of the invention are that the metal can be obtained in the molten form and it is very easy to handle the metal without oxidation since it is obtained in a massive form under the protective layer of the electrolyte.

This is a one-stage process. This avoids beneficiation of the ore such as reduction, leaching of the ore or like pre-treatments; and it is possible to produce manganese metal in massive form from manganese ore by directly feeding the said ore at -100 mesh size onto the molten bath of fluor spar and manganese fluoride at any ratio between 1 fluor spar to 1 manganese fluoride to 1 manganese fluoride to 3 fluor spar.

This process avoids the intermediate steps of either production of aluminium metal as in the conventional aluminothermic process or melting of electrolytic manganese metal obtained through intermediate production of very pure chloride/sulphate of manganese.

Furthermore, by this process, it is possible to operate the cell at higher current densities, say, the order of 2 to 2.5 A/cm² as opposed to 0.04 A/cm² in aqueous electrolysis.
The present invention accordingly consists of a one stage process for the production of metallic manganese in a compact form both from manganese oxide ore and manganese oxide concentrates by an improved fused salt electrolysis procedure wherein suitable mixtures of calcium and manganese fluorides are employed to obtain massive manganese at the cathode in a molten state with simultaneous evolution of oxygen at the anode carbon. This one stage process is in contact to the production of pure manganese chloride or manganese sulphate solution from the ore in a number of stages, electrolyzing the salt solutions employing very low current densities with very high inventories due to equipment and space. This procedure is also more economical compared to the aluminothermic reduction of manganese oxide to obtain massive manganese metal.

The process is further described with reference to the accompanying drawings. Figure 1 shows an electrolytic cell according to this invention for the production of manganese metal by electrolysis. The cell consists of a refractory lined metal cell(1) which has a mild steel plate cathode(3) at its bottom and a graphite rod anode(4). The electrolytic bath comprises molten mass of calcium fluoride (7) and manganese fluoride (6) to which is added as cell feed manganese oxide or manganese ore as a powder(5). The manganese metal formed collects at the bottom of the cell(8) and carbon dioxide or carbon monoxide
formed escapes at (2). The electrode distance is adjusted between 3.0 and 5 cm at the current density of the cathode adjusted at 2 to 2.5 A/cm$^2$ and that of the anode at 9-10 A/cm$^2$. The refractory lining used for the mild steel electrolytic cell preferably consists of magnesite bricks.

The invention is further illustrated by the following examples:

**EXAMPLE 1**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Calcium fluoride and manganese fluoride in the ratio 1:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed material</td>
<td>0.75 kg of pure manganese dioxide obtained by the decomposition of pure manganese carbonate</td>
</tr>
<tr>
<td>Temperature of electrolysis</td>
<td>1200°-1250°C</td>
</tr>
<tr>
<td>Quantity of metal obtained</td>
<td>250 grams</td>
</tr>
<tr>
<td>Composition of the metal obtained</td>
<td>Manganese : 99.3%</td>
</tr>
<tr>
<td></td>
<td>Silicon : 0.7%</td>
</tr>
<tr>
<td>Cell voltage and amp</td>
<td>5.2 V ; 200 amp</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>25%</td>
</tr>
</tbody>
</table>

**EXAMPLE 2**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Calcium fluoride and manganese fluoride in the ratio 2:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed material</td>
<td>2 kg of -100 mesh manganese ore containing 40% manganese content as such (i.e. untreated ore)</td>
</tr>
<tr>
<td>Temperature of electrolysis</td>
<td>1200°-1300°C</td>
</tr>
</tbody>
</table>
Quantity of metal obtained: 900 grams

Composition of the metal obtained:
- Manganese: 80%
- Iron: 17%
- Silicon: Rest

Cell voltage and amp: 5.5-6; 450 A

Current efficiency: 34%

**EXAMPLE 3**

Electrolyte: Calcium fluoride and manganese fluoride in the ratio 3:1

Feed material: 2.5 kg of 100 mesh manganese ore containing 48% manganese content partially reduced with charcoal

Temperature of electrolysis: 1200-1250°C

Quantity of metal obtained: 1200 grams

Composition of the metal obtained:
- Manganese: 83.612%
- Iron: 11.708%
- Silicon: 1.420%

Cell voltage and amp: 6.8V; 600 A

Current efficiency: 52%

**WE CLAIM**

1. An improved process for the production of manganese metal by electrolysis of manganese oxide in a stable molten bath consisting of alkaline earth fluoride in an electrolytic cell comprising a refractory lined mild steel vessel fitted with a mild steel plate cathode and a graphite rod anode, the inter-electrode distance being maintained at 3.8 to 5 cm at a temperature range of
1200-1250°C the manganese metal being obtained in a massive form at the bottom of the cell over the cathode.

Process as claimed in claim 1 wherein the electrolyte used comprises calcium fluoride and manganese fluoride in the ratio of 1:1 to 3:1 and manganese oxide in the form of -100 mesh pyrolusite (manganese ore) is used as cell feed.

3. Process as claimed in claims 1 and 2 wherein the electrolysis is carried out at a bath temperature of 1200°C with cathodic and anodic current densities of 2-2.5 and 9-10 A/cm² respectively.

4. Improved process for the production of manganese metal by electrolysis of manganese oxide substantially as herein described and illustrated.

Dated this 11th day of September, 1979

Sd/-

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